Novel Fumed Mixed Silica-Titania (FM-Si/Ti) Core Materials for a New Class of External Toner Additives

Masanobu Kaneeda*, Akira Inoue*, Yuki Amano*, Paul Brandl*, Maria R Nargiello**, Kai Schumacher***
****NIPPON AEROSIL CO., LTD.,Yokkaichi, Mie, Japan, ** Degussa Corporation, Piscataway, NJ, USA, *** Degussa GmbH, Hanau, Germany***

Abstract

Fumed mixed silica-titania (FM-Si/Ti) core materials and their corresponding hydrophobized counterparts are compared with respect to their applicability as external additives for electrophotographic toners using toner flowability and Tribo-Electrostatic Charge (T-ESC) stability under extended activation periods as well as L/L and H/H conditions. Flowability studies, which included angle of repose and tapped density measurements, showed differences in the toner flow enhancement with titania and FM-Si/Ti compared to silica alone, both under static and dynamic conditions. The influence of silica in FM-Si/Ti on the initial charge-up behavior was also observed in T-ESC measurements. The differences were explained by TEM investigations, indicating the importance of the silica/titania ratio of the nano-particle structure. In addition, volume resistivity (Ω•cm) studies showed that the structure strongly relates to the electro-physical properties of the FM-Si/Ti. The influences of a thin, encapsulating silica layer on the titania core of mixed oxides are described in detail.

1. Introduction

In order to meet the advancing requirements of electrophotography such as better image quality and higher process speeds, toner quality has been rapidly evolving. Properties such as toner particle size and toner resin Tg are getting smaller and lower, respectively.

A variety of advances and new approaches are observed in both conventional milled toners and newly developed chemical toners. Though both types of process technologies are very different, both their objective is the production of toners with high performance and excellent overall print quality.

To address the demanding requirements of more optimized toners, the development of more advanced external additives has been ongoing [1-2]. Additive development is focused on improving flow characteristics, controlled tribo-electrostatic charge stability in various environments and under extended activation periods as well as durability.

Ongoing trends show most formulated toners, whether made by conventional or chemical processes, using two or more kinds of specific external additives to meet the required properties. In recent times, as toner resins are getting softer, larger external additives are used as spacer material and development is ongoing to improve their performance. Trends also show that the average loading level is increasing.

With increased expectations towards performance, more development efforts are focused on finding the optimum combination of external additives. Optimum combinations are very much influenced by toner characteristics such as the production process (milling versus chemical), particle shape and size, black versus color, one component versus two components and positive versus negative charge. The desired toner performance will determine the optimum combination of external additives, which will still be a very small percentage of the entire formulation.

Historically, external additives have been based on surface modified metal oxide such as fumed silica, titania and alumina.

Recently, new fumed mixed silica-titania cores have been developed and this paper will discuss their characteristics based on basic toner application data.

2. Experimental procedures

2.1. Materials

2.1.1. Core materials

The FM-Si/Ti types were obtained from Degussa [3]. Fumed titania and fumed silica types were obtained from Nippon Aerosil Corporation (NAC). The key properties of all core materials are summarized in Table 1.

Table 1: Fumed mixed silica-titania, fumed titania and fumed silica core materials used for this investigation

Sample designation	Si/Ti ratio (g/g)	BET surface area (m^2/g)
S1	100/0	90
S2	15/85	80
S3	0/100	90
S4	97/3	300
S5	100/0	300
S6	10/90	50
S7	30/70	50
S8	50/50	50
S9	70/30	50

2.1.2. Surface treated materials

In order to investigate the differences in the influence of the FM-Si/Ti on toner flowability, the raw materials were surface treated using an existing method with hexamethyldisilazane (HMDS), to render them hydrophobic. The properties of surface treated samples are summarized in Table 2. To define the amount of chemical adsorption / reaction on the surface of particles, carbon contents of the surface treated samples were measured with a carbon analyzer EMIA-110 (Horiba). Additionally, carbon contents of extracted samples were determined. To do this, 0.5g of each additive tested was weighed, dispersed in 30g of chloroform under sonication, centrifuged and decanted to remove the chloroform. Samples were subjected to this extraction procedure twice. Afterward, they were dried and the carbon content was measured. The results are also summarized in Table 2. This test ensured that the trimethylsilyl group was fully chemically reacted to the surface of not only silica (H1 and H5) but titania (H3) and the FM-Si/Ti (H2 and H4).

Table 2: Surface treated external additives used for this investigation

Additive Sample designation	Core material	Si/Ti ratio (g/g)	C-content (wt.-%)	C-content after $CHCl_3$ extraction (wt.-%)
H1	S1	100/0	0.98	0.96
H2	S2	15/85	0.90	0.86
H3	S3	0/100	0.73	0.75
H4	S4	97/3	2.97	2.99
H5	S5	100/0	3.25	3.31

2.1.3. Toner formulations

The toner used for this investigation was a conventional, milled, negative, styrene-acrylic based toner with an average diameter of 8 μm. 2.5 % of each of the surface treated 90 m^2/g external additives S1, S2, and S3, and 1.0 % of each of the surface treated 300 m^2/g additives S4 and S5 were added to the toner as summarized in Table 3, respectively, prior to blending the mixture for 1 minute at 600 rpm, and subsequently for 3 minutes at 3,000 rpm in a high-speed mixer.

Table 3: Composition of toner mixtures investigated in this paper

Toner Sample designation	Additive	Addition amount to toner (%)
T1	H1	2.5
T2	H2	2.5
T3	H3	2.5
T4	H4	1.0
T5	H5	1.0

2.2. Methods

2.2.1. TEM investigation of the FM-Si/Ti materials

In order to investigate the structural differences of the various FM-Si/Ti products, Transmission Electron Microscopy (TEM) studies were performed.

2.2.2. Volume resistivity measurement

Volume resistivities (Ω•cm) of the FM-Si/Ti, fumed titania and fumed silica core materials were measured with a resistivity meter Hiresta-UP MCP-PD-41 (Mitsubishi Chemical) and calculated according to the equation provided by the manufacturer.

2.2.3. FE-SEM analysis of toner mixtures

In order to confirm that the toner and the respective additives from Table 2 were adequately mixed and dispersed, Field Emission-Scanning Electron Microscopy (FE-SEM) analyses were conducted.

The mixture of toner and each external additive was examined using JSM 6340F (JEOL). Each mixture was fixed on an aluminum sample holder using a double-adhesive conductive carbon tape and coated with a 5 nm osmium layer prior to examination using an osmium plasma coater OPC80 (Nippon Laser & Electronics Lab.). The micrographs were taken at 3 kV and at magnifications of 10,000 and 50,000, respectively.

The results obtained with the toner mixtures T2 and T4 are shown in Figure 2. The pictures show that the additives are not only well dispersed on the toner surface as small aggregates, but also dispersed uniformly on the surface.

2.2.4. Determination of toner flowability

2.2.4.1. Angle of repose

The angle of repose of the toner formulations in Table 3 was measured with a powder tester PT-S (Hosokawa Micron). 20g of a toner formulation were put on a 355 μm sieve. Sieving was conducted with vibration through a glass cone onto a round table. The glass cone was mounted above the top of the round table, the distance between the cone and the round table was 6.5 cm, and the diameter of the round table was 8 cm. Measurements were conducted in triplicate for each toner sample.

2.2.4.2. Tapped density

Tapped bulk density measurements were conducted using a tapped density determination equipment STAV2003 (Engelsmann). 70g of each toner mixture were weighed in a 250 ml graduated cylinder, and then the level in the cylinder was read after 1250 taps.

2.2.5. Tribo-Electrostatic charge (T-ESC)

T-ESC was measured using a blow-off type electrostatic charge meter TB-200 (Toshiba Chemical). 2g of each toner formulation with 48g of a non-coated ferrite carrier were stored under the condition at high temperature / high humidity (H/H: 40ºC, 85% relative humidity) and low temperature / low humidity (L/L: 10ºC, 20% relative humidity) for 18 h. After storage, under both environmental conditions, each toner / carrier was agitated with a Turbula mixer for 1, 5, 30 and 120 minutes, respectively.

3. Results and discussions

3.1. TEM investigation

Figure 1 depicts the corresponding TEM images of the core materials S2, S4 and S6-S9 from Table 1.

FM-Si/Ti grades with a small silica ratio (10, 15 and 30 g/g respectively) feature a core-shell structure with a layer (several nanometer thick) of silica around a titania core as shown in the images S6, S2 and S7 of Figure 1. In comparison, the FM-Si/Ti core material with a high silica ratio of 70/30 g/g consists of a silica core with small titania particles dispersed on its surface and throughout its bulk (S9). The core material with a silica/titania ratio of 50/50 g/g (S8) consists of both large and small titania particles which are distributed throughout the silica bulk. It is, however, difficult to identify the titania domains in the structure of S4, presumably because the titania is dissolved in the silica phase as already observed in an investigation of the optical properties of various FM-Si/Ti materials [4]. Thus the structures of the FM-Si/Ti particle were observed to vary with their Si/Ti ratios, and it will be shown that these differences significantly influence their respective electro-physical properties.

3.2. Volume resistivity

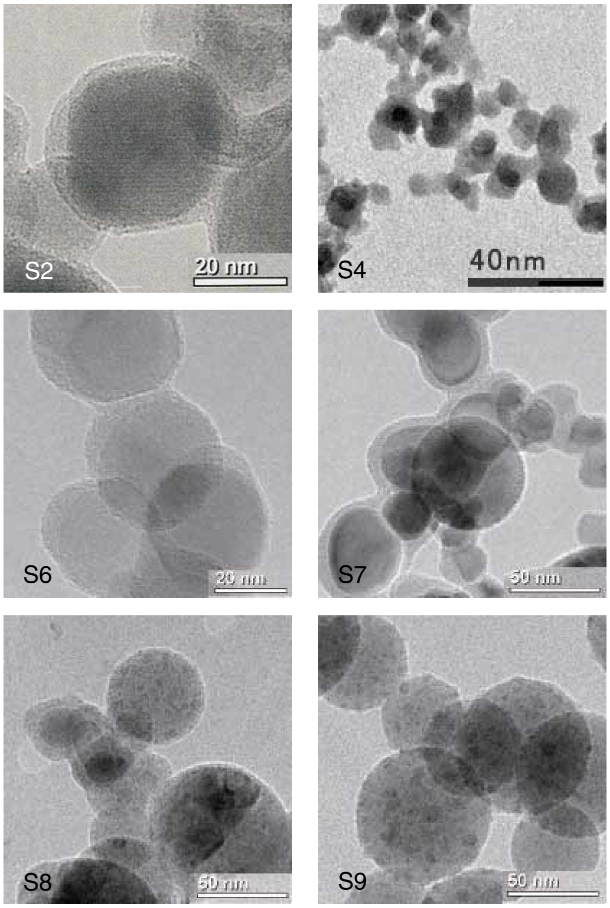

***Figure 1:** TEM pictures of various FM-Si/Ti core materials*

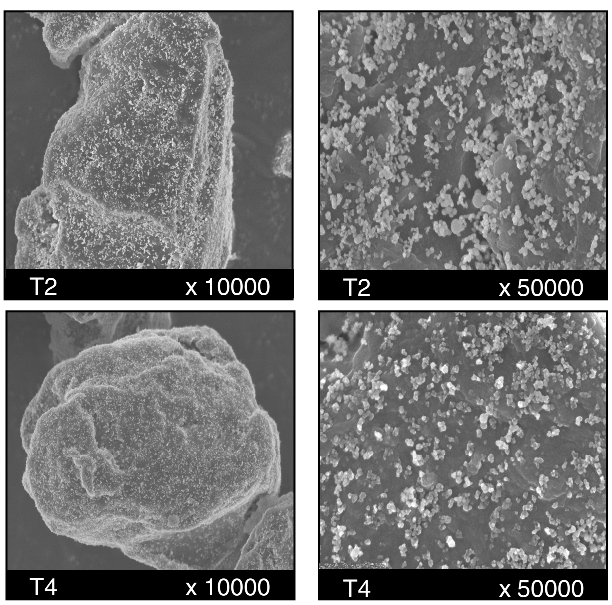

***Figure 2:** SEM pictures of toner mixture surface*

To assess the influence of the structure on the electro-physical properties, the volume resistivity of various FM-Si/Ti core materials with varying BET surface areas and Si/Ti ratios were measured. The results are shown in Figure 3. While the volume resistivity is approx. 10^5 Ω•cm for pure titania and 10^{14} Ω•cm for pure silica, the volume resistivity of the FM-Si/Ti was observed to generally increase with rising silica content at lower silica ratios. However, the silica content does not linearly relate to the increase in resistivity of FM-Si/Ti. The curves seem rather to be dependant upon the specific nano-structure of each FM-Si/Ti, in which the dispersed titania influences the overall electro-physical character of the mixed oxide.

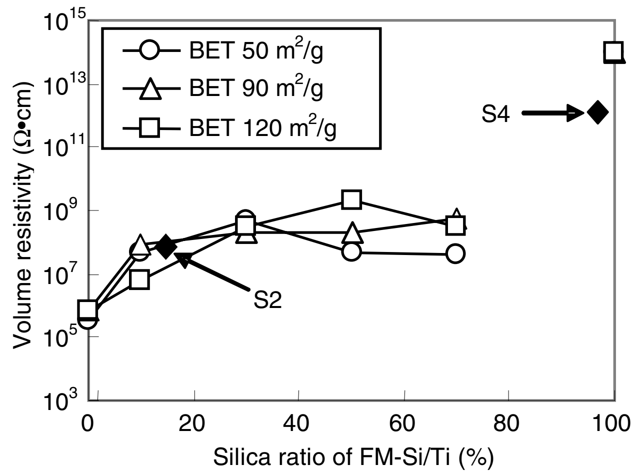

***Figure 3.** Volume resistivity of various FM-Si/Ti core materials*

3.3. Toner flowability

The flowability of toner / additive mixtures is shown in Figure 4. As expected, each type of toner mixture featured a clearly improved flowability versus the "as is" toner with no additive. The surface treated 80 m^2/g FM-Si/Ti with a Si/Ti ratio

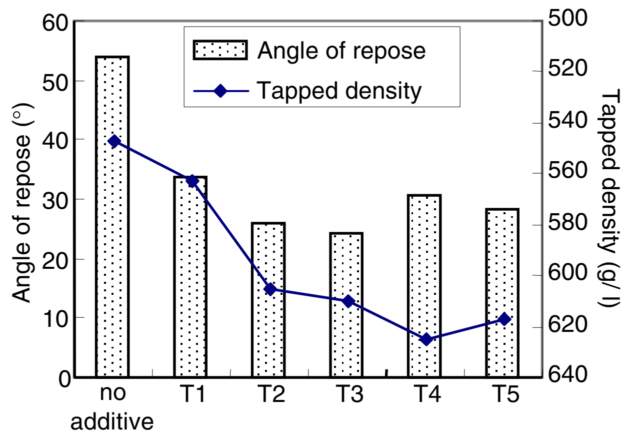

***Figure 4.** Toner flowability*

of 15/85 (H2) and the surface treated 90 m^2/g titania (H3) gave the best flowabilities (T2 and T3), even better than the surface treated 90 g/m^2 fumed silica H1 (T1). Tapped density data support the results. Surprisingly, H2 and H3 enhance the flowability (angle of repose) of the toner to a larger extent than the high surface area materials H4 and H5. On the other hand, the tapped densities of T4 and T5 were much higher than the ones of T1, T2 and T3.

3.4. T-ESC

One of the most notable advantages of the surface treated FM-Si/Ti core materials is their effect on the T-ESC stability of the toner mixtures. In order to assess the influence of surface

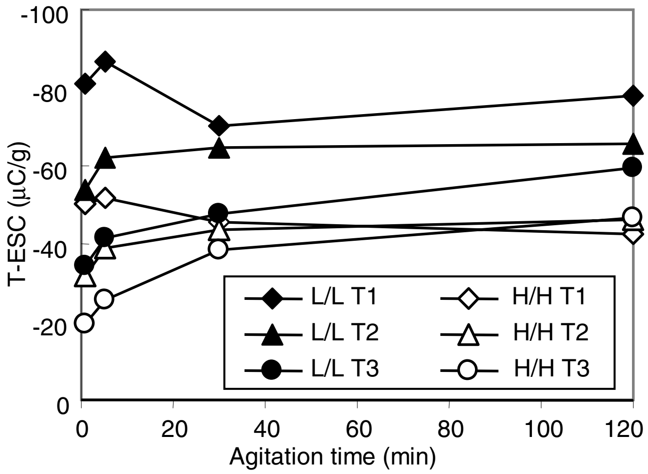

Figure 5. *T-ESC of T1, T2 and T3 (BET surface area 90m^2/g)*

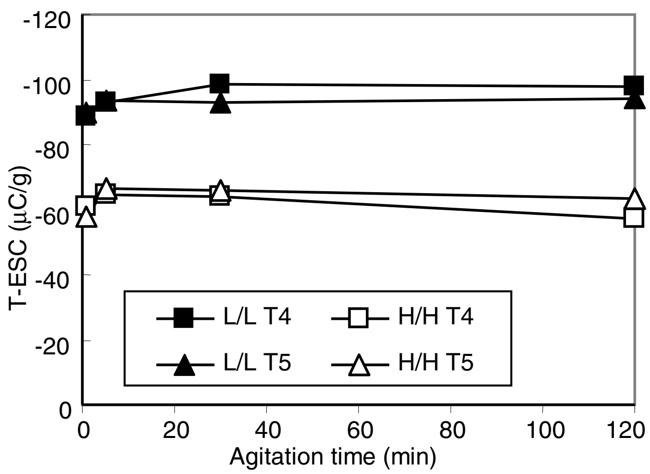

Figure 6. *T-ESC of T4 and T5 (BET surface area 300m^2/g)*

structure and Si/Ti ratio, the T-ESC stability of the toner mixtures as a function of agitation time was measured under L/L and H/H conditions, respectively. The results are shown in Figure 5 and Figure 6.

The T-ESC of T1, T2 and T3 were compared in Figure 5. The T-ESC of all mixtures were generally higher under L/L conditions with pure silica (H1) giving the greatest T-ESC differences between L/L and H/H conditions. The smallest differences were observed for the mixture with pure titania (T3). A result to note is that the FM-Si/Ti (H2) gave a quick charge-up in the first 5 minutes, and the charge level was kept for 120 min under both L/L and H/H conditions (T2).

The T-ESC of T4 and T5 were also investigated and compared. The results are shown in Figure 6. H4 and H5 enhanced the toner charge at higher levels than H1, H2 and H3 in both L/L and H/H conditions. In H/H condition, both T-ESC of T4 and T5 were gradually decreased after the first 5 min. This decrease may be explained by faster embedding into the toner particle of the smaller primary particle size of these additives.

4. Conclusions

(1) The structure of the FM-Si/Ti core materials strongly depends on the Si/Ti ratio. These structural variations causes considerable differences in the electro-physical properties.

(2) Both pure titania (H3) and core shell FM-Si/Ti (H2) enhanced the flowability of the investigated toner to a greater extent than the high surface silica (H5) and silica with low titania content (H4).

(3) One of the most significant features of the surface treated fumed mixed silica-titania is their effect on the T-ESC stability of the toner mixtures.

(4) On the other hand pure titania (H3) showed the strongest environmental stability under H/H and L/L conditions.

Investigation of this novel class of core materials is still ongoing, but preliminary results indicate that the FM-Si/Ti with a silica content of 15 weight.-% and a specific surface area of 80 m^2/g is the most promising material to enhance charge stability and provide a fast charge-up behavior.

References

[1] M. R. Nargiello, P. Brandl and H. Shirono, Study of the Effect of External Additives on Toner Performance, Proc. IS&T's NIP18, pg. 278 (2002).

[2] A. Inoue, Y. Amano and P. Brandl, Performance Optimization of Functional Fumed Metallic Oxide Based External Additives for Toner, Proc. IS&T's NIP21, pg. 558 (2005).

[3] M. Ettlinger, W. Hartmann, D. Kerner and J. Meyer, US Patent 6022404.

[4] P. C. Schultz, J. Am. Chem. Soc., **59**, 214 (1976).

Author Biography

Masanobu Kaneeda received his Master degree in Applied and Synthetic Chemistry at Nagoya University in 1995. After 7 years experience in organic synthesis at Toray Pharmaceutical Research Center, he joined NIPPON AEROSIL in 2002. The main focus of his work is basic research on surface modification of fumed oxides for toner application.