

The Role of Water in the Triboelectric Charging of Alkylchlorosilane-Treated Silicas as Toner Surface Additives

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Abstract

Fumed silicas are commonly used to modify the charge and flow of toners. However, little work has been done to understand the origin of relative humidity (RH) sensitivity of toner charging with silica surface additives. In this work, toner triboelectric charging using a hydrophilic silica and silicas modified by a surface-attached long-chain hydrocarbon or fluorocarbon silane was studied as a function of silica water content. The silica water content was measured by infrared spectroscopy. It is shown that the toner charging is controlled by the silica water distribution. Water is necessary for charging of hydrophobic silica; the charge increases with increasing water content up to 20% RH. Above 20% RH, the charge decreases linearly with water content, and this transition at 20% RH coincides with a change in the water adsorption isotherm. In contrast, the charge of hydrophilic silica decreases with relative humidity. Linear extrapolation of the toner charge with all silicas reaches a common point of zero charge at about 2.4 ± 0.4 molecules $\text{H}_2\text{O}/\text{nm}^2$. The drop in charge with relative humidity is consistent with a leaky dielectric model, where charge is dissipated by the formation of a contiguous water layer on the silica. On the hydrophobic silicas, this transition to a contiguous water network occurs near 20% RH.

Introduction

In xerography, fumed silica particles are blended onto the surface of the toner particles to improve the flow of the toner,¹ to control the triboelectric charge level,²⁻⁵ and to reduce the adhesion of the toner particles to substrates.⁶ In essence, the toner surface takes on the characteristics of a silica surface. Therefore, in principle, it should be possible to control the properties of the toner in a well-defined manner by a controlled modification of the surface of the silica.

Methylchlorosilanes are commonly used to modify fumed silicas through a high-temperature gas-phase reaction:



The replacement of the surface hydroxyl group with a methyl silyl group renders the silica hydrophobic in nature. These hydrophobic silicas are commercially available and are preferred to the untreated hydrophilic silicas in toner

additives because they impart better flow properties.⁴ Furthermore, the methyl silylated silicas typically give a triboelectric charge that is higher in value but one that is very sensitive to changes in relative humidity (RH).⁴

The triboelectric charge (in $\mu\text{C}/\text{g}$) measured at low relative humidity is usually higher (more negative) than the values measured at high relative humidity. One aim of our activity is to produce toner additives with the highest negative triboelectric charge and lowest relative humidity sensitivity. Thus silicas containing a minimum amount of surface water (i.e., hydrophobic silicas) would be expected to perform the best. In a previous study,⁵ we compared the triboelectric charge of commercial methyl silylated silicas at 20% RH with the charge obtained using modified silicas containing either a long alkyl chain or a fluoro-alkyl chain silane. The long alkyl chain and fluoro-alkyl chain treated silicas were selected because it has been well established (from contact angle measurements^{8,9}) that these materials are more hydrophobic than their methyl silylated counterparts. Thus it was expected that a long alkyl or fluoro-alkyl silylated fumed silica should be more hydrophobic than the commercial methyl silylated silicas and thus should impart more favorable triboelectric and flow behavior. This earlier work showed that a covalent Si-O-Si surface bond between the alkyl silane and the surface was important in defining the triboelectric behavior of the silica. However, the relationship between adsorbed water and the triboelectric charge was not clear. There was no correlation between the total amount of adsorbed water (measured at 20% RH) and the triboelectric charge.

The current work now makes use of these modified silicas containing covalently attached silanes to explore the relative humidity dependence of triboelectric charging, thus to understand better the role of surface water. In particular, infrared (IR) spectroscopy is used to measure the surface water content on the modified silica as a function of relative humidity, and these data are then correlated with the triboelectric charging of the toner.

Experimental

The fumed silica used was Aerosil 380 (A380), a fully hydroxylated fumed silica from Degussa (Teterboro, NJ) with a measured (BET N_2) surface area of $375 \text{ m}^2\text{g}^{-1}$. $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiCl}_3$ (FTS) and $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ (OTS)

were obtained from Petrarch (Piscataway, NJ). Triethylamine (TEA) and cyclohexane were obtained from Aldrich (Milwaukee, WI).

The silica denoted as A380/TEA/OTS was prepared using a two-step amine-promoted process.¹⁰ The amine-promoted reaction is used to attach the OTS to the silica by way of a surface Si-O-Si bond. The cell used to prepare the treated silica is described in detail elsewhere.¹¹ A380 (500 mg) was evacuated (10^{-6} torr) for 15 min, then exposed to an excess of triethylamine vapor (TEA) for 5 min, followed by evacuation for 5 min. A suspension of 500 mg A380 dispersed in cyclohexane (the cyclohexane was added under vacuum) was stirred for 30 min, followed by the addition of 140 mg OTS. The suspension was further stirred for 1 hr. filtered, then washed several times with methanol to remove the salt, triethylammonium chloride, and finally allowed to dry by evaporation.

The sample denoted A380/FTS was prepared by adding 175 mg FTS to a suspension of 500 mg A380 dispersed in cyclohexane (added under vacuum). The suspension was stirred for 1 hr. filtered, and then allowed to dry by evaporation. In the case of FTS, the formation of a surface Si-O-Si bond does not require the two-step amine-promoted reaction.¹²

No difference was found between a sample prepared using the two-step process and the A380/FTS sample with respect to triboelectric behavior.⁵ The amounts of FTS and OTS were chosen to be equivalent to the hydroxyl density on the silica (about 3.0 OH/nm^2).

The silicas were blended on Xerox 1075 toner by roll milling with steel shot for 35 min. In practice, triboelectric charge depends on silica coverage. All experiments were conducted at 100% coverage¹³ (based on silica and toner surface areas) to eliminate this coverage dependence. Uniformity in coverage from sample to sample was confirmed by scanning electron microscopy. The Xerox 1075 toner (2 wt%) with surface additives and Xerox 9200 carrier were conditioned overnight at an RH between 5 and 80%, before charging in a sealed bottle for 15 min on a roll mill. The toner charge was determined by using the standard total blow-off tribo.¹⁴

The amount of water on the silica was measured by IR spectroscopy, using the cell shown in Fig. 1. A self-supporting 1-in. disk of silica (100 mg) was prepared, using minimal pressure (50 p.s.i.), and placed in the center of the IR cell. The cell was mounted in the spectrometer, and air at various relative humidity values was passed through the cell. The relative humidity of the air was measured at the air outlet, using a Vaisala HMP 35B relative humidity probe (Woburn, MA) controlled by an HMI 36 data processor. The accuracy of the relative humidity probe was $\pm 1\%$. The amount of adsorbed water was determined from the integrated intensity of the H_2O deformation mode at 1628 cm^{-1} (see Fig. 2). The band at 1628 cm^{-1} is superimposed on a region containing various Si-O overtone and combination modes. The overtone and combination bands were removed by subtracting a spectrum of the silica disk subjected to evacuation at 10^{-6} torr for 30 min. The spectrum of the evacuated silica was recorded at the end of each experiment. The intensities of the Si-O overtone and combination modes were used to compute the amount of silica in the IR beam and to compensate for any sample-to-sample variation in this amount.

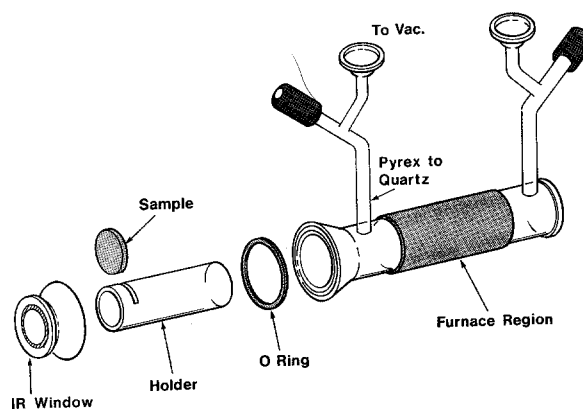


Figure 1 IR cell used to measure adsorbed water on silica.

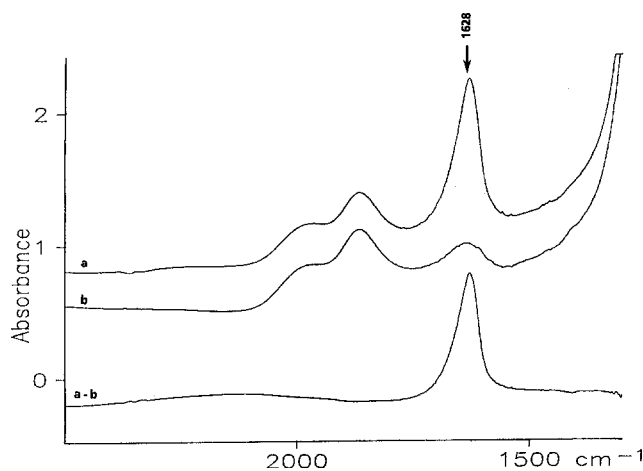


Figure 2. IR spectra at (a) 50% RH, (b) after evacuation (10^{-6} torr) for 15 min, and (c) (a) - (b).

For each measurement, the relative humidity of the air was held constant and spectra were recorded until there was no detectable change in the intensity of the 1628 cm^{-1} band. In practice, this required about 5 min. Errors due to localized heating by the IR beam were negligible. This was tested in a separate control experiment, in which the IR beam was attenuated by 90%, using a neutral density filter. In this case, the intensity of the 1628 cm^{-1} band recorded with the neutral density filter was the same as the intensities obtained in experiments recorded without the filter. The integrated intensity of the 1628 cm^{-1} band was converted to the amount of adsorbed water ($\text{H}_2\text{O}/\text{nm}^2$ silica) by calibrating to the weight change of 1 g of silica powder after equilibration at 20 and 80% RH.

Results and Discussion

In general, toners containing silica tend to charge negatively. It is well known that the triboelectric charge of the toner is sensitive to relative humidity and thus to surface water.⁴ Typically, the triboelectric charge (in $\mu\text{C/g}$) measured at low relative humidity is higher than that measured at high relative humidity. The decrease in toner charge with relative humidity is reasonably ascribed to the increase in water content of the silica with relative humidity. The curves

obtained of total adsorbed water versus relative humidity for A380, A380/TEA/OTS, and A380/FTS are shown in Fig. 3. All three curves show an initial steep rise in water adsorption up to about 20% RH, followed by a slower rate of increase at RH values greater than 20%.

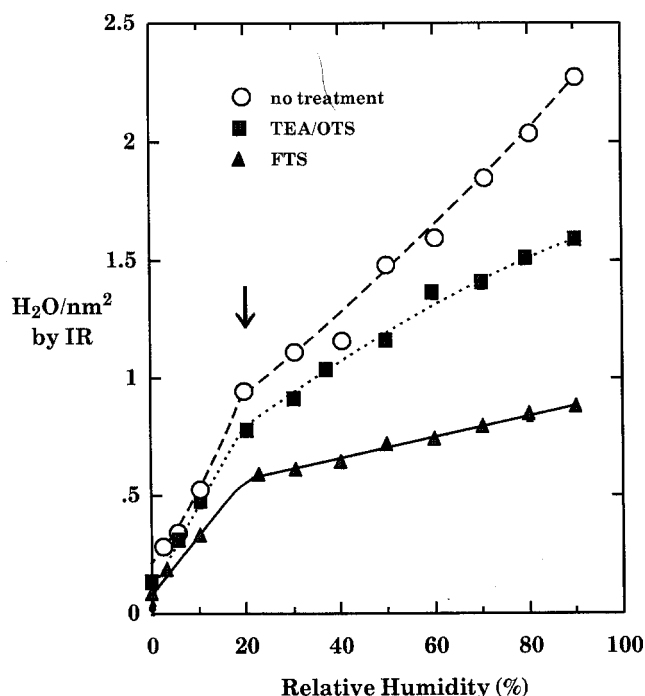


Figure 3. Adsorbed water level on silica versus % RH. The arrow indicates the inflection point for reference in Fig. 4.

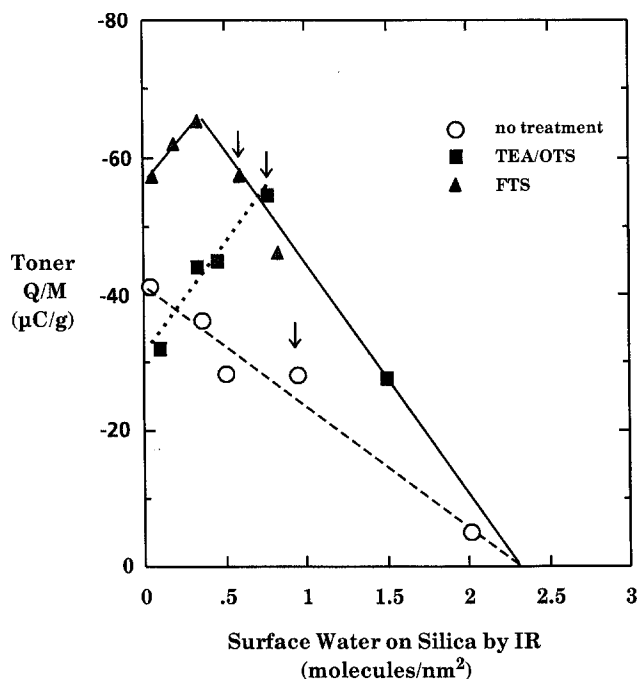


Figure 4. Triboelectric charge versus amount of adsorbed water on silica. The arrow refers to the water content at the inflection point in Fig. 3.

The triboelectric charge (Q/M) of each toner blended with silica additives versus the total adsorbed water is shown in Fig. 4. The bare toner has a negligible contribution to the charge. The charge of the 1075 toner alone is $-7 \mu\text{C/g}$ at 20% RH and drops to $0 \mu\text{C/g}$ at 80% RH. At an RH value near 0% (i.e., very low and equal surface water content) there was a measured difference in charge in the toners coated with the three silicas used in this study. Whereas the charge of the OTS-treated silica was similar to the value obtained using A380, the charge was about $20 \mu\text{C/g}$ more negative with the FTS-treated silica. Because the water content was very low and similar in value for all three silicas near 0% RH, the difference in charge must be due to the difference in chemical nature of the FTS and OTS.

In the curve of A380/FTS, the charge increases linearly with RH from 5 to 10% (i.e., in the region of steep rise in water adsorption curve in Fig. 3), passes through a maximum at 20% RH, and then decreases linearly as relative humidity increases. The change from increasing charge with water content, to decreasing charge with water content (denoted by the arrow in Fig. 4) occurs near the inflection point of the water adsorption curve in Fig. 3.

The trend in the curve for A380/TEA/OTS shown in Fig. 4 is very similar to the curve obtained for A380/FTS. Again, the charge initially increases linearly with increasing water content, passes through a maximum, and drops linearly with further increases in water content. Furthermore, the maximum in the charging-versus-water curve occurs at nearly the same relative humidity as the inflection point in the water-versus-relative humidity curve. At relative humidity values above the maxima, the charge of both FTS- and OTS-treated silicas is identical at the same water content. Thus, above 20% RH the drop in charge is controlled not by the chemistry of the surface, but only by the water content. Finally, both treated silicas show the same water content of $2.4 \pm 0.4 \text{ H}_2\text{O}/\text{nm}^2$ at zero charge at high relative humidity (from the linear extrapolation to high water content).

For A380 there is no maximum in the charge curve. The charge drops in value with water content, even below the inflection point of the water curve (see Fig. 4). Nevertheless, the untreated hydrophilic A380 shows the same approximately linear decrease in charge with increasing water content; the extrapolation to the point of zero charge is $2.4 \pm 0.4 \text{ H}_2\text{O}/\text{nm}^2$, which is the same value as that obtained for the two treated silicas. Because the charge of the toner with silica correlates well with the water content of the silica alone, it is clear that the toner itself has a minimal contribution to the overall charge of the toner with additive. That is, the charging of the toner with silica is controlled solely by the silica.

We envisage two possible mechanisms to explain the charging behavior of toner additives with respect to relative humidity. The first is that the water acts to block a charging site. The assumption with this mechanism is that water covers the silica charging sites, preventing their charge exchange with the carrier. In addition, the model assumes that the water on the silica itself does not exchange charge with the carrier or that the adsorbed water on the toner transfers to the carrier. In the latter case, charging drops because the same amount of water is present on both toner and carrier. No charge exchange occurs between carrier and toner sites,

because they are both blocked by water. However, our data show that water is necessary to have charge exchange to explain the initial increase in charge at low relative humidity. Thus, the weakness of this model is that it does not explain the maxima in the water curve with relative humidity.

The second possible model postulates that water makes the surface of the silica conductive. As the water content increases, the surface becomes more conductive and thus dissipates the charge. The conductivity is due to a contiguous network of water on the silica. This we call a leaky dielectric model. In our case, the presence of the hydrophobic chains disrupts the conductive water paths on the surface of the silica, at least at low water content.

It is interesting to note that at RH values below 20% RH, the charge with the hydrophobic treatment *increases* with water content. This shows that water is a source of charging or aids in charging on the surface. We recall that the offset in the charge curves between these two materials was observed near 0% RH, which indicated that the offset in charge was due to the difference in nature of FTS and OTS. Whereas the charge levels on the FTS- and OTS-treated silica are different, due to this initial offset, they both have the same rate of increase in charge with the adsorbed water level. This would occur when water is adsorbing on similar sites on both silicas. We conclude that these sites that are common to both surfaces are sites that have not been affected by the silane treatment. The water adsorption curves in Fig. 3 shows that the OTS-treated silica contains about twice as many of these surface sites as does the FTS-treated material.

At a critical relative humidity, all available free sites on the surface are filled with adsorbed water. Additional water would then form a contiguous network between the adsorbed water molecules on the surface. This conductive network would dissipate toner charge. At this point, charge begins to decrease with increasing water adsorption. Our data show that this drop in charge occurs between 10 and 20% RH, close to the position of the inflection point of the water-versus-relative humidity curves shown in Fig. 3. This inflection point in the water adsorption curve reflects a change in the mode of adsorption of water on the surface. We believe it is at this point that a contiguous water layer forms on the surface, resulting in an increase in conductivity and thus a loss of toner charge. For the hydrophilic silica, A380, there is no alkylsilane present to disrupt the formation of a contiguous water network on the surface. The charge drops continually as relative humidity increases.

Conclusions

The charging and water content of hydrophilic silica, as well as silicas that have been modified by a *surface-attached* long-chain hydrocarbon or fluorocarbon silane have been studied. The surface water content of the silica was determined by IR spectroscopy. The charging of the hydropho-

bic silica, when used as a toner surface additive, is controlled by the water distribution on the silica. At RH values below 20%, charge increases with increasing water content. This shows that water is necessary in some way for charging. At RH values above 20%, the adsorption of water on the silica occurs at a lower rate than for RH values below 20%. At high relative humidity, the charge on the hydrophobically modified silica decreases linearly with increasing water content and is solely controlled by the amount of adsorbed water. The hydrophilic untreated silica does not appear to show an increase in charge with water content at low relative humidity, despite also showing an inflection in the rate of water adsorption. Linear extrapolation of the charge of all of the silicas leads to a common point at high relative humidity where all of the toners with silica show no charge at all. The common point of zero charge corresponds to about $2.4 \pm 0.4 \text{ H}_2\text{O}/\text{nm}^2$.

Our results show that some water is necessary to develop optimal charge on the silica surface. We believe that the drop in charge at RH values above 20% is consistent with a leaky dielectric model, where charge is dissipated by the presence of contiguous conductive paths of water on the silica surface. The transition to the contiguous water layer would coincide with the inflection point in the rate of water adsorption. When the surface of the silica is totally covered with a monolayer of water, no charge can accumulate.

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