New Submicron Silica Produced by Hybrid Production Process

Yusuke Tosaki[1], Yuki Amano[1], Yukiya Yamashita[1], Paul Brandl[2] Dr. Robert E. Johnson[3]; [1]NIPPON AEROSIL CO., LTD., Yokkaichi Mie, Japan, [2] Evonik Degussa Specialty Chemicals (Shanghai) Co. Ltd., Shanghai, China, [3] Evonik Corporation, NJ, USA

Abstract

New surface modified submicron silicas produced by a hybrid production process are compared to commercially prepared surface-modified colloidal silica with respect to their applicability as external additives for electrophotographic toners. The principal metric for comparison is tribo-electrostatic charge (T-ESC) stability under an extended activation period, but relative dispersibility on toner and the influence of environmental extremes on tribo-charge properties are also examined. 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.

1. Introduction

In an effort to improve the mechanical robustness of toner particles to the demands of current electrophotographic printing processes, a new class of external additives has emerged under the generic term: submicron silica. Submicron silicas contrast with well-known silica additives by their average primary particle size – greater than 100 nanometers for submicron silica.

Two routes to these large particle additives have been identified: flame pyrolysis and wet-process colloidal silica. In this paper we introduce a new submicron silica produced by a hybrid production process. This hybrid method results in a combination of attractive characteristics: spherical, monodisperse particles, as from the wet-process, and the ability to vary the silica surface modification at will, as is typical for flame-process silica.

Achieving greater flexibility for surface chemistry allows the new submicron silica greater control of tribo-charge (negative charge to positive charge, mixed modification, strong charge to weak charge, etc.). The new process also results in less residual water or alcohol, common to wet-process submicron silica. Along with greater control of the type and degree of tribo-charge, the hybrid process submicron silica allows for better charge stability and, as a result, enhanced print quality.

2. Experimental procedures

2.1. Materials

2.1.1 Core materials

The core materials used in this study were produced by well-known techniques previously outlined: the flame pyrolysis or fumed process (here called "dry-process") and the colloidal or sol-gel process (here called "wet-process"). [1][2] We further contrast the wet process samples by their modes of surface modification: for the hybrid case, techniques similar to those applied to fumed silica were employed; for the colloidal case, a commercially available sample was used. This material is prepared by treating wet-process silica with an organosilane but under conditions that result in the final product containing much more residual moisture [see Table 1.]

Table 1: Process and properties of submicron silica

	Dry process	Wet process	
Sample Name	Fumed	Hybrid	Colloidal
Core material process	Flame pyrolysis	Sol-gel	Sol-gel
Surface modification	Variety	Variety	Limited
Residual moisture content	Very Low	Low	High
Particle size distribution	Broad	Narrow	Narrow
Easiness of dispersion	Good	Good	Moderate

2.1.2 Surface Modification Agent

Surface modified submicron silicas produced by the wet-process have been utilized as toner external additives for approximately twenty years[3]. However, the variety of surface chemistry available is somewhat limited because the water-based origin for the particles means that some treatments such as dimethyldichlorosilane or silicone oils, common for fumed silica additives, cannot be easily employed. As a consequence, the most commonly available wet-process silica has HMDS (hexamethylenedisilaze) and/or alkyl surface modification. Fumed silica, used widely as a small-particle toner surface additive, in contrast can be readily modified with many reagents – one in particular: silicone oil treatment (PDMS) has found wide use. [4] This diversity of treatment options is attractive and so we investigated a new technique in which a wet-process silica core is surface modified in a like manner as is used for fumed silica – here called the "hybrid-process."

In this study we will focus 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 [see Table 2.].

Table 2: Physicochemical properties of submicron silica in this investigation

	Hybrid-Process Sample A	Hybrid-Process Sample B	Colloidal-Process Sample
Surface Treatment	HMDS	PDMS	Silane coupling agent
BET [m^2/g]	30	25	30
Bulk Density [g/l]	ca. 400	ca. 500	ca. 350
Carbon Content [wt%]	0.3-0.6	1.0-1.5	0.7-1.2
Hydrophobicity [%]	> 70	> 90	> 90
Moisture [%]	< 0.5	< 0.5	> 2.0

2.1.3 Toner formulations

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

2.2. Methods

2.2.1 TEM investigation of new submicron silical

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

2.2.2 FE-SEM analysis of new submicron silica on toner surface

A Field Emission-Scanning Electron Microscopy (FE-SEM, Hitachi SEM S4100) imaging was used to check dispersibility and embedding of new submicron silica aggregates into the toner particle.

Samples were prepared by combining toner with hybrid submicron silicas (3wt %) followed by agitation with a Turbula mixer for 4 min.

2.2.3 Tribo-Electrostatic charge (T-ESC) of surface treated submicron silica

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 career (50 g) and agitated with a Turbula mixer from 30sec to 30 minutes. All sample preparation and measurement was carried out in a constant temperature/constant humidity room.

2.2.4 Thermogravimetry of surface treated submicron silica

Thermogravimetry was measured using the TG/DTA 6200 (Seiko Instrument EXSTAR series).

2.2.5 Water vapor adsorption of surface treated submicron silica

Water vapor adsorption and desorption isotherms at several pressures were measured using the BELSORP-max (Microtrac).

3. Results and discussions

3.1. Structure investigation through TEM analysis.

Figure 1 shows the TEM images of the core silica used for the hybrid-process surface modification and of fumed silica with a relatively large primary particle size (average: 80 – 100 nm). As is typical, the fumed silica shows an aggregated morphology. The core used for the hybrid-process in contrast is much less aggregated and, through optical analysis of the TEM image, the average primary particle size was estimated as 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 and colloidal-process cores appear similarly spherical, monodisperse, and with equivalent average primary particle size (approximately 110 nm) indicating that both samples should readily disperse on the toner surface.

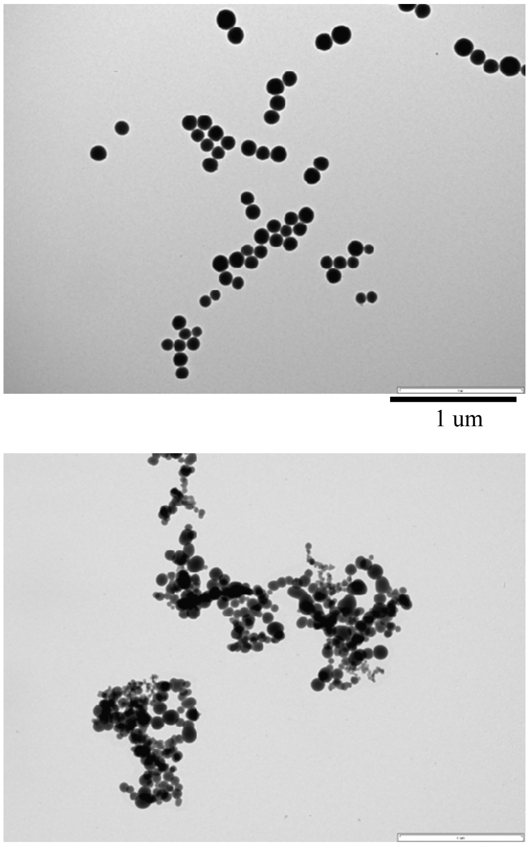

***Figure 1**. TEM images of hybrid process sample A (top) and fumed process sample (down)*

3.2. FE-SEM analysis of wet-process silica – dispersibility on toner

In order to examine relative dispersibility, the two wet-process silicas were each mixed with toner for a short period (agitation time: 4min) and SEM images of the toner surfaces compared [Figure 2]. The good dispersibility of the hydbrid-process submicron silica is evident in the image on the left and contrasts significantly with the colloidal-process silica/toner sample (right image) where agglomeration is still present.

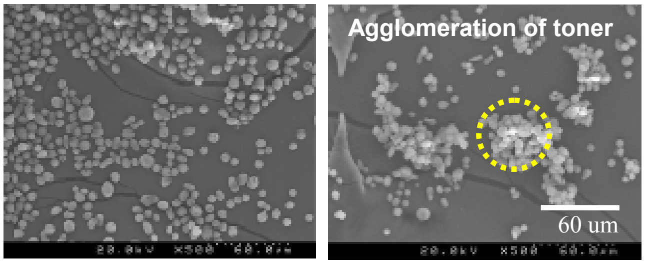

***Figure 2**. SEM images of toner with hybrid process sample A (left) with colloidal process sample (right)*

Further evidence of the good dispersiblity of the hybrid-process submicron silica on toner surface is shown in Figure 3 and Figure 4. Both images were taken for silica/toner samples after a short period of mixing (agitation time: 4 min).

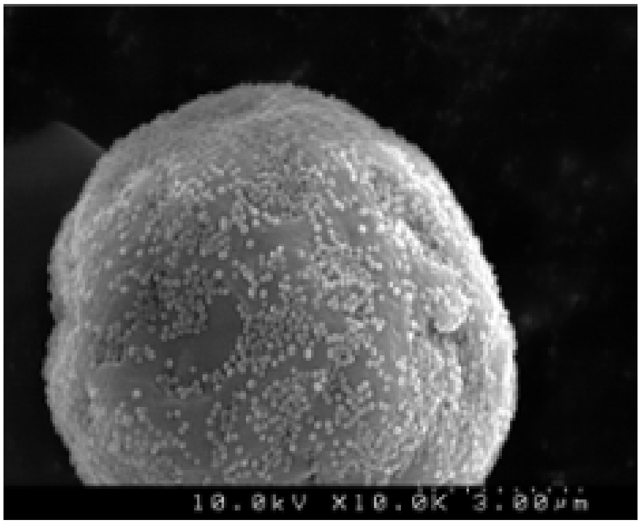

***Figure 3**. SEM images of toner with hybrid process sample A (agitation time is 4min)*

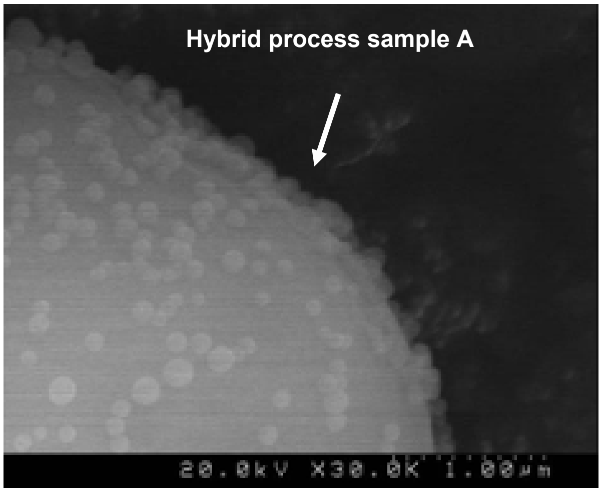

***Figure 4**. SEM images of function as spacer of hybrid process sample A on toner surface*

What is particularly evident in Figure 4 is demonstration of the spacer-attribute for the hydrbid-process submicron silica. Because of their size, even after the 4 minutes of mixing, these silica particles extend well beyond the toner surface. When combined in a toner additive formulation with much smaller fumed silica, typically used to provide free-flow and charge behavior characteristics, act as a physical barrier between impacting toner particles. This spacing keeps the smaller silica from embedding beneath the toner surface even under shearing conditions.

3.3. Charge characteristic and charge stability

T-ESC results for the samples are shown in Figure 5 – Hybrid-Process Sample A increases charge during agitation and progresses from strong negative charge to moderate charge; Hybrid-Process Sample B retains charge strength around the middle negative charge range; it also retains its charge strength around a slight negative charge value. As expected, surface modification has a strong impact on the additive charge and, clearly, PDMS modification brings an important charge capability to spacer-effect silica.

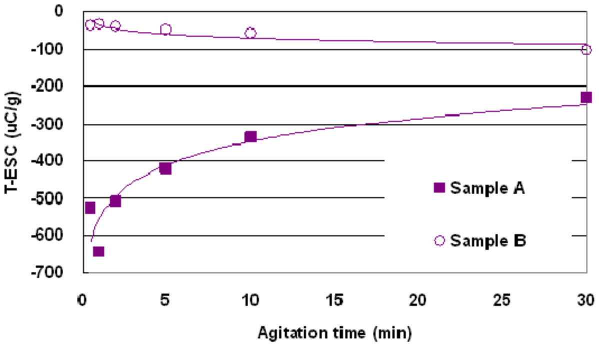

***Figure 5**. Charge characteristics of hybrid process sample (sample A and B)*

In addition to its charge value, the charge stability of Wet-Process Sample A was measured under typical environmental extremes of humidity and temperature: HH (80% RH, 40° C) and LL (15% RH, 10° C) [Figures 6 & 7].

The figures show that this new submicron silica produced by the hybrid production process has excellent environmental stability with little change in charge observed even after one week at either set of conditions.

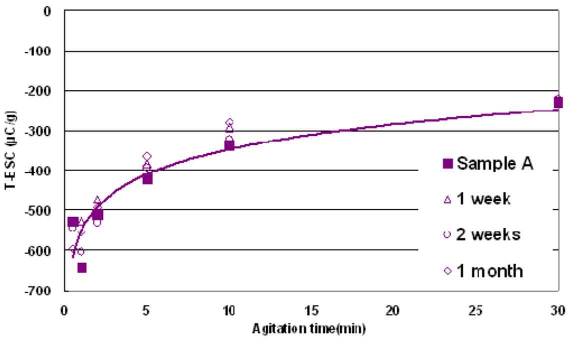

Figure 6. *Charge stability of hybrid process sample A on HH condition*

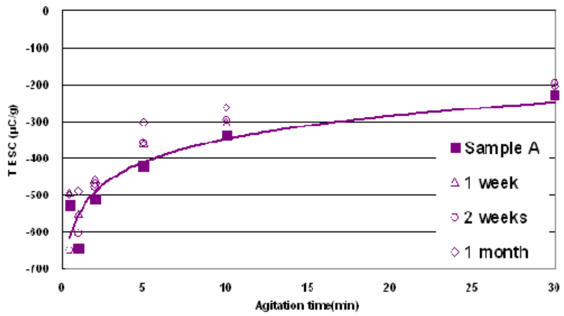

Figure7. *Charge stability of hybrid process sample A on LL condition*

3.4. Thermogravimetry of surface treated submicron silica

The source of this environmental stability was sought by measuring the TGA of Samples A & B (HMDS treated hybrid silica and PDMS treated) and contrasting those with the commercially available silica external additive (HMDS treatment) [Figure 8]. The results show that sample A and sample B retain a much lower level of volatiles (presumably water) than the colloidal sample. This lower level of retained moisture would clearly aid charge stability and powder flow for the hybrid process silica versus those for the commercial colloidal grade.

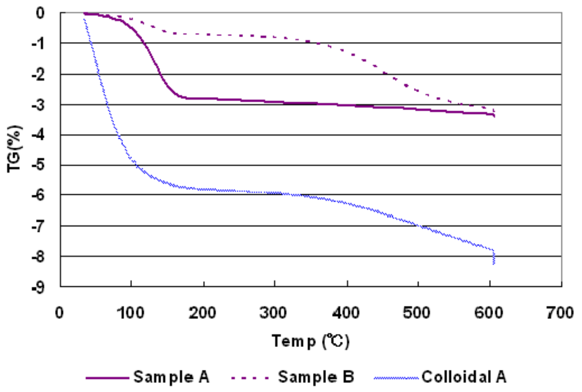

Figure 8. *Thermo gravimetry data of hybrid process sample (Sample A and B) and colloidal process sample*

3.5. Water vapor adsorption and desorption of submicron silica

Further investigation for the source of this environmental stability was sought by carrying out a water vapor adsorption/desorption study on the three wet-process silicas [Figure 9]. The results show that hybrid-process Sample A and Sample B exhibited much lower water vapor adsorption than the Colloidal grade and desorption levels for the hybrid origin silica are again far below that of the Colloidal. Also interesting to note is that the PDMS treated silica (Sample B), because of its greater hydrophobicity, exhibits the lowest adsorption/desorption levels of all. Although not shown here, it should be noted that water vapor adsorption/desorption levels for fumed-process spacer-effect silica are even lower, but only the hybrid-process silica can approach this superior environmental stability.[5]

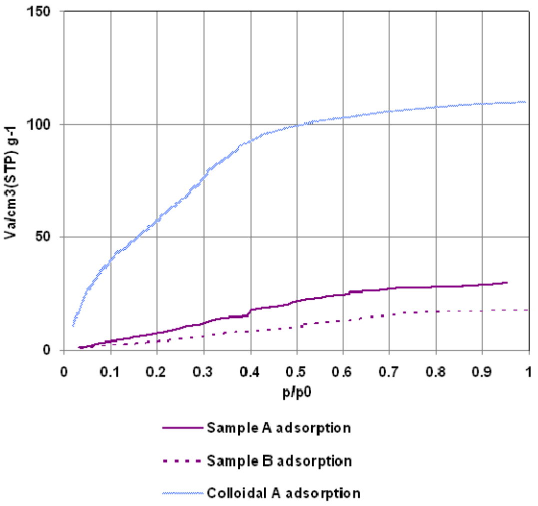

Figure 9. *Water vapor adsorption of hybrid process sample (Sample A and B) and colloidal process sample*

4. Conclusions

New submicron silica manufactured by a hybrid production process displays a good spacer attribute. The function of these submicron materials as spacers between toner particles was confirmed by SEM studies under mixing conditions. The hybrid-silica additives also demonstrated the ability to ensure stability for charge characteristics, i.e. charge level and distribution, at HH-LL conditions – especially when compared with colloidal spacer-effect silica. Under extreme environmental conditions, the hybrid submicron silica, while outperforming the commercial material, has nearly the same water-vapor adsorption/desorption behavior of fumed-process spacer-effect silica.

References

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Author Biography

Yusuke Tosaki received his Masters 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 / fumed metal oxides and their application as external additives for toner.