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Electrostatic Charging of Fumed Silica Particles: Effect of Surface Treatment with Fluoroalkylsilanes

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Abstract. *Hydrophobically modified fumed silica particles are widely used in toner formulations to enhance toner free flow and triboelectric charging. Despite the important role that dielectric powders have in electrophotography, the triboelectric charging of such powders is still poorly understood. In this article, the authors present experimental data on the charging properties of toners formulated with fumed silica additives that were modified with different levels of fluoroalkylsilanes. The results show that at high ambient relative humidity (RH) conditions, the triboelectric charge correlates with the fluorine content of the additive, whereas at low RH, the triboelectric charge is effectively constant with respect to fluorine content. The same result was obtained with two different types of toner particles. The authors attempt to rationalize these results in terms of surface conductivity at high RH conditions and charge saturation at low RH conditions. They also present a series of zeta potential measurements that show a correlation with tribocharge at high RH and interpret the results in terms of the ion-transfer model for triboelectric charging.* ©*2012 Society for Imaging Science and Technology.*

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INTRODUCTION

Electrostatic charging of dielectric materials, also known as contact electrification or tribocharging, is a complex physical and chemical phenomenon, which is still not fully understood. Discussions concerning the mechanism for triboelectric charging of dielectric materials—whether due to electron or ion transfer—and on the role of surface moisture are on-going.[1–7] Charges that develop on the surfaces of two dielectrics when they are brought into contact and then separated are known to depend on the surface chemistry of the contacting solids,[8–10] the temperature and humidity conditions of the environment,[11–13] and the contact pressure and nature of the contact between the surfaces.[14] A number of qualitative triboelectric charge series which include a wide range of synthetic and natural materials have been reported in the literature.[5,14]

There are several important industrial applications dealing with electrostatically charged particles. These applications include electrophotography,[4,15,16] powder coatings,[17] and electrostatic precipitation of fine particles from various tail gases.[18] In the case of electrophotography, it is important to control the triboelectric charge of the toner particles.[4] Toner particles that are charged too high or too low may not accurately transfer from the development roll to the surface of the optical photoconductor drum, leading to poor print quality.[15]

In almost all modern toner formulations, small quantities (0.5–2.0 wt%) of hydrophobically treated fumed silica are added into the formulation to reduce the cohesion between toner particles and improve toner free flow.[4,19,20] Figure 1 presents field emission scanning electron microscopy (FE-SEM) photographs of toner particles and the hydrophobically treated fumed silica which coats the individual toner particles. Hydrophobic modification of fumed silicas is usually obtained by treating the silica surface with alkylsilanes or siloxanes.

Surface treatment of fumed silica generally enhances the triboelectric charge of the toner formulation but has limited impact on charge variations that occur with changes in the relative humidity and temperature of the environment even though the hydrophobic surface treatment reduces moisture adsorption. The ratio of triboelectric charge measured at low (20%) and high (80%) relative humidity for toners formulated with hydrophobically treated fumed silica is typically between 2.5 and 1.6. One of the unmet technical challenges in the toner industry is to eliminate or decrease these variations due to changes in ambient humidity and temperature. There is an on-going search for surface treatments of fumed silica that will improve electrostatic charge stability over a range of humidity conditions without sacrificing the magnitude of the charge.

Several years ago, it was reported that fumed silica treated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane, $CF_3(CF_2)_5CH_2CH_2SiCl_3$, shows a higher triboelectric charge than silica treated with a silane that does not contain fluoroalkyl groups.[8,13] It is also well known that fluorinated polymers are generally located at the far negative end of the triboelectric series, implying that these materials are capable of supporting the highest negative electrostatic charges.[5,14] Because of the increase in the number of available fluoroalkylsilanes and a decrease in their cost, the commercial development of fluoroalkylsilane treated fumed silica presents a possible option for developing toner additives with improved triboelectric charge humidity resistance.

To the best of our knowledge, systematic studies of the electrostatic charging properties of silica or other metal oxides treated with fluorine containing treating agents have not been reported in the literature. The goal of the

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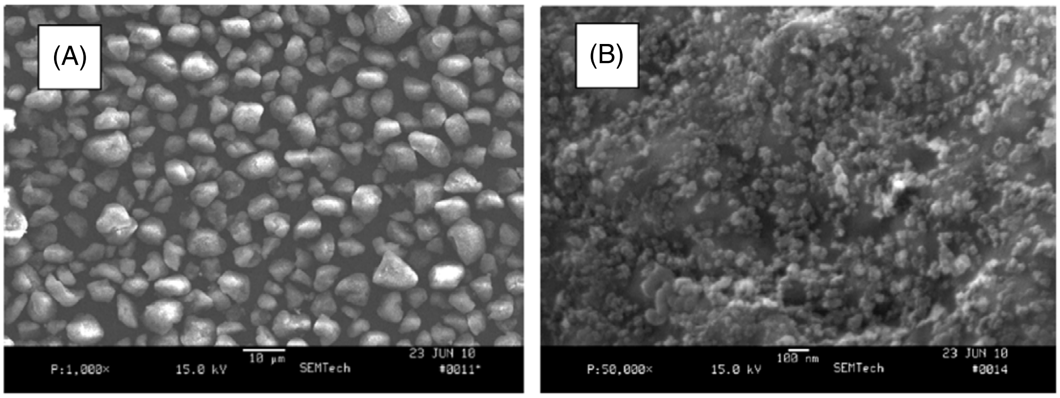

Figure 1. FE-SEM images of commercial toner (A) and hydrophobically treated fumed silica on the toner surface (B). The scale bars are 10 µm in (A) and 100 nm in (B).

present work is to fill this gap by exploring the effect of fluoroalkylsilane treatment on water adsorption on the silica and on the electrostatic charging of toners formulated with these treated silicas.

MATERIALS AND METHODS

Materials

CAB-O-SIL® LM-130 fumed silica—surface area 130 m^2/g—is a product of Cabot Corporation. 1,1,1,3,3,3-hexamethyldisilazane (HMDZ), (3,3,3-trifluoropropyl) trimethoxysilane (F_3-silane) and nonafluorohexyl-trimethoxysilane (F_9-silane) were purchased from Gelest Inc. All chemicals were used as received.

Sample Preparation

A series of eight surface treated fumed silica CAB-O-SIL® LM-130 samples (1–8) was prepared by spraying calculated amounts of an F_3- or F_9-silane/HMDZ mixture and 4 g of water on 130 g of CAB-O-SIL® LM-130. The total amount of HMDZ and fluoroalkylsilane initially added to the silica was kept constant at 5 molecules per nm^2 of silica surface area.

The fumed silica and the treating agents were thoroughly mixed and then transferred to a 2 L Parr reactor. The reactor temperature was brought up to 95°C and the mixture was heated and agitated for 3 h. Subsequently, the temperature was raised to 150°C and nitrogen gas was blown through the reactor for 2 h at a rate of 100 mL/min to remove any unreacted treating agents and the reaction by-products (NH_3 and methanol). The treated silica was removed from the reactor after cooling. Sample data are summarized in Table I, which lists the compositions of the treating mixtures, the results of the carbon measurements before and after extraction with toluene, the fluorine content for the extracted samples, and the calculated concentration of F_3- or F_9-silane per unit silica surface area.

Carbon Content Measurements

The carbon content of all samples was measured using a LECO-C200 carbon analyzer. In order to assess the degree of attachment of the treating agents, the carbon content of the prepared samples was measured both before and after Soxhlet extraction (Table I). The extractions were performed with toluene in Soxhlet apparatus for 3–4 h. The extracted samples were dried overnight in a vacuum oven at 120°C. As shown by the data in Table I, extractions with toluene had minimal effects on the carbon content.

The fluorine content of the extracted samples was analyzed by Galbraith Laboratories, Inc., Knoxville, TN. The concentrations of fluoroalkylsilanes on the surface (Table I) were calculated from the fluorine content data assuming the surface area (BET) of the untreated fumed silica—130 m^2/g.

Samples were extracted only to assess the effectiveness of attachment of the treating agents. The as-prepared samples were used for moisture adsorption, triboelectric charge, and zeta potential measurements.

Water Adsorption Measurements

Water adsorption isotherms of the treated fumed silicas were measured at 25°C using a dynamic vapor sorption balance from Surface Measurement Systems. 100 mg samples were dried in glass vials in an oven for 30 min at 125°C before the analysis. The dried samples were immediately loaded into the instrument after briefly holding them under a Haug point-ionizer. Adsorption measurements were made at twelve relative humidity steps between 0 and 95%. At each humidity value, the sample was allowed to equilibrate for 20 min. Equilibrium was closely approached at each individual step. The corresponding desorption isotherms were recorded for three selected samples.

Zeta Potential Measurements

Dispersions of treated fumed silica (2.0 wt%) in ethanol/water (80/20 w/w) were prepared. Small vials of the dispersions were sonicated for about 5 min in an ultrasonic bath before the measurements. The measurements were performed with a ZetaProbe from Colloidal Dynamics Inc. The ZetaProbe utilizes the electro-acoustic effect, which involves generation of sound waves when alternating voltage is applied to a suspension of charged particles. From the measurements of the electro-acoustic effect, a frequency dependent electrophoretic mobility of the particles can be

Table I. Treatment compositions, carbon content for the as-prepared and extracted samples, fluorine content for the extracted samples, and the calculated surface concentration of fluoroalkylsilane molecules (based on F content after extraction) for the set of eight samples.

Sample	Treatment (molar %)	wt% C as prepared	wt% C after extraction	wt% F after extraction	Calculated conc. of F_3- or F_9-silane for the extracted samples (molecules/nm^2)
1	100% HMDZ	1.15	1.10	0	0
2	25% F_3-silane/75% HMDZ	1.32	1.33	0.63	0.51
3	50% F_3-silane/50% HMDZ	1.04	1.04	1.2	0.97
4	75% F_3-silane/25% HMDZ	1.65	1.63	2.31	1.87
5	100% F_3-silane	1.34	1.30	2.04	1.65
6	25% F_9-silane/75% HMDZ	1.97	1.78	2.95	0.80
7	50% F_9-silane/50% HMDZ	2.19	2.14	5.47	1.48
8	100% F_9-silane	2.55	2.59	5.78	1.57

determined and the zeta potential calculated.[21] The following parameters were used for calculation of the zeta potential: particle dielectric constant 4.5; solvent dielectric constant 34.0; solvent viscosity 1.881 cP; speed of sound 1302.9 m/s. The instrument was calibrated with the standard solution of $K_4[SiW_{12}O_{40}]$ in water with conductivity 0.25 ± 0.01 S/m at 25°C provided by Colloidal Dynamics Inc.

Preparation of Toner Samples and Triboelectric Charge Measurements

Toners were formulated using two different types of toner particles obtained from different suppliers. One toner was a polyester (chemical) toner manufactured via the phase-separation/aggregation method[22] (Toner #1, chemical toner, particle size 8–12 µm). The other toner was a conventional pulverized styrene–acrylic toner (Toner #2, conventional toner, particle size 9–14 µm). For both toners, the density of a toner particle was assumed to be 1.2 g/cm^3. The chemical toner was formulated with 1.5 wt% of treated silica while the conventional toner was formulated with 1.2 wt% of silica because of the slight difference in the average toner particle size. Toner surface coverage was calculated using the following relationship:

$$C = [w/(100\% - w)] \cdot [(\rho_t \cdot d_t)/(\pi \cdot \rho_a \cdot d_a)] \cdot [\sqrt{3}/2], \quad (1)$$

where w is the wt% of additive and ρ_t, d_t and ρ_a, d_a are the density and diameter of the toner and additive particles, respectively. The factor $\sqrt{3}/2$ arises from the assumption of cubic close packing of the additive on the toner surface. Fumed silica aggregates are fractal-like structures composed of clusters of primary particles. Estimates of the aggregate particle density can be obtained from the Stokes diameter or from image analysis studies of transmission electron microscopy (TEM) micrographs. Typical aggregate particle density values are about 1.3 g/cm^3. The average aggregate size for Cab-O-Sil ® LM-130 is 185 nm. In other cases, coverage is often calculated based on the size and density of the primary particles in an aggregate. For the primary particles in LM-130, $d_a = 21$ nm and $\rho_a = 2.2$ g/cm^3.

Table II. Environmental conditions at which the developers were conditioned before the triboelectric charge measurements.

	RH (%)	T (°C)	Abbreviation in the text
Toner #1	15	25	LN
Toner #1	80	25	HN
Toner #2	15	18	LL
Toner #2	80	30	HH

The toner and treated silica were mixed in a laboratory blender for 3 min. The blender was operated in a pulse mode (1 s blender on and 4 s blender off) to keep the toner from heating above its glass transition temperature.

Developers were prepared by mixing the formulated toner with a (60–90 µm) silicone resin coated Cu–Zn ferrite carrier (purchased from Powdertech Co., Ltd.) at a toner to carrier weight ratio of 2:98. Developers prepared with toners #1 and #2 were conditioned at relative humidity (RH) and temperatures as specified in Table II. After conditioning, the developers were placed in glass jars and charged by rolling for 30 min at 185 rpm on a roll mill.

Electrostatic charge measurements were performed using the blow-off method that has been generally adopted in the field of electrophotography. The charge measurements were made using a Vertex T-150 tribocharge tester, manufactured by Vertex Image Products, Inc., Yukon, PA. Approximately 1 g of the developer was placed inside a Faraday cage and a high pressure air jet was used to blow the toner from the carrier. The charge on the carrier, which remains in the cage, was measured with the electrometer in the Vertex T-150 tribocharge tester. The amount of blown-off toner was determined by weighing the cage with the developer before and after the measurement. Each measurement was repeated three times and the average and standard deviation of the measurements are reported.

RESULTS AND DISCUSSION

A series of eight surface modified CAB-O-SIL® LM-130 fumed silica samples (1–8) was prepared, as listed in Table I. The fluorine content of the samples (after extraction) was between 0 and 5.8 wt% and increased both with the concentration of the fluoroalkylsilane in the treatment mixture and with the fluorine content in the silane (F$_3$- versus F$_9$-silanes). The samples were generally found to have low levels of extractable carbon, which suggests a high level of chemical attachment of the treating agents to the silica surface.

Although surface treatment of fumed silica with alkoxysilanes is quite important from an industrial point of view, relatively few studies of this reaction are reported in the literature when it is performed without a solvent.[23] The liquid phase treatment of fumed silica with alkoxysilanes in organic solvents has received more attention.[24–28] The calculated concentrations of 1.65 F$_3$-silane/nm^2 and 1.57 F$_9$-silane/nm^2, for samples 5 and 8, respectively, are in reasonable agreement with attachment concentrations of 1.2 and 2.0 molecules/nm^2 reported for a fumed silica (preconditioned at 75% RH), which was treated with methyltrimethoxysilane and butyltrimethoxysilane in toluene without a catalyst.[25]

In contrast, the treatment of fumed silica with HMDZ either in the gas phase[29] or in solution[30] has been much more widely studied. The surface concentration of 1.4 trimethylsilyl groups/nm^2 for sample 1 is close to the maximum concentration of 1.7 trimethylsilyl groups/nm^2 obtained by treating CAB-O-SIL® HS-5 fumed silica with HMDZ in benzene in the presence of an amine catalyst, as reported by Blitz and co-workers.[30]

Water adsorption isotherms at 25°C for samples 1, 2 and 4–8 are presented in Figure 2. Desorption isotherms were also recorded for samples 1, 4 and 7. The desorption isotherm for sample 1 is shown in Fig. 2; the desorption isotherms for samples 4 and 7 practically overlaid the adsorption isotherms and were therefore not included in Fig. 2. Fumed silica is generally considered to be non-porous, even though some pore filling phenomenon is observed, as shown by the isotherm of sample 1. The presence of interstitial areas (necks) between primary particles in a fumed silica aggregate presumably yields some porosity. However, with increasing fluorine content the shape of the isotherms changes systematically. Whereas samples 1 and 2 show a type II isotherm, which is common for adsorption on fine particles, samples 4, 5, 7 and 8 all exhibit a type VI isotherm expected for a non-wetting adsorbate–adsorbent system.[31,32] A silica surface treated with fluoroalkylsilane is more hydrophobic than a silica surface treated with HMDZ (covered with trimethylsilyl groups).

With increasing fluorine content, the hydrophobic layer effectively prevents access of water to the interstitial regions of the particles and restricts multi-layer condensation, as noted by the absence of the upturn in the water adsorption isotherms at high relative humidity levels. Slightly lower amounts of water are adsorbed on silica reacted with F$_9$-silane (samples 6–8) than on silica treated with F$_3$-silane, as might be expected because of the higher fluorine content and longer alkyl chain in the former case.

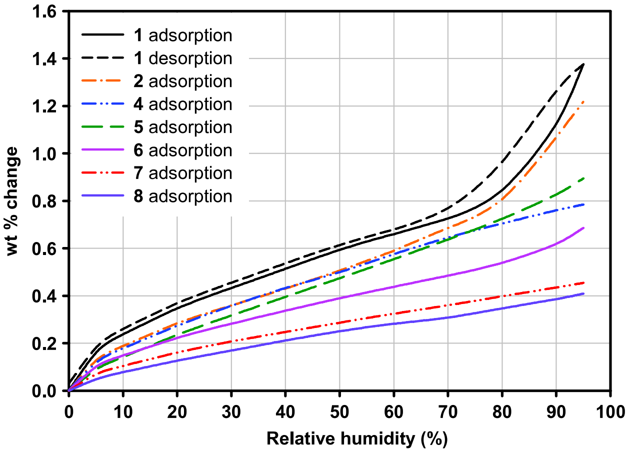

Figure 2. Water adsorption isotherms for samples 1, 2 and 4–8 recorded at 25°C. The desorption part of the isotherm is shown for sample 1. The adsorption and desorption curves for samples 4 and 7 are not distinguishable.

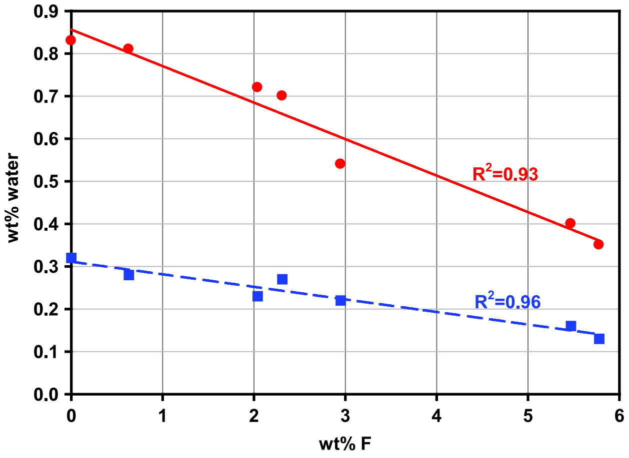

Figure 3. The amount of water adsorbed by the as-prepared samples 1, 2 and 4–8 at 20% RH (blue squares) and 80% RH (red circles) at 25°C as a function of fluorine content measured for extracted samples.

The isotherms also clearly show that samples with a higher fluorine content are more hydrophobic over the entire RH range. This is not surprising and reflects the well-known fact that perfluorocarbons participate very weakly in intermolecular interactions because of the low polarizability of fluorine. This results in lower surface energies than are typical of hydrocarbons.[33,34] The correlation between fluorine content and the amount of water adsorbed at 20 and 80% RH is linear, as shown by the data in Figure 3.

Assuming that the cross-sectional area of a water molecule absorbed on a silica surface is 13.3 Å^2, Ref. 35, the theoretical monolayer coverage for 130 m^2/g silica occurs at ~3.0 wt% water. Since all samples adsorb less than 1.2 wt% water, none have reached monolayer coverage; for most of the fluorine treated samples, the maximum surface coverage of water is between 12 and 25% of a monolayer.

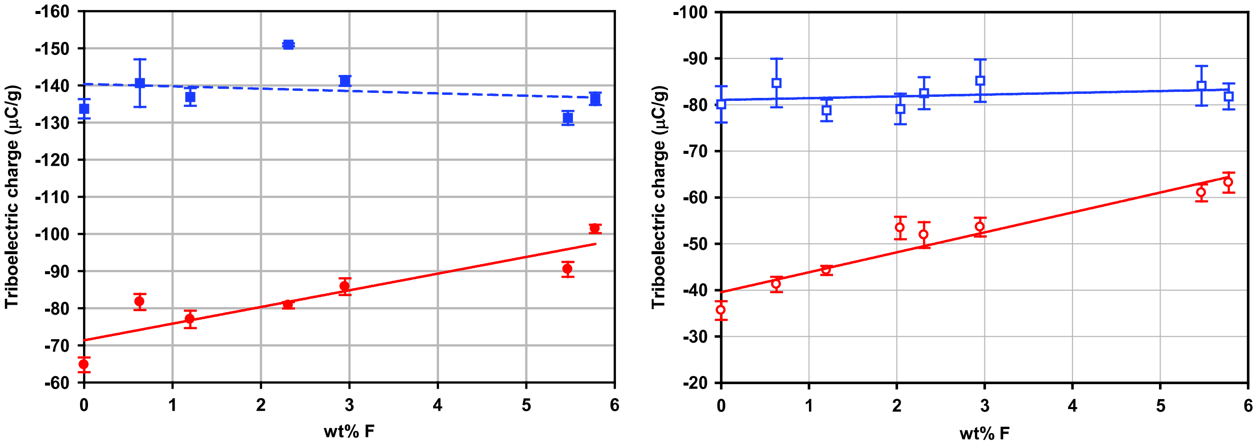

Figure 4. Results of triboelectric charge measurements for toner #1 (left plot) and toner #2 (right plot) formulated with surface modified fumed silicas 1–8 as a function of wt% F in the silica. Data for toner samples conditioned at high humidity are shown as red circles and for toners conditioned at low humidity as blue squares.

Table III. Results of triboelectric charge measurements for toners formulated with samples 1–8.

Sample	HN (μC/g) Toner #1	LN (μC/g) Toner #1	LN/HN Toner #1	HH (μC/g) Toner #2	LL (μC/g) Toner #2	LL/HH Toner #2
1	−65 ± 2	−134 ± 3	2.08	−36 ± 2	−80 ± 4	2.22
2	−82 ± 2	−142 ± 6	1.72	−41 ± 2	−85 ± 5	2.08
3	−77 ± 2	−137 ± 2	1.79	−44 ± 1	−79 ± 2	1.80
4	−81 ± 1	−151 ± 1	1.85	−52 ± 3	−83 ± 3	1.59
5	—	—	—	−53 ± 2	−79 ± 3	1.49
6	−86 ± 2	−141 ± 1	1.64	−54 ± 2	−85 ± 5	1.56
7	−90 ± 2	−131 ± 2	1.45	−61 ± 2	−84 ± 4	1.37
8	−101 ± 1	−136 ± 2	1.35	−63 ± 2	−82 ± 3	1.30

The moisture adsorption measurement for sample 8 is noted to be in good agreement with previously published data for an Aerosil 380 ® (380 m^2/g) fumed silica surface treated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane, $CF_3(CF_2)_5(CH_2)_2SiCl_3$.[13] When normalized with respect to the surface area of the silica, the amount of water adsorbed on sample 8, which is closest chemically to the sample from Ref. 13, is nearly the same. At 20 and 80% RH, sample 8 adsorbs 0.3 and 0.9 molecules/nm^2, respectively, compared to 0.6 and 0.8 molecules/nm^2 for the treated Aerosil 380 ® sample.[13] The Henry's law regime, where a change in the slope of the adsorption curve occurs, is at an RH of about 5% for all samples 1–8, whereas the measurements in Ref. 13 for Aerosil ® treated with either an alkylsilane or the fluoroalkylsilane showed a broader Henry's law regime—up to 20% RH.

The results of triboelectric charge measurements for toners #1 and #2 formulated with samples 1–8 and conditioned at HN or HH and LN or LL, are summarized in Table III and shown in Figure 4.

For both types of toner the triboelectric charge at high humidity conditions increases (i.e., becomes more negative) with increasing fluorine content, whereas at low RH conditions—both LN and LL—the tribocharge is constant and independent of the fluorine content. From a practical perspective, because of the different triboelectric charge behavior at high and low RH, the ratio of triboelectric charge at LL and HH, which is often regarded as a measure of ambient charge stability, decreases with increasing fluorine content from 2.08 to 1.35 and from 2.22 to 1.30 for toners #1 and #2, respectively.

It is known that hydrophobic treatment of the silica surface can significantly reduce the surface conductivity.[36] The increase in triboelectric charge from sample 1 to sample 8 observed at high humidity conditions (Fig. 4) is most likely due to a decrease in surface conductivity, which in turn is due to a decrease in the amount of surface adsorbed water.

Interestingly, if the triboelectric charge is plotted as a function of the amount of adsorbed water (Figure 5) rather than fluorine content, the relationship between charge and water content is similar to that reported earlier by Veregin and co-workers.[13] However, here the charge is constant over the range of 0.3 and 0.8 molecules/nm^2, and it decreases with increase in water content between 0.8 and 2.2 molecules/nm^2.

At low RH conditions, the charge density is apparently not determined by the amount of adsorbed water, but instead may be limited by dielectric breakdown of air. Although

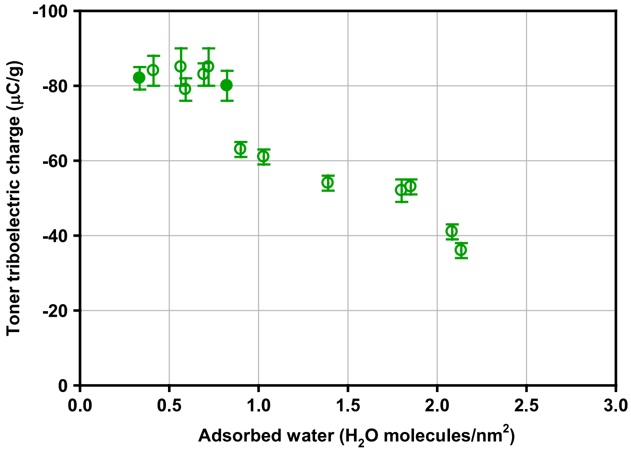

Figure 5. Triboelectric charge as a function of concentration of water on the additive's surface (data for toner#2). Triboelectric charge data for samples 1 and 8 at LN and HN, respectively, are shown as filled circles.

Table IV. Calculated $\sigma_{\text{max theor.}}$ and σ_{exp} for toners #1 and #2 at LN and LL conditions.

Toner #	Toner particle radius (nm)	$\sigma_{\text{max theor.}}$ (e/1000 nm^2)	σ_{exp} (e/1000 nm^2)
1	5000	2.0	1.7
2	5500	2.0	1.0

a precise breakdown field cannot be easily calculated for a system such as this, an upper limit for the charge density for an ideal sphere of radius R expressed in e/nm^2 can be calculated using the equation provided by Harper,[5]

$$\sigma_{\text{max theor.}} \approx 0.026 \cdot R^{-0.3}, \tag{2}$$

where R is in nm.

The experimental charge density in e/nm^2 for toners #1 and #2 can be calculated using the following equation:

$$\sigma_{\text{exp.}} = 6.241 \cdot (q/m)/S_{\text{toner}}, \tag{3}$$

where q/m is the triboelectric charge per mass in Coulomb/g and S_{toner} is the surface area of the toner in m^2/g. The surface area of the toner can be estimated assuming that the toner particles are spheres with a density of 1.2 g/cm^3. Using 140×10^{-6} and 80×10^{-6} C/g as the triboelectric charges for toners #1 and #2 at LN and LL, respectively, and 0.50 and 0.45 m^2/g as the surface areas of toners #1 and #2, it is easy to calculate the upper bound charge densities. Values of $\sigma_{\text{max theor.}}$ and $\sigma_{\text{exp.}}$ for both toners are listed in Table IV.

Eq. (2) was proposed by Harper and is frequently used to determine the breakdown field for spherical particles. The data in Table IV give the upper bound charge values for toners #1 and #2. Although the experimental triboelectric charge levels are different for each toner, they do not exceed the upper bound values.

We had inferred above that the charge is probably located on the additive rather than being uniformly distributed on the surface of the toner itself, based on the observation that the triboelectric response at the two RH conditions is the same for the two different toners. This suggests that it is primarily the response of the additive rather than the toner itself to the ambient humidity conditions that affects the triboelectric charge. However, the magnitude of the charge, which is different for toners #1 and #2, is affected by the chemical compositions of the toners.

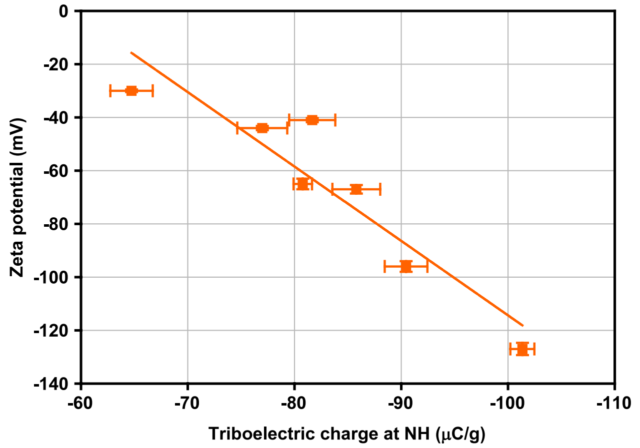

Figure 6. The correlation between the triboelectric charge measured for toner #1 formulated with samples 1–4 and 6–8 and conditioned at 80% RH/25°C and the zeta potential measured for samples 1–4 and 6–8 dispersed in ethanol/water ($R^2 = 0.86$).

In contrast, at high RH conditions (either HN or HH), the tribocharge level correlates with either the fluorine or the moisture content of the additive, although the moisture content alone does not seem to be sufficient to explain the differences in tribocharge. For example, samples 1 and 2, which are predominantly trimethylsilyl treated, adsorb about the same amount of water at 20% RH as samples 7 and 8 (predominantly F_9 treated) at 80% RH, but the tribocharges of the two samples at the corresponding humidity conditions of LN and HN, respectively, differ by at least 33 μC/g, as shown by the data in Fig. 5. It is likely that other factors affect the magnitude of the electrostatic charge under high humidity conditions.

The fact that fluoropolymers (e.g., polytetrafluoroethylene) develop strong negative electrostatic charge has been reported previously.[8,14,37] To the best of our knowledge, neither has a complete scientific understanding of this phenomenon been achieved nor has an understanding of the origin of electrostatic charging in hydrophobic polymers been formulated. Recently, McCarty and Whitesides[1,14] have suggested that contact electrification of many hydrophobic materials, which do not have mobile and fixed ions on the surface, may be due to unequal partitioning of hydroxyl and hydronium ions between the surfaces. They demonstrated a correlation between the triboelectric charge and the zeta potential for a series of organic polymers and proposed an explanation in terms of a partitioning of hydroxyl ions in the system.

To test whether there is a relationship between the magnitude of contact electrification and the zeta potential of

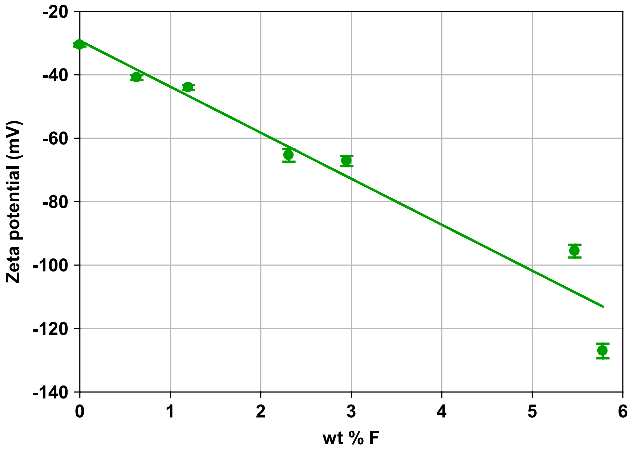

Figure 7. The correlation between the fluorine content in the silica treatment (wt% F) and the zeta potential measured in ethanol/water ($R^2 = 0.94$).

Table V. Results of zeta potential measurements for samples 1–4 and 6–8 in ethanol/water (80/20 w/w).

Sample	Zeta potential (mV)
1	−30.6 ± 0.5
2	−40.9 ± 0.8
3	−44.0 ± 0.8
4	−65.4 ± 2.0
6	−67.2 ± 1.6
7	−95.6 ± 2.0
8	−127.1 ± 2.3

the surface, the zeta potentials of samples 1–8 were measured. The results of these measurements are summarized in Table V and are plotted as a function of the HN tribocharge in Figure 6. The observed negative sign of the zeta potential and the correlation of the zeta potential with the triboelectric charge provide some evidence to support the proposal of McCarty and Whitesides that the triboelectric charge is related to the preferential adsorption of hydroxyl ions on the hydrophobic surfaces. The higher the fluorine content, the higher is the concentration of hydroxide ions adsorbed on the surface (Figure 7). This is in agreement with previously reported observations that there is a strong preference for hydroxide adsorption at a water/fluorinated surface interface.[38]

CONCLUSIONS

A series of fluoroalkylsilane and HMDZ treated fumed silica samples has been prepared and characterized by elemental analysis, water adsorption, and zeta potential measurements. The amount of water adsorbed by the samples decreases with an increase in fluorine content, and the shape of the adsorption isotherm shifts to one that is characteristic of a non-wetting surface.

Triboelectric charge measurements of two model toner formulations showed a correlation between triboelectric charge and moisture content for samples conditioned at HN or HH but the absence of such a correlation for samples conditioned at LN or LL. The results show that the electrostatic charge at high humidity conditions monotonically increases with an increase in fluorine content, while the charge at low humidity remains constant and independent of fluorine concentration. This difference in behavior is interpreted in terms of connectivity between regions of moisture on the fluorinated surface affecting the surface conductivity at high RH conditions and electric field breakdown at low RH conditions.

A correlation is observed between the zeta potential of samples 1–8 dispersed in an ethanol/water (80/20 wt/wt) solution and the triboelectric charge of toner formulated with samples 1–8 and conditioned at HN. It is proposed that the enhancement of the triboelectric charge of silicas treated with alkylflourosilanes is due to the preferential adsorption of hydroxyl ions on fluorine containing surfaces. These hydroxyl ions originate from the dissociation of water molecules at the interfacial region during contact electrification.

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