Comparison between De-agglomerated and Traditional Fumed Silica External Additives and Their Performance in Toner Formulations

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Abstract

De-agglomerated hydrophobized fumed silica is compared to corresponding traditional agglomerated fumed silica as an external additive for electrophotographic toners. The first finding is that the Tribo-Electrostatic Charge (T-ESC) of toner treated with de-agglomerated silica is as strong as that with traditional silica after agitation. Charge distribution analysis however indicates faster charge-up for de-agglomerated silica. These characteristics apply for both milled conventional toner and chemically produced toner and are explained by the superior dispersibility of de-agglomerated silica. The shelf-life (storage stability) was also tested and demonstrated that de-agglomerated silica maintained performance under normal appropriate storage conditions.

1. Introduction

One certainty of the current market for high speed and high quality electrographic printing/copier machines is that as performance demands ratchet up so do requirements for superior raw materials used in toners. A critical component to this evolution has been the development of various products based on silica, titania and alumina as electrophotographic developer external additives. These additives act as powerful influences on the charging and flow for the developer; a behavior defined by the interplay of such fundamentals as the nature and size of the core particle and the degree and type of particle surface modification.

This paper presents application data for another key parameter: *agglomeration.* While all pyrogenic oxides: fumed silica, titania, and alumina exhibit nano-structured aggregation of primary particles, agglomeration is the result of softer inter-particle interactions and is significantly influenced by the oxide surface modification. On a practical level, the effectiveness and efficiency of breaking down agglomeration and dispersing the aggregates over the toner particle surface has a large impact on the ultimate performance and economy of a toner/external additive formulation.

2. Experimental procedures

2.1. Materials

2.1.1. Core materials

The surface modified fumed silica used, supplied by Evonik Degussa GmbH and NIPPON AEROSIL CO., LTD., was produced by familiar processes previously described [1]. The pyrogenic process to make fumed silica has great versatility and can produce average primary particle sizes ranging from 7 to approximately 100 nm [2]. In this study the average particle size is 12 nm in diameter [Table 1].

Table 1: BET and Particle Size of Fumed silica

Product name	BET surface area [m^2/g]	Primary particle size [nm]
AEROSIL® 200	200	12

2.1.2. Surface Treatment Agent

Surface treated fumed silicas have long been used as toner external additives. In earlier technology, the treated silica provided hydrophobicity to the toner particle and thereby ensured good powder flow. It was soon apparent that surface modification also greatly influenced the nature, speed, and stability of tribo-electric charging for toner and so a variety of reagents have been employed [3]. Of the three most commonly encountered: DDS (dimethyldichlorosilane), HMDS (hexamethyldisilazane), and PDMS (poly-dimethylsiloxane) we will focus in this study on the last. Additives with PDMS treatments are of interest because of their very high hydrophobicity but also present challenges from the nature of their agglomeration: PDMS agglomerate particles tend to be large and their agglomeration forces tend to be greater.

2.1.3. Aggregation and agglomeration

It was recognized early in the development of the pyrogenic process that the powders formed were made up of complex structures resolvable to the submicron level. The so-called primary particle of fumed oxides averages in size from 7 to 100 nanometers depending on the manufacturing conditions, however these particles are always found in an aggregated state that is to the most part non-divisible. Aggregates are characterized with strong forces between primary particles and typically average in size between 100 and 300 nanometers.

There is another level of structure always encountered that is termed agglomeration. Agglomeration is the result of weak forces between aggregates that nevertheless results in macro-structures ranging from a few to many microns in diameter. This knowledge of structure is important since the utility of fumed oxides depends on the complete break-down of agglomeration and the homogeneous dispersion of aggregates. Fortunately, this can be achieved by the external application of shear. The dynamics of these structural changes can be examined by a laser scattering particle sizing technique further described in Section 3 below.

In this investigation, regular agglomerated structure PDMS treated fumed silica, RY 200, and special process de-agglomerated grade, RY 200 L were used. The core particle, PDMS treatment type, and treatment level were all held constant for this study; only the agglomeration structure was changed.

Table 2: Surface treated external additives used for this investigation

	RY 200	RY 200 L
Core material/ Surface Treatment	AEROSIL® 200/ PDMS	AEROSIL® 200/ PDMS
Agglomerate Structure	Regular Agglomeration	De-agglomerated
BET [m²/g]	110	110
Bulk Density [g/L]	ca. 40	ca. 20
Carbon Content [wt%]	5.0	5.0
Hydrophobicity [%]	> 98	> 98

2.1.3. Toner formulations

For this investigation 8 micron polyester negative black toner was blended with 1 wt% of the surface modified silica using a Henschel-type mixer.

2.2. Methods

2.2.1. Dispersibility (Particle size distribution)

The particle size distribution of the dispersed external additive on a toner particle surface is a notoriously difficult measurement. We sought an indirect means that could approximate especially the dynamic process of additive dispersion. In this method a sample of the additive powder is mixed in ethanol for ten minutes with a 300W Ultrasonic homogenizer and the particle size distribution is measured (Horiba Laser Scattering Particle Size Distribution Analyzer LA-920). By carefully controlling the time and conditions for the samples in ethanol, the relative dispersibility can be judged.

2.2.2. SEM analysis of toner mixtures

A Scanning Electron Microscopy (SEM) image was used to check the dispersibility of fumed silica aggregates on the toner particle (Hitachi SEM SU8000, samples coated using an osmium plasma).

2.2.3. Tribo-Electrostatic charge (T-ESC)

T-ESC was measured using a blow-off type electrostatic charge meter (Kyocera Chemical TB-220). A sample of toner (2 g.) was combined with a non-coated ferrite carrier (48 g.) and agitated with a Turbula mixer. All sample preparation and measurement was carried out in a constant temperature/constant humidity room.

2.2.4. Charge distribution

The charge distribution was determined with a q-test (Epping GmbH). The toner formulation was agitated with non-coated ferrite carrier by Turbula mixer before measurement.

3. Results and discussions

3.1. Dispersibility

Using our indirect technique to characterize dispersibility, we recorded the particle size distribution for the agglomerated silica in ethanol vs. that for the de-agglomerated silica [Figure 1]. The combined data plot clearly indicates that the de-agglomerated product (RY 200 L) can be dispersed more readily than the agglomerated (RY 200). Note that the average particle size for the well dispersed de-agglomerated additive is between 100 and 300 nanometers, the typical aggregate size. This implies that the de-agglomerated grade more easily disperses to the fullest extent possible. Also note that the regular grade shows a significant fraction of agglomerated silica (i.e. particle fraction between 10 and 80 micron) even after sonication. If the sonication power or length of time is increased, the regular sample will be driven to the fully dispersed state too, so for the purposes of this study it is important to adjust the test conditions such that distinctions can be made.

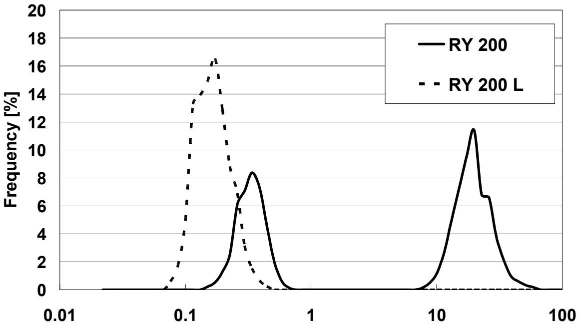

Fig. 1 particle size distribution

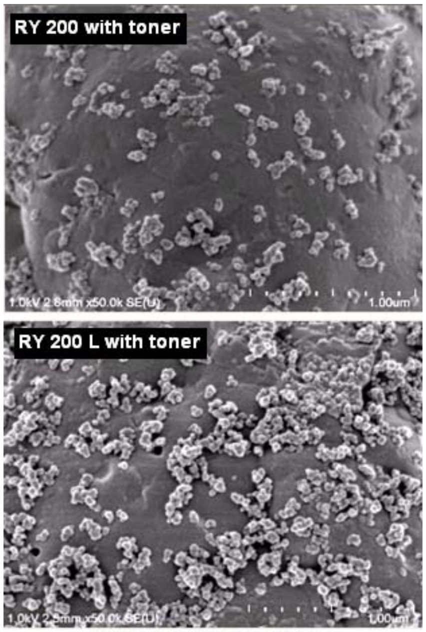

Fig.2 SEM image of toner

Figure 2 shows SEM images of toner mixed with agglomerated and de-agglomerated grades, respectively. The larger amount of external additive on the toner surface observed for the de-agglomerated sample is direct evidence of the superior dispersibility possible from de-agglomeration. With matching formulations and mixing conditions, the regular agglomerated grade can result in free isolated silica whereas the de-agglomerated grade is fully dispersed on the toner surface.

3.2. Charge stability and charge distribution

Charge stability was evaluated by tribo-electrostatic charge and charge distribution as a function of agitation time [Figures 3 & 4]. The plots show that while there is a difference in initial charge related to agglomeration, the differences are less distinct upon mixing. This would be expected as the two samples have in effect the same formulation. Importantly, the de-agglomerated grade clearly demonstrates tribo-charge stability, a sharper charge distribution, less wrong sign toner, and a faster charge-up.

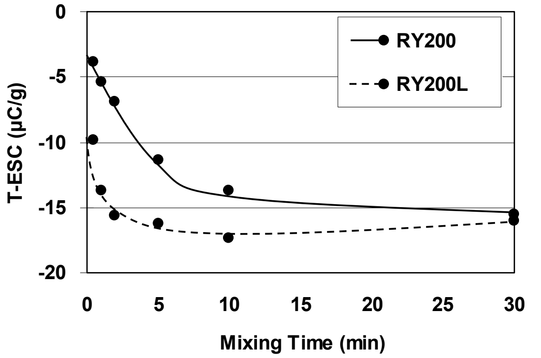

Fig.3 Tribo-electrostatic charge of toner with silica

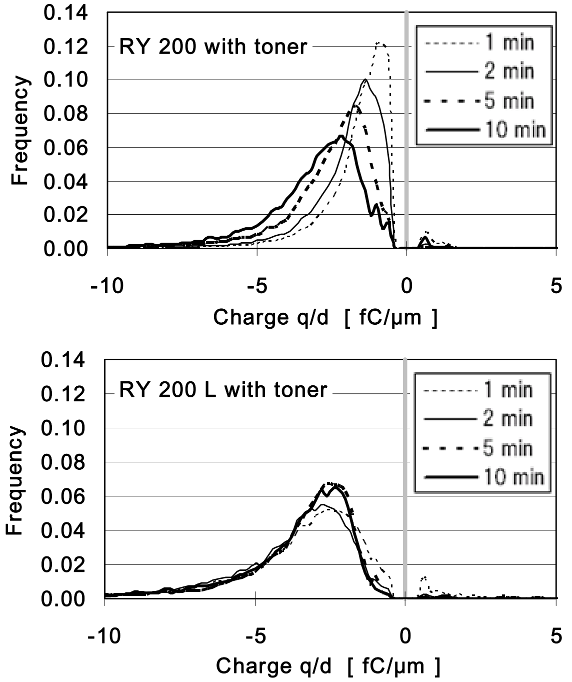

Fig.4 Charge distribution of toner

3.3 Stability of de-agglomerated silica

A final, practical question arises whether de-agglomeration is itself steady or reverts to the original agglomerated state upon storage of the product. The de-agglomeration technology represented here was tested by real-time storage and did not show re-agglomeration after two years under normal warehouse conditions. All properties (physico-chemical analytical along with the measured dispersibility) remained unchanged. Further studies on the mechanism of de-agglomeration and re-agglomeration remain for future research.

4. Conclusions

The agglomeration structure of fumed silica can be manipulated to benefit in superior external additives for electrophotographic toners. While only one example was presented in this paper, this technology can be applied to a broad array of nano-structured materials. The de-agglomerated product shows better dispersibility, faster charge-up behavior, less wrong sign toner, and sharper charge distribution than the regular agglomerated grade and similar charge strength. Finally, under normal long-term storage the de-agglomerated product fully maintained its attractive properties.

References

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Author Biography

Yuki Amano received his Masters degree in Functional Materials Science from Saitama University (Japan) in 1998. He joined Mitsubishi Materials Corporation in the same year. Since 1999, 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.