The Effect of Surface Modified Fumed Metallic Oxide Additives on the Performance of Toners

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Abstract

A wide variety of surface modified fumed metallic oxides has been proposed and successfully applied as toner additives for improvement of such characteristics as free-flow properties, tribo-electrostatic charge (ESC) level, and charge stability at the activation time and ambient variations. When the Selenium (Se) was mainly used as image drum component, dimethylsilyl treated fumed silica with negative charge was an effective additive. According to the introduction of the new technologies, such as Organic Photo Conductor (OPC) or amorphous silicon (a-Si) drum, the requirements for the toner, and hence for the toner additives have diversified extensively. The type of polymer for toner, e.g. polystyrene-acrylic type or polyester type, and the type of the machine, e.g. monochrome, color or multifunctional unit, also helped diversification of such requirements. To meet with the specific requirement in the respective system, the various surface modified fumed oxides, ranging from positive charged to negative charged, from high BET surface fine particles to low BET coarse particles, for example, have been developed. This paper describes the typical proposed material designed to suit for the respective system, with the physicochemical data, and then discusses the effect of the types of surface treatment reagents on the performance of the toner.

Introduction

Toner is composed with binder, colorant, charge control agent, wax and outer additive. The surface modified fumed metallic oxide (SMO) is used in toner as an outer additive. The properties required for the outer additive at high hydrophobicity, high dispersibility, good free-flow effect and stable ESC for toners.[1] These properties of SMO influence on the image quality and image density, fogging, cleaning, adhesion, abrasion properties. The type of SMO is normally selected depending on the copying system and type of toner. Table 1 shows the copying system, type of toner and the type of outer additive. The combination of the toner and outer additive is further optimized depending on the copying system (machine type, monochrome/color, analogue/digital, photo conductor).

Table 1. Toners and fumed oxides required in various copying systems

System				Toner		Outer Additive		
Machine Type	Monochrome /Color	Analogue /Digital	P/C*	Binder	ESC*	Type of metallic oxide	ESC*	Group
PPC*	Monochrome	Analogue	Se	St-Ac*,PS*	Negative	Fumed Silica	Negative	1
	Monochrome	Analogue	OPC	St-Ac*,PS*	Positive	Fumed Silica	Positive	4
	Monochrome	Digital	OPC	St-Ac*,PS*	Negative	Fumed Silica	Negative	2, 3
	Monochrome	Analogue	a-Si	St-Ac*,PS*	Positive	Fumed Silica	Positive	2, 3
	Color	Digital	OPC	Polyester	Negative	Fumed Silica, Titania	Negative	5
LP*	Monochrome	Digital	OPC	St-Ac*,PS*	Negative	Fumed Silica	Negative	2, 3
	Monochrome	Digital	a-Si	St-Ac*,PS*	Positive	Fumed Silica	Positive	4
	Color	Digital	OPC	Polyester	Negative	Fumed Silica, Titania	Negative	5
Multi	Monochrome	Digital	OPC	St-Ac*,PS*	Negative	Fumed Silica	Negative	2, 3
	Monochrome	Digital	a-Si	St-Ac*,PS*	Positive	Fumed Silica	Positive	4

PPC*; Plane Paper Copier   LP*; Laser Printer   P/C*; Photo Conductor
St-Ac*; Styrene-Acrylic Copolymer   PS*; Polystyrene   ESC*; Electrostatic charge

The outer additive of SMO proposed by the authors are classified into five groups according to the core material and type of reagent and resulting varied ESC levels.

Types of Fumed Metallic Oxides used for Toners

ESC and hydrophobicity of the SMO can be controlled by the core material, BET surface area, primary particle size and the type of reagent. Table 2 shows overviews of five groups of SMOs used for toners. The detailed application of SMOs is explained as follows.

Group 1 is dimethyldichlorosilane (DDS) treated fumed silica and is negatively charged. Generally type of the outer additive is chosen so that the ESC of the additive is same to that of toner. The SMOs in group 1 are suitable to the analogue –Se drum system.

Group 2 is dimethylpolysiloxane (DMPS, silicone oil) treated fumed silica and group 3 is hexamethyldisilazane (HMDS) treated fumed silica. Both group 2 and 3 are negatively charged. The SMOs in group 2 and group 3 are mostly recommended for the digital-OPC drum or the analogue-a-Si drum system. DMPS treated fumed silica has high hydrophobicity and is suitable to toners to achieve better cleaning effect. HMDS treated fumed silica is recommended for the high speed copying machine because of better free-flow effect.

Group 4 is aminosilane (AS) and HMDS or DMPS treated fumed silica and is positive charged. The SMOs in group 4 are recommended for the analogue-OPC drum or the digital-a-Si drum system. These SMOs have less hydrophobicity than other groups due to introduction of a hydrophilic property of amino group.

Group 5 is alkylsilane (RS) treated fumed silica or fumed titania. This type of SMOs shows weakly negative charged and is recommended to the color copying system.[2]

Properties of SMO Required as Toner Additive

The properties of SMO are important for characterizing toner performance because SMO adheres on toner. The requirements for SMO to attain good image quality are hydrophobicity,[1] uniform hydrophobicity,[2] high dispersibility,[3] improved free flow behavior and ESC control and stability. Taking these requirements for SMO into consideration, the properties of SMO and its application to toner are explained in this section.

Table 2. Type of SMOs using for toner

Group	Core Material	BET [m^2/g]	Primary particle size [nm]	Reagent*1	ESC	MW*2 (Hydrophobicity)
1	Fumed Silica	130 200 300	16 12 7	**DDS**	**Negative**	**40-55**
2	Fumed Silica	50 50 200 130 150	40 30 12 16 15	**DMPS**	Negative	60-70
3	Fumed Silica	50 50 200 300	40 30 12 7	HMDS	Negative	60-70
4	Fumed Silica	50 200 200 50 200	30 12 12 30 12	HMDS+AS HMDS+AS HMDS+AS DMPS+AS DMPS+AS	Positive	30-70
5	Fumed Titania Fumed Titania Fumed Silica	50 90 200	21 14 12	RS	Negative	65-80

*1 DDS: Dimethyldichlorosilane DMPS: Dimethyl polysiloxane *2 MW: Methanol Wettability
HMDS: Hexamethyldisilazane AS: Aminosilane
RS: Alkylsilane

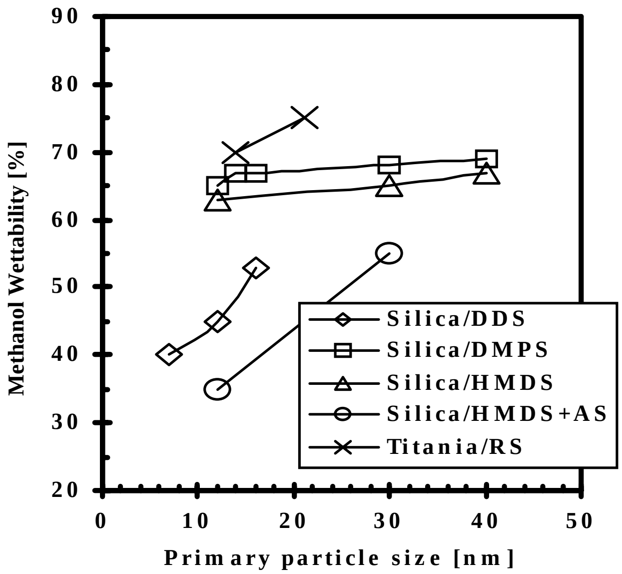

Figure 1. Methanol Wettability of SMOs

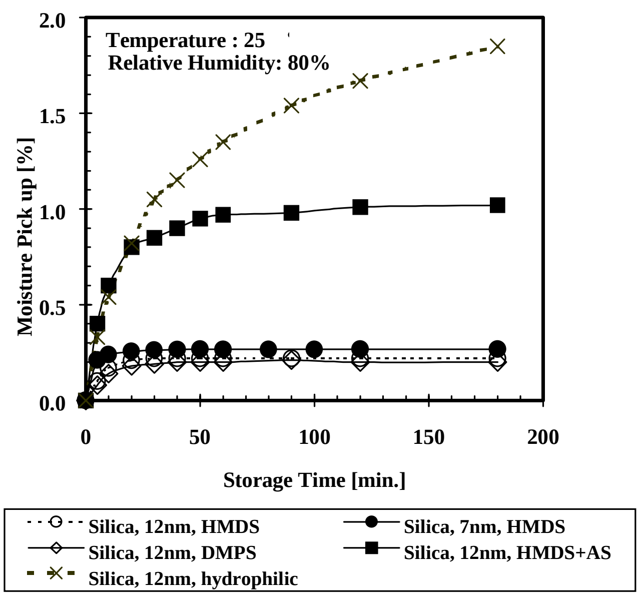

Figure 2. Moisture pick up behavior of SMOs and hydrophilic fumed oxide

1. Hydrophobicity

Hydrophobicity is one of the most important SMO property required for improvement free-flow and con-trolling ESC of toner. Hydrophobicity can be explained by methanol wettability value (MW) and moisture pick up characteristics of SMO under an ambient condition. MW value is measured by following procedure. Weigh 0.2g of SMO in a 250ml glass beaker and pour 50ml of pure water. Add methanol into water (not on to SMO) and stirred until SMO is wetted completely in water/methanol. The vol. % of methanol consumed is defined the MW value. Figure 1 shows MW values for SMOs as a function of primary particle size of core material. The MW values for HMDS+AS and DDS treated silicas are lower than that for RS, DMPS and HMDS treated silica. These results are thought to explain that AS is hydrophilic property and dimethylsilyl group on DSS treated silicas is less surface coverage than other type of alkylsilyl groups such as trimethylsilyl group and dimethylpolysiloxane.

The influence of reagent on the moisture pick up characteristics of SMOs was evaluated. The ambient condition of the measurement was controlled at 25°C and 80% relative humidity. As depicted in Figure 2, the mois-ture pick up of SMOs is lower than that of the untreated hydrophilic fumed silica. Hydrophilic fumed silica of 12nm primary particle size absorbed moisture up to 1.8% during 180 minutes. On the other hand, SMOs did not pick up moisture so much. In case of HMDS+AS treated silica, the level of moisture pick up is higher than other SMOs. This is due to lower hydrophobicity.

Under normal storage and transportation conditions, powder toners have tendency to agglomerate due to moisture pick up. This influences their flow and charging behavior. Through a special production process, SMO ensures hydrophobic property. Due to the hydropobicity, primary use of SMOs in toners is used to improve flowability, to reduce pick up moisture and to quench reaglomeration of toners. Typical loading volume of SMOs onto toner to improve flowability and to reduce moisture pick up is ranging from 0.1 to 2%.

2. Uniformity of Hydrophobicity

Uniform hydrophobicity of SMO is important property for toner performances which are narrow ESC distribution, stable ESC during activation, and good image density. That can be evaluated by measuring sedimentation volume in the different volume ratio of methanol and water mix-ture. This method enables to judge uniformity and degree of hydrophobicity. The measurement method is; prepare different volume ratio of methanol and water; weigh SMO and put it in the mixture; after shaking the mixture for certain time, sedimentation volume of SMO is measured. Figure 3 shows methanol wettability behavior that can judge uniformity of SMO hydrophobicity. If the sedimen-tation curve is steeper, uniformity is better. And if the value of methanol at which SMO starts wetting is large, hydrophobicity of SMO means high. HMDS treated fumed silica shows better hydrophobic uniformity and higher hydrophobicity than DDS treated silica.

3. High Dispersibility

Dispersibility of SMO is also important factor for toner application. If agglomerates of outer additive are remained in toner, white spots are appeared in the copied paper or photo conductor is damaged by agglomerates. Dispersibility of SMO is influenced by the type of reagent. If agglomerates are remained in SMO, pulverizing process is sometime taken to make them smaller size. Figure 4 shows the SEM photographs of 7 µm toner with silica (silica average primary particle size; 40nm and 12nm). SMO adhered on the toner particle uniformly and appears well dispersed. This is very important for improvement of toner flowability.

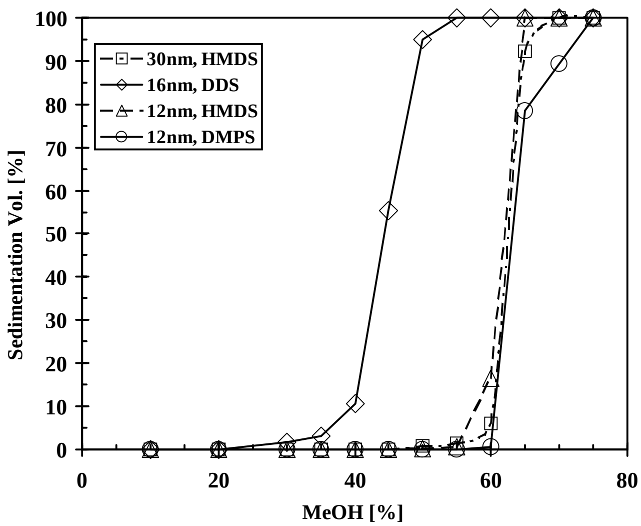

Figure 3. Uniformity and degree of SMO hydrophobicity

4. Improved Flow Behavior

According to the development of high image quality and high speed copying system, the particle size of toner became smaller.

The addition quantity of outer additive should be increased in order to improve free-flow property due to low flowability of very fine toner. The free-flow evaluation of toner with SMO was performed according to the measurement of repose angle.

The flow behavior of toner (average particle size 7 µm) in addition with SMO was evaluated by a POWDER CHARACTERISTICS TESTER (by HOSOKAWA MICRON CO., LTD.). Figure 5 shows the repose angle of toner with different type of SMO. Low repose angle means good free-flow. Most of SMOs used on toner additive improve the flowability of the toner in comparison with a toner without SMO (52-degree). It is observed that the repose angle of toner is in the range of good level if the primary particle size is less than 16nm irrespective of reagent. However, the repose angle is largely depended on the type of reagent if the primary particle size is more than 16nm. Therefore, the improper selection of a SMO negatively impacts flow behavior. The improvement of flowability is influenced by the type of hydrophobic treatment and the primary particle size.

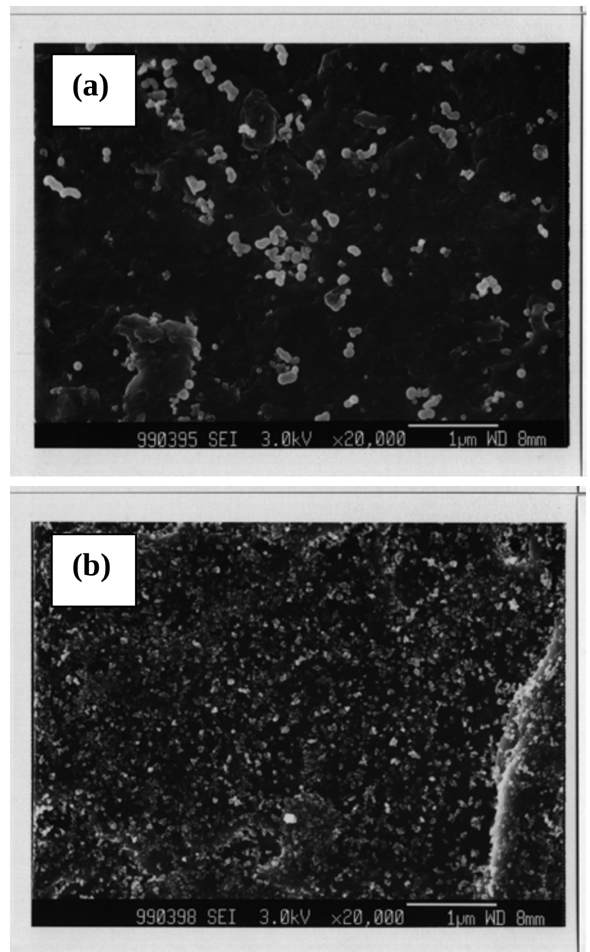

Figure 4. SEM photograph of toner with surface modified silica (a; 40nm and b; 12nm)

5. ESC Control and Stability

In addition to dispersibility and hydrophobicity, ESC level of SMO is important factor. Fumed metallic oxides are surface modified with different types of reagents in order to give a wide range of ESC level controlling from positive to negative. The ESC level of SMOs can be selected to control the overall charge level of the toner and maintain the ESC of the toner during the storage under ambient conditions. Adjustment of the amount of charge controlling reagents is resulted in change of the ESC level of SMOs.

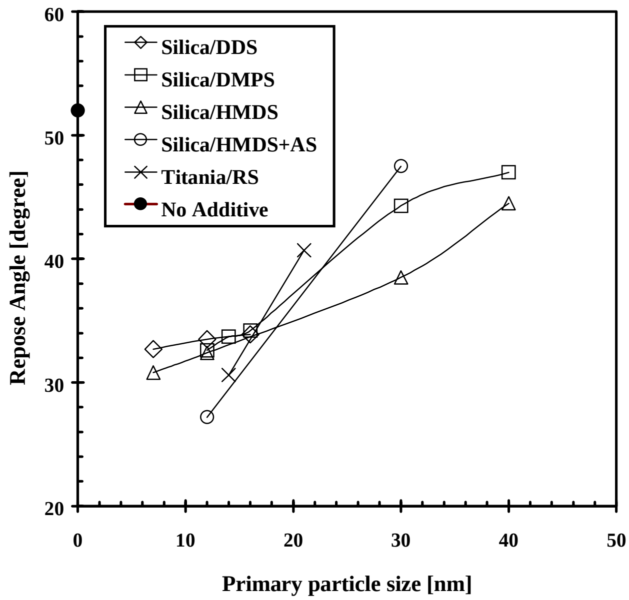

Figure 5. Repose angle of toner applied with different type fumed metallic oxide

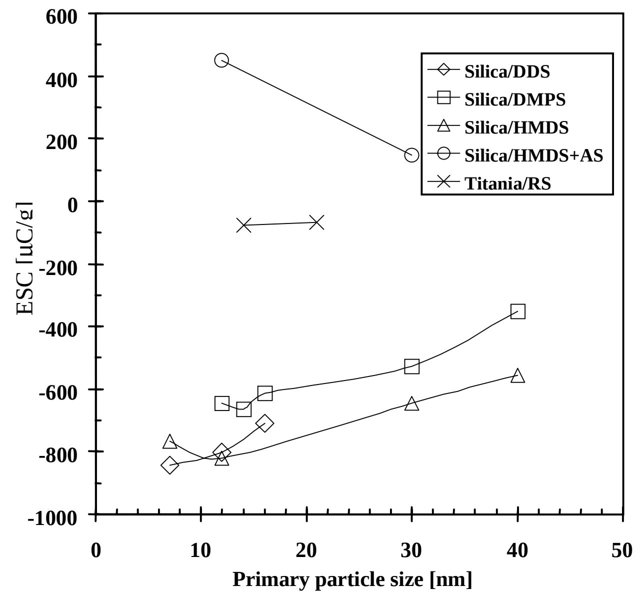

Figure 6. ESC of SMOs as a function of primary particle size (against iron carrier)

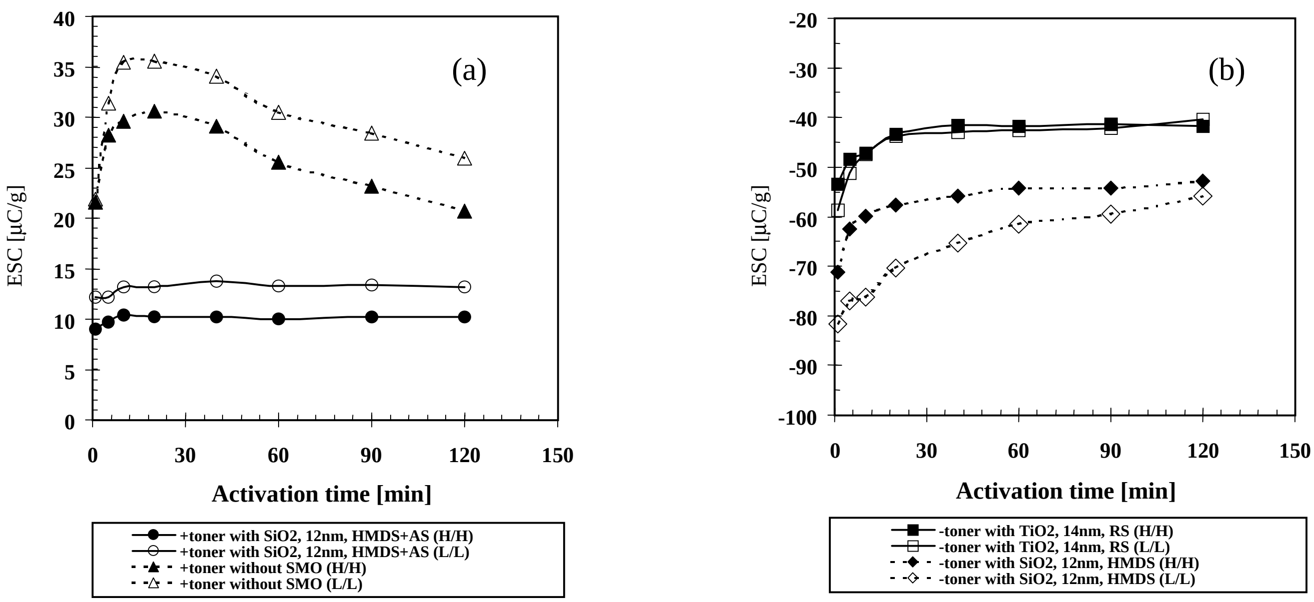

Figure 7. ESC of a positive (a) / negative (b) toner with and without SMO under the condition of H/H and L/L as a function of agitation time (L/L: 10℃, 20%RH, H/H: 40℃, 85%RH)

It is required in toner that instant charge up soon after activation to the targeted ESC and constant charge level should be attained during activation under ambient conditions. A selection of SMO according to a copying system; a strongly / a weakly charged, type of core material, or type of reagent / reagent combination, is a key factor to attain these requirements.

Figure 6 shows ESC of SMO as a function of primary particle size (against iron carrier). HMDS, DDS, and DMPS treated fumed metallic oxides are strong negative ESC. On the other hand, a weakly negative ESC can be attained by RS treated fumed titania. These SMOs are applied to negative toners. Positive charged SMOs (HMDS+AS) are varied from 100 to 450 μC/g. The charge level depends on the amount of molar ratio of amino group. These positive charged SMOs are applied to positive charged toners.

Charge up speed and ESC stability of toner were evaluated according to following procedure. The toner with SMO was prepared by mixing the components with a high-speed mixer. The addition quantity of SMO is 0.5phr against toner. The toner / SMO mixture (4%) and an iron carrier (96%) were dry-blended with a TURBULA MIXER. Then the ESC was measured by a Blow-off-typed electrostatic charge meter.

Figure 7(a) shows ESC behavior of a positive toner with and without a positive charged SMO (HMDS+AS) as a function of activation time under H/H (40°C/80%RH) and L/L (10°C/20%RH) conditions. The positive charged toner with the SMO shows instant charge up and stable ESC during activation time, but the positive toner without SMO shows slow charge up and unstable ESC. Figure 7(b) shows ESC behavior of negative toner with RS treated fumed titania or HMDS treated fumed silica. In this case RS treated fumed titania has much better performance than that of HMDS treated fumed silica.

Conclusion

Due to a variety of toner systems many SMOs have been developed to meet various technical requirements. Core material of fumed metallic oxides and reagents for surface modification are the key factors to improve toner performance. Requirements for fumed metallic oxides, as toner additives will probably be even more diversified in the future with development of new toners.

References

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Biography

Hirokuni Shirono received B.S. degree from the Tokyo Science University in 1981. Since 1981 he had worked at Mitsubishi Material Corporation in Japan. Three months later, he transferred to Nippon Aerosil Co., Ltd. In Yokkaichi, Japan. His work has primarily focused on the development of new surface modified fumed metallic oxide for toner and silicone rubber application.