

The Surface Modification of Silicas on the Free Flow and Charging Properties of Monocomponent Magnetic Toners

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Abstract

The efficient reduction of the high surface energy of virginal flame born silica by silylation of its active surface silanol groups is an essential task for a free flow additive in a toner system. A series of surface modified, i.e. silylated silicas, were prepared using functional organosilicon compounds. Characteristic features of the chemical surface modified silicas are compared to experimental findings of silica loaded model toners with regard to toner free flow and charging. The toner properties are influenced by the silica properties and also by the mixing process of the silica-toner blend. We discuss our results with respect to silica surface properties and the impacts of the silica-toner mixing process.

Introduction

Numerous papers and patents deal with the benefits of synthetic silicas as a free flow additive in toners.^{1,2} Fumed silicas based on a flame process are of first choice, however. The very particular process of flame hydrolysis of chlorosilanes to yield fumed silica is given in Figure 1.

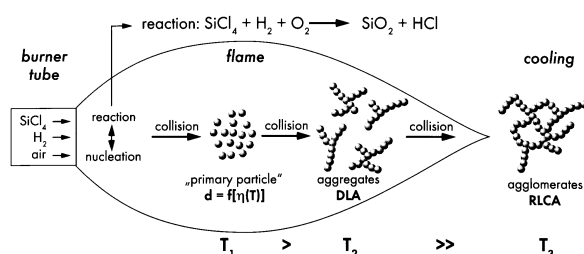


Figure 1. Flame process of fumed silica.

In the flame “primary particles” of amorphous silicon dioxide are formed. They are sintered together to build up stable submicron sized “aggregates” of fumed silica. Leaving the flame, these aggregates form micron sized “agglomerates” by physico-chemical surface interactions. In a two-component system, e.g. a silica-toner blend, these agglomerates will be dispersed down to form aggregates, when using an appropriate mixing technique. Further characteristic features of fumed silica are the extremely high and active surface area ranging from 100 - 400 m²/g and the low bulk density of the product. Typical density values for

aggregates are of about 0.7 mg/cm³ and for agglomerates of about 0.1 mg/cm³, respectively.

Model of Toner Deagglomeration

In a recent report experimental data were presented which demonstrate that newly designed silica grades can be used to improve toner free flow and charging stability. These data underline the necessity of a high hydrophobicity of the free flow additive and, additionally, the advantage of distinct chemical surface functions on the modified silica.³ However, the two components of the silica-toner mixture differ in a large part of their material properties, e.g. density, particle size, surface area and surface chemistry. Therefore, segregation may occur and would counteract the mixing process. Distinct impacts on the toner performance with regard to toner free flow and toner charging could be the consequence. The interaction of the toner particles and the silica additive is of main importance in order to control the stability and properties of silica-toner mixtures. However, the mechanisms of interactions between toner and silica are still an open topic of discussions. Toner-silica interactions are influenced by both the silica surface modification and the energy of the mixing and dispersion process. In this report, we compare two mixing techniques of basically different energy inputs along with different surface modifications of fumed silica additives in negatively and positively charged monocomponent toners. Toner properties are discussed with regard to the quality factors free flow and charging of the total toner system.

Experimental

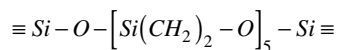
Fumed Silica Grades

All silica grades used were prepared at WACKER-CHEMIE GmbH. The starting materials, i.e. hydrophilic silicas and all organosilicon compounds for surface modification, were received from WACKER-CHEMIE GmbH. For laboratory scale, the chemical surface modification was performed as follows: Fluidizing 100 g of a hydrophilic fumed silica with a BET surface area of 200 m²/g in a lab-sized flow-bed reactor and injecting 10 g of water, 20 g of a OH-terminated polydimethylsiloxane with a viscosity of 30 mPas at 25°C dissolved in 20 g of 2-propanol and 10 g of the functional organosilicon compound at a temperature of 70°C. The reaction with the active silica surface silanol groups was completed by heating up to 200°C for 2 h. To

avoid degradation of heat sensitive organo silanes, e.g. amino functions, all reactions were carried out under nitrogen. The silica sample characteristics are given in Table 1.

Silica Samples and Silica Surface Functions

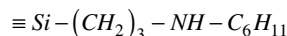
Silica A: dimethylsiloxo



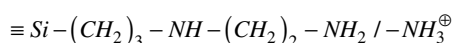
Silica B: amino-ethyl-amino-propyl



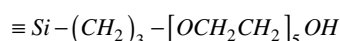
Silica C: cyclohexyl-amino-propyl



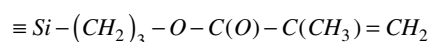
Silica D: amino/quart. ammonium



Silica E: polyethylene oxide



Silica F: methacryloxy



Silica G: sodium phosphinato

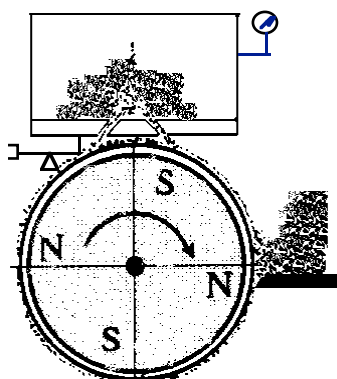
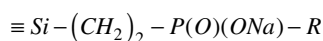


Figure 2. Schematic illustration of the Q/M-Mono DEVICE with toner charging and toner mass flow determination (EPPING GmbH, D-85375 Neufahrn, Germany). A detailed description of the device was given elsewhere.³

Toner Flow and Charging Testing Systems

The toner charging and free flow after dry blending with the surface modified silicas were analyzed by a new device recently developed by Epping (see Figure 2). This device combines standard charge-to-mass measurement techniques with the capability to simulate the toner mass release from the activation unit of a copier machine to the PC. The numerical data for the toner flow were obtained by balancing the toner mass flow from the activation unit to a removable measurement cell. The repeatability analysis to evaluate the equipment variation provided an error < 5%. Toner systems used were of the crushed type and the binder resins of both toners were of the type styrene/acryl-

ics. The mean particle size for the positive toner system was found to be 11 μm , and for the negative toner system 15 μm , respectively.

The numerical q/m-values for the silica charging are easily measured by using a common charge-to-mass unit (hard-blow-off conditions, device from EPPING GmbH). The silica charging was measured after an overall mixing time of 5 minutes on a roll mill vs. an 80 μm ferrite carrier. The silica concentration in the silica-ferrite mixture was 1 wt%. The silica charging data are given in Table 2.

To simulate the aging of a given toner in a copy machine, the data from the Q/M-MONO device were recorded after 20 minutes of activation on the developer roll at RT 23°C and R.H. 50%.

Comparative Testing of Mixing Equipment

The particular importance of the mixing quality for the overall performance of a toner is well known. This includes the dry blending of silicas with the toner. In this study we report on tests with two different types of batch mixers which differ markedly in their FROUDE numbers.⁴

Mixer Type 1 (FROUDE number $Fr \gg 7$)

High speed rotating high shearing mixer $v_1 = \omega r = 65$ m/s; $\omega = 2 \pi f$, $f = 415$ 1/s; drum inner radius $r_1 = 0.025$ m, total mixing time $t = 3$ min, the mixing was interrupted after each 15 sec for 20 sec to avoid toner damage, temperature control $T < 40^\circ\text{C}$.

Mixer Type 2 (FROUDE number $Fr = 0.6$)

Low rotating mixer, superposed by translation and inversion movements. $v_2 = \omega r = 0.4$ m/s, $\omega = 2 \pi f$, $f = 3$ 1/s, $r_1 = 0.025$ m, mixing time $t = 30$ min.

Volumetric filling level for both systems was 50%. Concentration range was 0.2 to 0.8 wt% silica loading.

Results and Discussion

Silica Characteristics

Table 1. Fundamental characteristics of silica grades.

silica	critical surface energy γ_s^c [*] mJ/m ²	carbon content %	residual SiOH [†] %	BET [‡] surface area (m ² /g)
A	29	4.5	16	131
B	33	7.9	19	91
C	33	9.8	16	88
D	31	7.5	15	92
E	38	7.1	25	94
F	38	7.5	31	107
G	31	7.2	13	84

* Critical surface energy γ_s^c was analyzed by wetting the silica with various contents of methanol in water

† Relative silanol content in respect to hydrophilic silica (200 m²/g, 2 SiOH / nm²) was calculated after potentiometric titration according to Sears, consumption V (ml) of 0.1 n NaOH in MeOH:WATER=50:50; SiOH=(1-(V_{silylated}) / (V_{hydrophilic})) 100.

‡ BET surface area, using nitrogen at 78 K. The low BET value is related to the low surface energy after surface modification.⁵

Silica Charging

The tribocharging of the surface modified silica versus the ferrite carrier is given in Table 2. The high tribocharging efficiency of the silicas is evident. Functionalizing the silica surface with amino and quart. ammonium groups

Table 2. Charge-to-mass data of modified silicas vs. ferrite

Silica A dimethyl siloxo	Silica B amino ethylaminopropyl	Silica C cylohexyl aminopropyl	Silica D quat. ammonium	Silica E polyethylene oxide	Silica F methacryloxy	Silica G sodium phosphinato
-600 ($\mu\text{C/g}$)	+200 ($\mu\text{C/g}$)	+120 ($\mu\text{C/g}$)	+290 ($\mu\text{C/g}$)	-410 ($\mu\text{C/g}$)	-400 ($\mu\text{C/g}$)	-430 ($\mu\text{C/g}$)

provides a distinct positive charging behavior. Hydrophobization of the silica with dimethylsiloxo groups and oxygen functions lead to high negative tribocharging. However, organic functions containing C - O, C = O, C = C or P = O groups reduce the high negative charging of the silica in comparison to the silicon dioxide bulk covered by a dimethylsiloxo layer only.

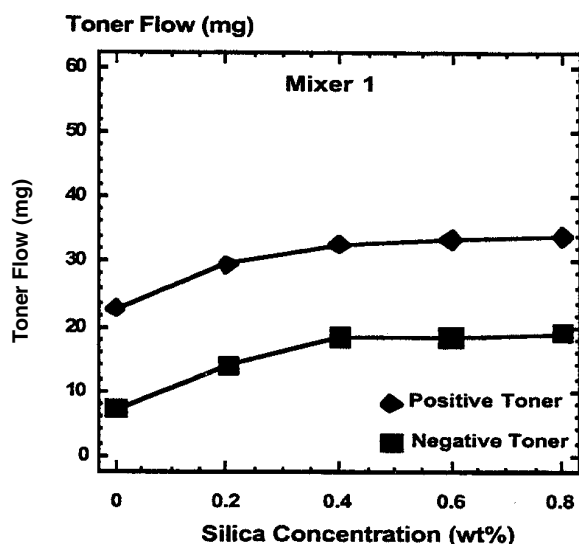


Figure 3. Toner flow versus silica concentration. Rectangles represent Silica A in the negative toner, rhombuses represent Silica B in the positive toner. Mixing process with Mixer 1, mixing time 3 min.

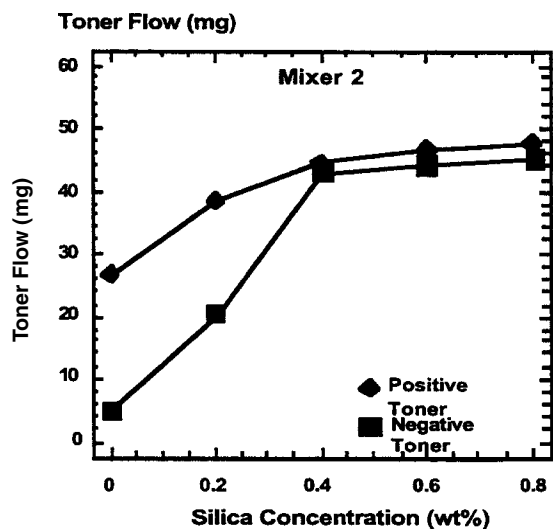


Figure 4. The toner flow versus silica concentration. Rectangles represent Silica A in the negative toner, rhombuses represent Silica B in the positive toner. Mixing process with Mixer 2, mixing time 30 min.

Free Flow of Silica-Toner Mixtures

In Figure 3 different rates of the toner free flow are shown for silica-toner mixtures using Mixer 1 at 5 increasing levels of silica concentrations.

In Figure 4 different rates of the toner free flow are shown for silica-toner mixtures using Mixer 2 at 5 increasing levels of silica concentrations.

Obviously, the increase of toner free flow with growing silica concentrations is most pronounced between 0.2 and 0.6 wt% of silica. In order to detect, with highest sensitivity, quality differences of silica-toner mixtures, we decided to use a silica loading of 0.4 wt% for further investigations.

To prove the significance of the observed differences between Mixer 1 and Mixer 2, with respect to the toner flow, an analysis of the batch-to-batch variation at a fixed silica concentration of 0.4 wt% was performed. For this purpose, we sampled 10 batches of the appropriate silica-toner mixture, prepared by using Mixer 1 and Mixer 2, respectively.

Figure 5 shows the graphical display of the distribution of toner flow data for the negative toner system with Silica A along with the median, the range, and the extreme values for each mixer, by using box-and-whisker plots.

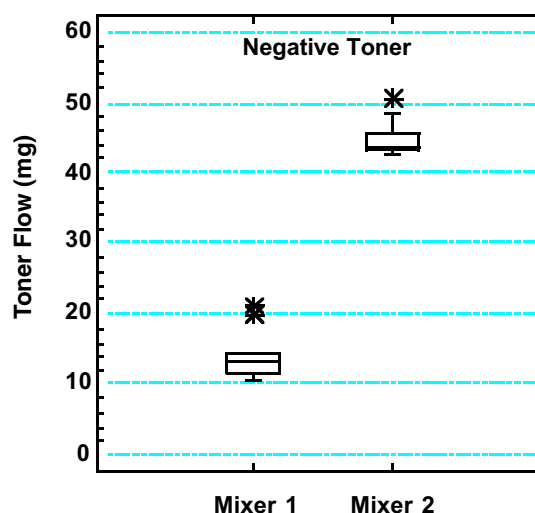


Figure 5. Distribution for the free flow data as a function of the mixing process, Mixer 1: FROUDE No. $\gg 7$, Mixer 2: FROUDE No. = 0.6; silica type = Silica A, silica loading in the negative toner was 0.4 wt%, sample size = 10.

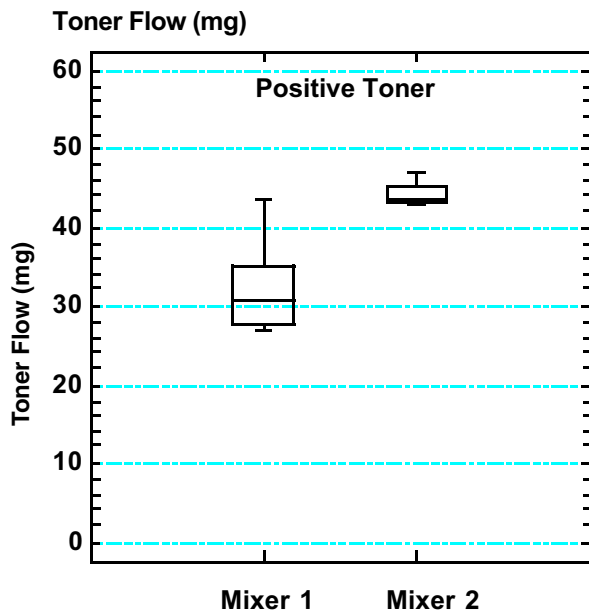


Figure 6. Distribution for the free flow data as a function of the mixing process, Mixer 1: FROUDE No. $\gg 7$, Mixer 2: FROUDE No. = 0.6; silica type = Silica B, silica loading in the positive toner was 0.4 wt%, sample size = 10.

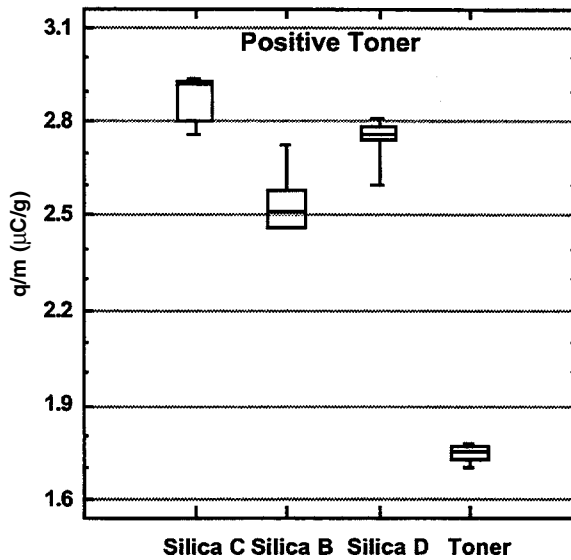


Figure 8. Variation of charge-to-mass ratio of positively charged model toners with respect to silica surface modification; silica loading 0.4 wt%; dry blending by Mixer 2.

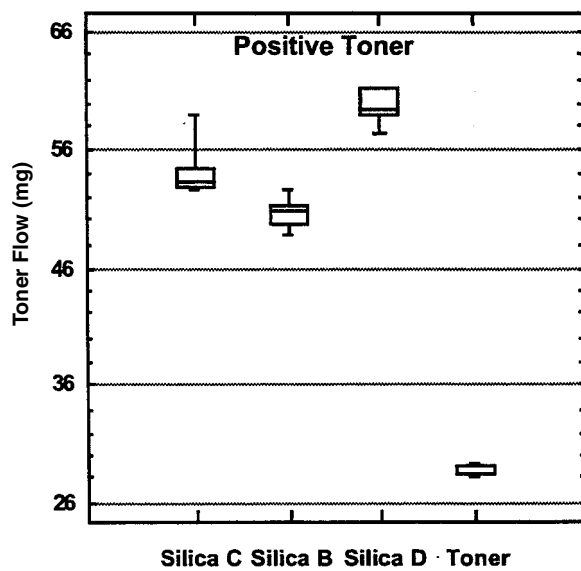


Figure 7. Variation of toner free flow of positively charged model toners with respect to silica surface modification; silica loading 0.4 wt%; dry blending by Mixer 2.

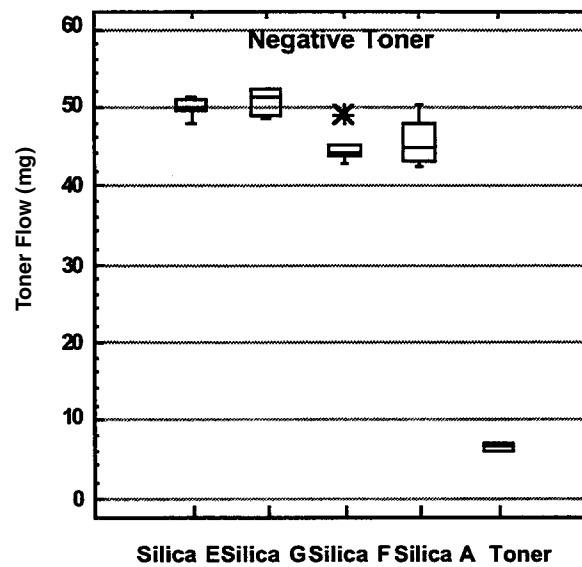


Figure 9. Variation of toner free flow of negatively charged model toners with respect to silica surface modification; silica loading 0.4 wt%; dry blending by Mixer 2.

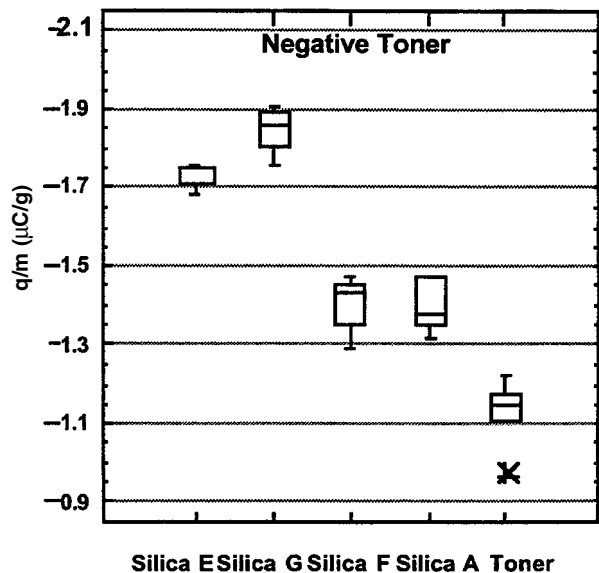


Figure 10. Variation of charge-to-mass ratio of negatively charged model toners with respect to silica surface modification; silica loading 0.4 wt%; dry blending by Mixer 2.

Figure 6 shows the data for the positive toner system blended with Silica B.

It is obvious that the mean values of the toner flow differ significantly: Mixer 1 produces silica-toner mixtures with lower free flow compared to those produced with Mixer 2. Additionally, the variation in the toner free flow data from Mixer 1 is higher compared to those provided by Mixer 2, in particular as with regard to the positive toner system.

From our results, we may conclude that a mixing device based on gravity and powder friction provides advantages over devices applying high centrifugal forces and mechanical impacts on the silica-toner mixture. This reveals that the silica-toner interactions are dominated by physico-chemical surface interactions. Silica surface interactions are also controlled by the chemical functionalization of its surface. To detect distinct differences in silica performance resulting from the silica surface modification the silica loading was fixed to 0.4 wt% and the dry blending was performed by using Mixer 2, respectively. The experimental results of silica loaded model toners with regard to toner free flow and charging are shown in Figures 7 to 10.

As it can be seen from Figure 7, the improvement in free flow of the positively charged model toners is more than 100%, using surface modified silica. With regard to silica loaded model toners, the use of secondary alkylated

amino functions, see Silica C, is more preferable than simple primary amino groups, see Silica B. However, high performance toner properties is only achieved by a combination of amino- and quat. ammonium groups for silica surface modification, see Silica D. The surface modification of the silica does not have such a distinct impact on the toner charging, see Figure 8. As shown in Figure 9, the enhancement in free flow of the negatively charged model toners is up to five times, when adding surface modified silica. Functionalizing the hydrophobic silica surface by C - O and P = O groups enhances the toner free flow. This correlates well with higher chargeability of the silica-toner system, see Figure 10.

Conclusions

We investigated the influence of silica surface modification on free flow and charging of two monocomponent magnetic toner systems, positively and negatively chargeable, respectively. A high surface hydrophobicity of the silica in use is a main requirement to achieve satisfying free flow and charging behavior of the toner systems. For the positive charging toner system we found that combining amino and quaternary ammonium functions provide further advantages. In the negative charging toner system the free flow is enhanced by C - O and P = O functions grafted on a highly hydrophobic silica surface.

Comparing high “hard” and “soft” dry blending techniques, described by FROUDE numbers < 1 and $>> 7$, respectively, we conclude that a soft contact of the surface modified silica and the toner resins will lead to more favorable toner properties. From our results we propose a model of physico-chemical interactions between the silica particles and the toner surface, rather than incorporation of the silica particles into the toner resin.

References

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