Study of the Effect of External Additives on Toner Performance

Maria R. Nargiello-Tetreault, Paul Brandl**, and Hirokuni Shirono***
**Degussa Corporation, New Jersey*
***Nippon Aerosil Co., Ltd., Mie, Japan*

Abstract

External additives for toners such as hydrophobic fumed silica and hydrophobic titania have been widely used for improvement of toner performance. Toners formulated for use in laser printers and PPC (Plain Paper Copiers) are being developed, aimed at high speed copying, high image quality and downsizing. To meet the challenges of more demanding requirements, toners are designed utilizing both smaller and larger particle size external additives to achieve better flowability, higher durability, higher image density and stable electrostatic charge under ambient conditions. Usage levels are also increasing. In addition to improved overall toner flow and charge properties, this trend is associated with improving cleaning properties such as reduced fogging and adherence of toner to paper.

As such properties can be influenced by external additives, it is important for the toner formulator to know which characteristics need improvement in the already design stage.

This paper describes the design and the selection of external additives. It will address the influence of mixing time of external additives on the tribo-electrostatic charge (T-ESC), charge distribution, and flowability of toners. In addition, the influence of surface chemistry of external additive on the admix performance is discussed. Finally, experimental results of the performance of color toner mixed with several kinds of external additives are reported.

Introduction

In recent years, raw material requirements for toners going into printer and copying machines have diversified due to a variety of system developments such as multi-purpose use, down-sizing, energy-saving, etc. Due to this increase in system complexity, more accurate material design is needed in the development of very fine toners, chemical toners, and color toners. To optimize selection of an external additive for toner several factors need to be considered; type of toner (monochrome or color), the type of machine (analogue or digital), and the type of photo-conductive (PC) drum (Amorphous-Silicon:a-Si or Organic Photo Conductor:OPC). An appropriate external additive is selected by considering its physicochemical properties (particle size and distribution, metal or metallic oxide, surface chemistry) and then confirming applications tests are needed to verify selection.

The classification and the role of external additives used for toners are depicted in Figure 1. Fumed silica, titania, and alumina are the most widely used external additives for toners. In addition, other metal oxides, mixed metal oxides, or organic resins can be applied depending on the technical requirements.[1,2,3] The average primary particle size of such external additives is ranged from 7~300nm for fumed silica, 10~1,000nm for titania, alumina and mixed oxides, and 10~10,000nm for organic resin. Most metallic oxides and mixed metallic oxides are surface modified with a variety of organic compounds to improve the toner performance, over their non-modified counterparts. External additives are loosely fixed on the toner (through attractive force or slight embedding). They function as aids to free-flow, charge control, heat resistance, anti-caking, abrasion control for the PC drums, cleaning for the PC drums, control the adhesion of toners, impart hydrophobicity, and improve toner durability. The associated copying process and the role required (typical function) for the external additive, are shown in Figure 2 and Table 1.

As external additives are expected to fill many roles, it is difficult to control all functions with one single additive. To meet diverse performance requirements, combinations of two, or more additives is recommended.

In this study, the measurement results of T-ESC for the external additives with a non-coated ferrite carrier and the toners are addressed with data from an evaluation of admixing properties and charge distribution of toner. Lastly, a newly developed external additive is introduced.

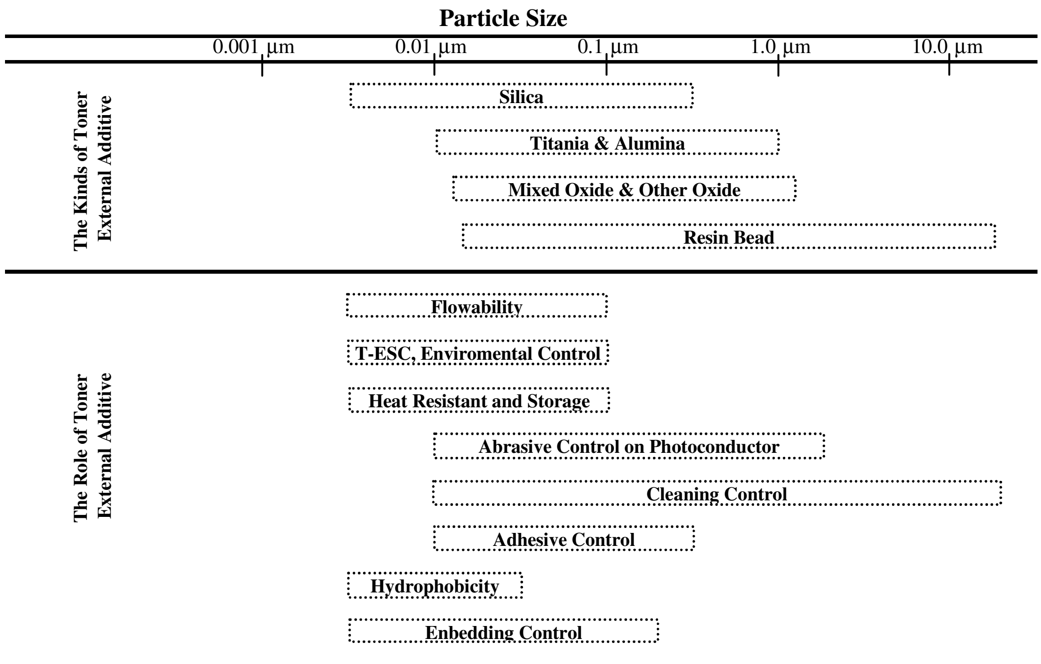

Figure 1. Classification and the Role of External Additives used for Toners

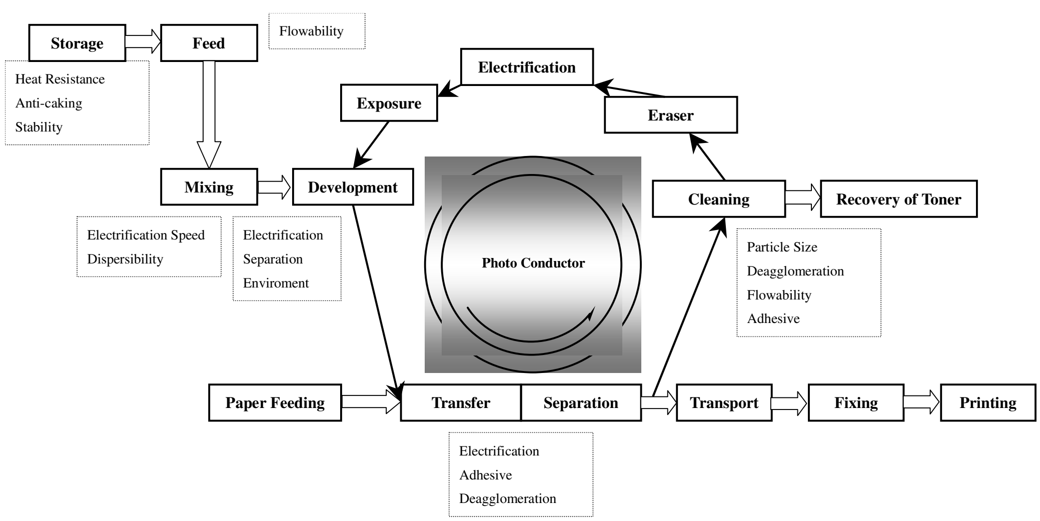

Figure 2. Copying process and Role Required for the External Additive at Each Copying Stage

Table 1. Roles Required for the External Additive at Each Copying Stage.

Copying Stage	Roles Required for External Additives
Storage	Heat resistance, Anti-caking, Charge stability
Feed	Flowability (Free-flow), Admixing [4]
Mixing	Electrification speed (Instant charge up), Dispersibility (Dust free), Admixing [4]
Development	Electrification, Separation (from carrier), Admixing,[4] Environment (less influence from ambient condition)
Transfer / Separation	Electrification, Adhesiveness, Deagglomeration
Cleaning	Particle size, Deagglomeration, Flowability, Adhesiveness

Experimental

(1) Preparation of Toner/External Additive Mixture

The toners used for this experiment are monochrome and color (yellow) toners with 7µm in diameter. The mixing of toner and external additive is carried out with a Henschel® mixer at 12,000 rpm for 1 minute. For negative charged toner, negative charged external additives are incorporated and for positive charged toner, positive charged external additives are used.

(2) Evaluation Method

Flow behavior after addition of toner with an external additive, repose angle and the passage rate of toner through a 45µm screen are evaluated by POWDER TESTER PT-N (Hosokawa Micron Co. Ltd.).

The T-ESC for the external additive is measured according to the following procedure. Add 0.1g of the external additive into 50g of non-coated ferrite carrier. Mix them with TURBULA® mixer (Type T2C : WBA) at 90 rpm for 5 minutes. Take out 0.1g of the mixture and measure the T-ESC by a blow-off type electrostatic charge meter TB-200 (Toshiba Chemical Co. Ltd.) after 1 minute, blow-off by N_2 gas.

The T-ESC, of the toner, is measured by the same equipment (mentioned above). Mix 48g of non-coated ferrite carrier and 2g of the mixture of toner/external additive by TURBULA mixer at 90 rpm for 5 to 90 minutes. Then take out 0.1g sample and measure the T-ESC by the blow-off meter after 1 minute, blow-off with N_2 gas.

At the end of the mixing of the toner after 90 minutes, the admixing test was performed, with 1g of uncharged toner being added to the charged toner. Then TURBULA mixing was made for 15~300 seconds. The T-ESC for each sample was measured according to the same proce-dure mentioned above. The charge distribution was mea-sured by E-SPART Analyzer (Hosokawa Micron Co. Ltd.).

Result

The External Additives for Toner

As reported in the NIP16, titled "The Effect of Surface Modified Fumed Metallic Oxide Additives on the Performance of Toner", the type of external additive is normally selected depending on the copying system and type of toner.[3] Table 2 shows overviews of five groups of the external additives used for toners.

Table 2. Type of External Additives used for Toner

Group	Core Material	BET [m²/g]	Primary particle size [nm]	No.	Reagent*1	ESC	MW*2 (Hydrophobicity)
1	Fumed Silica	130	16	1A	DDS	Negative	40-55
		200	12	1B			
2	Fumed Silica	50	40	2A	DMPS	Negative	60-75
		50	30	2B			
		200	12	2C			
		130	16	2D			
		150	15	2E			
3	Fumed Silica	50	40	3A	HMDS	Negative	60-70
		50	30	3B			
		200	12	3C			
		200	12	3D			
		300	7	3E			
		300	7	3F			
		300	7	3G			
4	Fumed Silica	50	30	4A	HMDS+AS	Positive	30-75
		200	12	4B	HMDS+AS		
		200	12	4C	HMDS+AS		
		50	30	4D	DMPS+AS		
		200	12	4E	DMPS+AS		
5	Fumed Titania	50	21	5A	RS	Negative	40-80
	Fumed Titania	90	14	5B	RS		
	Fumed Silica	200	12	5C	RS		
	Fumed Silica	200	12	5D	D4		
	Fumed Silica	300	7	5E	D4		

**1 DDS: Dimethyldichlorosilane DMPS: Dimethyl polysiloxane HMDS: Hexamethyldisilazane AS: Aminosilane RS: Alkylsilane D4:Octamethylcyclotetrasiloxane*

**2 MW: Methanol Wettability*

Table 3 shows the typical application data for the charge level of external additive after mixing with a non-coated ferrite carrier with a TURBULA for 5 minutes. The T-ESC differs largely depending on the type of core material, surface area, primary particle size, and surface chemistry. Table 4 shows the flow behavior of the toner (7μm) with addition of the external additive. The repose angle and the passage rate through a 45μm screen for the negative charged toner shows 51.2 degree repose angle and 0% passage rate respectively. All the toners with addition of the external additives show improvement of flow behavior. However, the flowability of the toner is largely depending on the primary particle size and surface chemistry of the external additive. In case of the positive charged toner, results indicate there is the same tendency in the effect of the external additives. From these results, the improvement of flowability is enhanced largely by a smaller particle size, treated with HMDS (Hexamethyl-disilazane) which results in trimethylsilyl groups on the surface of the external additive. It is theorized that additives based on larger particle size cores do not uniformly adhere to the toner surface, making them less effective as flow enhancers.

Table 3. Typical Application Data for the Charge Level of External Additives

	Group	Tribo Electrostatic Charge (μC/g)					
		Negative			Positive		
		-800～ -600	-600～ -400	-400～0	0～ +200	+200～ +400	+400～
Ferrite Carrier	I		1B	1A			
	II		2C 2D 2E	2A 2B			
	III	3F	3A 3B 3C 3E 3G	3D			
	IV				4A	4B 4D 4E	4C
	V			5A 5B 5C 5D 5E			

(2) Influence of the External Additive on Admixing Property

Figure 3 shows the T-ESC of a negative toner with and without external additive as a function of agitation time. The instant charge up to a consistently high level, after agitation is preferable in toner performance. The T-ESC of a toner with a negative external additive, in gen-eral, shows a stronger negative charge than that of a toner without external additive. This improved performance was observed in the toner with addition of hydrophobic fumed titania. Toner treated with this additive showed instant charge up which remained on a stable charge level after agitation. The reason behind why hydrophobic fumed titania (5B) gives better charge characteristic is presum-ably based on weaker electrostatic charge and lower electric resistance compared to fumed silica.

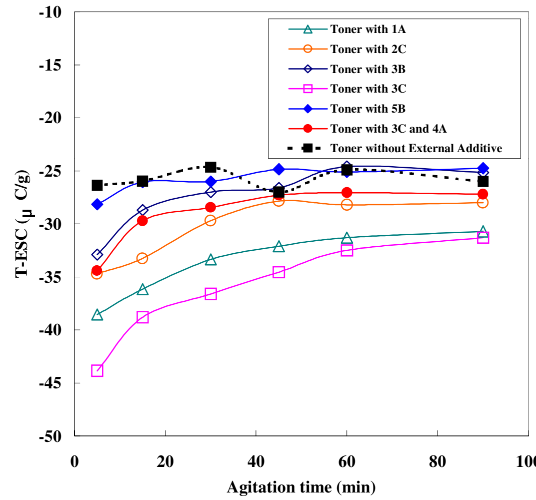

Figure 3. Tribo-electrostatic Charge (T-ESC) of a Negative Toner with and without External Additive as a Function of Agitation time

Table 4. Flow Behavior of Toner (7μm) with Addition of the External Additive

			Repose Angle*1 [degree]	Passage Rate under 45μm-Screen*2
Negative charged Silica	Group I	1A	33.9	84.0%
		1B	33.5	82.2%
	Group II	2A	47.0	13.5%
		2B	44.3	42.5%
		2C	34.2	84.5%
		2D	32.6	85.5%
		2E	33.7	83.0%
	Group III	3A	44.5	46.0%
		3B	38.5	63.0%
		3C	32.4	91.0%
		3D	33.0	89.0%
		3E	30.8	82.5%
		3F	37.5	90.0%
		3G	36.4	88.0%
	Group V	5A	40.7	81.5%
		5B	30.6	82.5%
		5C	35.7	85.5%
		5D	37.5	82.5%
		5E	30.2	86.0%
	Negative Toner		51.2	0%
Positive charged Silica	Group IV	4A	47.5	48.0%
		4B	22.5	91.0%
		4C	27.2	89.0%
		4D	43.9	41.5%
		4E	28.6	88.3%
	Positive Toner		52.2	2.6%

*1: Repose Angle : The low value means better flowability.

*2: Passage Rate under 45μm screen : The higher value is better flowability.

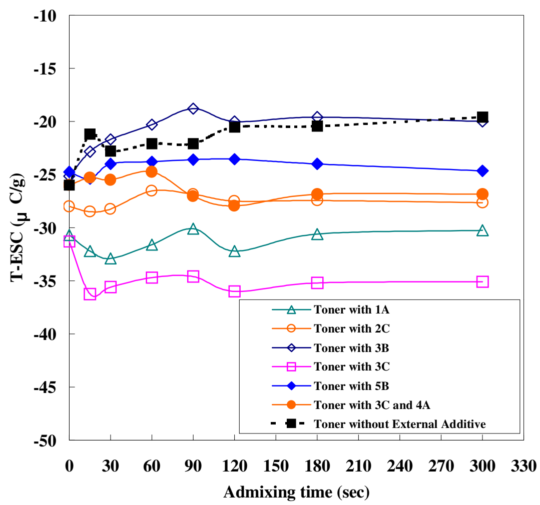

Figure 4. Admixing Property for the Toners with and without External Additive

After 90 minutes of agitation, an uncharged toner was added and then the T-ESC was measured after a short time on a TURBULA mixer (for 15~300 seconds). Figure 4 shows the admixing property for the toners with and without external additive. Admixing property, is observed to be largely influenced by the particle size and surface chemistry, as a function of mixing time. The hydrophobic fumed titania and the mixture of negative and positive charged fumed silica (3C and 4A) gives better admixing property. To control admixing property, the use of silica with a different polarity is suggested.

Figure 5(a) and (b) show the charge distributions of the toner with a hydrophobic titania and hydrophobic fumed silica. The preferable curve is supposed to contain sharper charge distribution and with reduced opposite charge area. The toner with hydrophobic titania shows sharper charge distribution and reduced opposite charge area.

Influence of the External Additive on the Performance of Color Toner

Figure 6 shows the T-ESC of a color (yellow) toner with and without an external additive as a function of agitation time. Formulators have requested instant charge up and less fluctuation of charge after agitation in toner performance. The T-ESC of the color toner with hydrophobic titania (5B) becomes weaker with agitation, however, the charge level is relatively constant as compared with the toner with hydrophobic fumed silica (2C and 3C).

The admixing behavior of the color toner with an external additive is also evaluated. The performance of the toner with hydrophobic fumed titania shows nearly the same behavior as the toner itself, but the toner with hydrophobic fumed silica shows slightly strong negative charge. Results show that admixing property of toner can be improved by the selection of a suitable external additive.

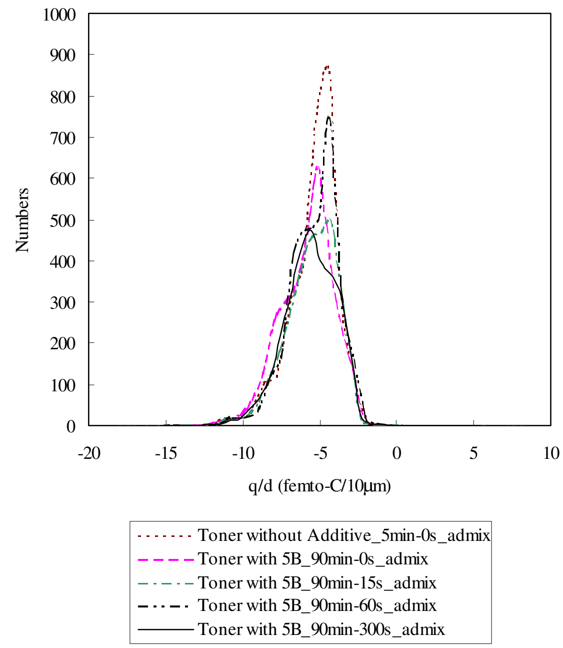

Figure 5(a). Charge Distribution of Toner with Hydrophobic Titania (5B) and without External Additive

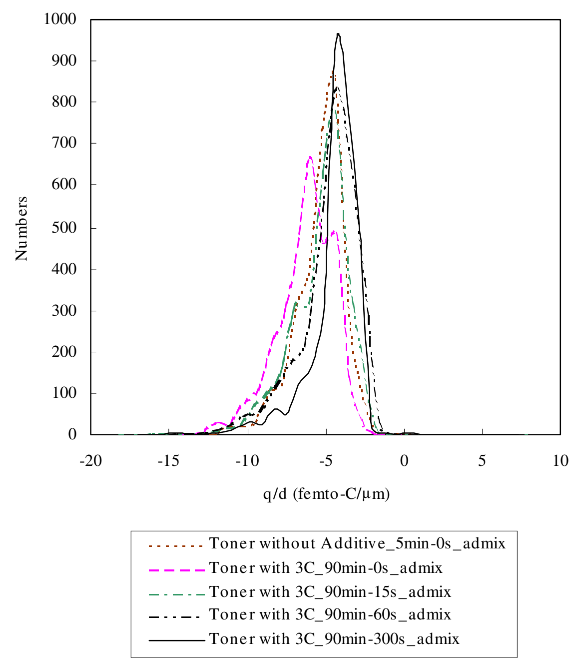

Figure 5(b). Charge Distribution of Toner with Hydrophobic Fumed Silica (3C) and without External Additive

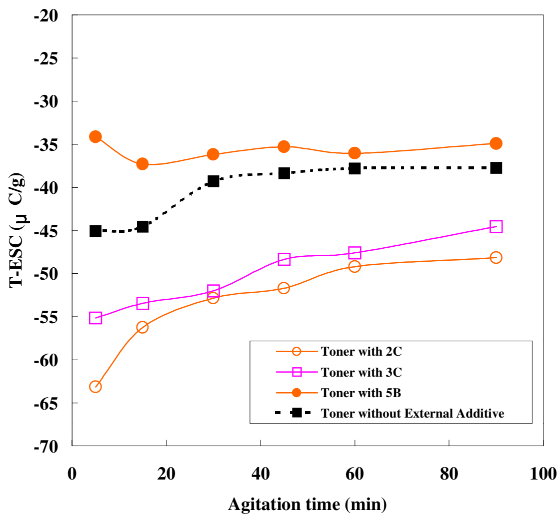

Figure 6. Tribo-electrostatic Charge of a Color (Yellow) Toner with and without an External Additive as a Function of Agitation Time

Conclusion

T-ESC of the toner using a non-coated ferrite carrier and a variety of external additives have been documented in this study. Results suggest that the use of fumed silica with different polarity and combinations with fumed titania improves charge stability, admixing property, and charge distribution pattern of toners.

Reference

1. H. Akagi et al, *The 9th International Congress on Advance in Non Impact Print on Technology Japan Hard Copy* (1993).
2. M. Murota, H. Shirono, *The 8th Annual Conference of the Korea Society for Imaging Science*, pg. 30. (1997).
3. M. Murota, E. Komai and H. Shirono, *IS&T's 16th International Conference on Digital Printing Technologies*, pg. 608. (2000).
4. R. J. Nash, M. L. Grande, R. Jiles and R. N. Muller, *IS&T's 16th International Conference on Digital Printing Technologies*, pg. 591. (2000).

Biography

Maria R. Nargiello-Tetreault received her BS degree in both Chemistry and Biology with a minor in Environmen-tal Science from Upsala College in E. Orange NJ in 1984. She has worked for Degussa Corporation as Technical Applications Manager for 18 years. She is responsible for coordinating technical Service and applied research for NAFTA countries in support of Aerosil Fumed silica and fumed oxides for several major industrial applications. Paints / coatings / resins and toners are target industries for support.