External Additives for Toners: Treatment with Functional Silanes for Active Triboelectrostatic Charge Control

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Abstract

Treated fine particles of metal oxides such as silica, titania, and alumina are commonly used in toner formulations to help to achieve the necessary level of toner free flow and trboelectrostatic charging. In most cases such particles are treated with hydrophobicity imparting agents such as alkylsilanes or silicone oils and their charging characteristics reflect the acidity of the base oxide and quality of the hydrophobic treatment. So far little has been reported on the effect of different chemical functional groups on charging characteristics of treated metal oxides.

This paper describes the treatment and characterization of fine particles of aforementioned oxides with two types of functional silanes containing nitro groups and fluorine atoms. Results of triboelectrostatic charge measurements demonstrate that both treatments significantly enhance negative charge and, in certain cases, greatly reduce tribocharge humidity sensitivity. Observed charge enhancement parallels the amount of functional silane present on the surface. Possible reasons for such behavior are discussed from the point of view of ion-transfer model of contact electrification and in conjunction with the available characterization data.

Using external additives modified with nitro and fluorine containing functional groups may allow formulators to reduce the number of formulation components and provide extra flexibility to achieve the target performance.

Introduction

An external additives package is one of the major components of modern toner formulations. Although polymeric nano-particles are utilized in some cases, most often hydrophobically treated nano-particles of silica, titania, or alumina are used as external additives. The additives are applied to improve toner free flow, increase efficiency of toner transfer from OPC to paper, prevent agglomeration of toner during storage, and improve control over toner triboelectrostatic charge (tribocharge). As a result of the ongoing technology shift towards smaller size polyester based toners produced via different polymerization methods, which sometimes can make the introduction of charge control agents (CCAs) into the toner difficult, the latter function of the external additives becomes more important. External additives with tunable triboelectrostatic charge and minimal dependence of tribocharge on humidity and temperature of the environment are continually sought by formulators.

It is important to note that mechanisms of tribocharging of dielectric materials are not fully understood and different explanations of this phenomenon have been proposed [1, 2]. It appears, however, that tribocharging of untreated metal oxides such as silica, titania, and alumina could be explained in terms of an ion transfer model and is determined by the acid-base properties of the metal oxide surface [3, 4]. Silica, for instance, is the most acidic out of these three oxides and it shows strong negative charge while alumina is slightly basic and its tribocharge is slightly positive.

Typically, metal oxide particles used as external additives are treated with silanes (e.g., octyltriethoxysilane, hexamethyl-disilazane) or with silicones (polydimethylsilicone oil) to make their surfaces hydrophobic. Hydrophobic treatments reduce the amount of water adsorbed on the surface and, thus, decrease surface conductivity, which is one of the possible discharge mechanisms. As a result, hydrophobicaly treated oxides charge higher than untreated metal oxides.

Except for additives treated with amino functional silanes, little has been reported regarding tribocharge properties of particles treated with silanes containing different functional groups (e.g., mercapto, nitro, or trifluoromethyl group). In this paper we report results of our study on the effect of treatment with silanes containing trifluoromethyl/nanofluorobutyl and nitrophenyl groups on the tribocharge of fumed silica and alumina.

Experimental

Materials. All silanes used in this work were purchased from Gelest Inc. and were used as received without further purification. Fumed alumina, SpectrAl81™ surface area 80 m^2/g, and fumed silica, CAB-O-SIL® LM-130 surface area 130 m^2/g, are products of Cabot Corporation.

General procedure for liquid phase siliane treatment of fumed alumina. SpectrAl81™ fumed alumina was treated with a silane or mixture of silanes in isopropanol. Ammonium hydroxide was employed to catalyze hydrolysis and condensation of the silane. Treatments were conducted at 70 ^{o}C for several hours. Treated solids were separated from the reaction mixtures, washed and dried in an oven at 100 ^{o}C for several hours.

General procedure for dry treatment of fumed silica with silane/silazane. CAB-O-SIL® LM 130 fumed silica was sprayed with desired amounts of water and fluorosilane/HMDZ mixture (different fluorosilane/HMDZ ratios were employed). Fumed silica, fluorosilane, and HMDZ were thoroughly mixed and transferred to 2 L Parr reactor where the mixture was heated for several hours. The reactor was allowed to cool down and treated powder was recovered.

Sample characterization. Carbon content was measured for all prepared samples using LECO-C200 analyzer.

In order to determine the amount of treating agent chemically attached to the surface, selected samples were extracted with toluene, dried in a vacuum oven at 120 °C and then analyzed for carbon content. Results of carbon content analysis were used to calculate silane coverage on oxide surface.

Samples treated with fluorosilanes, were analyzed for wt% of F while samples treated with silanes containing nitro groups were analyzed for wt% of N.

To verify silane attachment modes ^{29}Si CP MAS NMR spectra of selected samples were recorded.

Water adsorption measurements. Water adsorption isotherms of treated LM-130 fumed silica were measured at 25 °C using a dynamic vapor sorption balance from Surface Measurement Systems. 100 mg samples were dried in a glass vial in an oven at 125 °C for 30 min before the analysis. Dried samples were loaded into the instrument immediately after briefly holding them under the Haug Point-Ionizer. Data collection method included twelve 20 min steps at relative humidity values between 0 and 95 %.

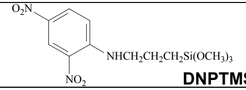
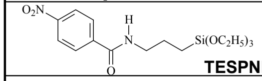
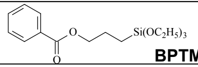
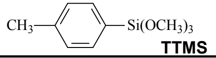
Zeta potential measurements. Dispersions of treated alumina samples in methanol (0.5 wt%) were prepared. The dispersions were sonicated for about 5 minutes in an ultrasonic bath before zeta potential measurement with a ZetaPLAS manufactured by Brookhaven Instruments Corporation (Holtsville, NY) using the technique of phase analysis light scattering. Mobilities were converted to zeta potential using the Smoluchowski equation.

Tribocharge measurements. Treated metal oxides (fumed alumina and silica) were milled to fine powders using laboratory grinder, and then formulated with polyester toner (conventional polyester black toner, size ~10 µm) in a laboratory blender for 3 min. The toner/additive ratio was: 98.5 wt% toner and 1.5 wt% of treated alumina; or 98.8 wt% toner and 1.2 wt% of treated LM-130 fumed silica. Mixing was conducted for approximately 20% of the time in order to keep the toner from heating above the glass transition temperature. Developers were prepared by formulating 2 wt% of the toner and 98 wt% of Cu-Zn ferrite based carrier coated with silicone resin (Powdertech Co., Ltd.). All developers were conditioned overnight in a temperature/humidity chamber at 18 °C/15% RH (LL conditions) or 30 °C/80% RH (HH conditions). After conditioning developers were placed into the glass jars and charged by rolling jars for 30 min at 185 rpm on a roll mill. Tribocharge measurements were done using Vertex T-150 tribocharge tester. Each measurement was repeated three times and the average is reported.

Results

Results of tribocharge measurements for fumed alumina particles treated with functional silanes. It has been reported that titania and alumina show considerably less negative tribocharge than silica [3]. Untreated fumed alumina often has even slightly positive tribocharge. Results of tribocharge measurements for fumed alumina treated with various silanes are summarized in Table 1. The data show that, while all prepared samples have approximately the same number of silane molecules per nm^2 of surface, tribocharge values span the range from 0 to close to -50 µC/g.

Table 1. Silane surface coverage and tribocharge data for fumed alumina samples treated with functional silanes.

Treating agent	Coverage* (molecules/nm^2)	Toner tribocharge at RH=20% (µC/g)
 **DNPTMS**	2.4	-47
 **TESPNB**	2.5	-32
$CF_3CH_2CH_2Si(OCH_3)_3$ **TFPTMS**	2.5	-30
$CH_3(CH_2)_7Si(OCH_3)_3$ **OTES**	2.8	-3.4
 **BPTMS**	2.6	-1.9
 **TTMS**	2.4	-0.8

** Silane coverage was calculated from the wt%C*
*** Uncertainty of tribocharge data is ≤2 µC/g*

Treatments with silanes containing alkyl (OTES), benzoyloxypropyl (BPTMS), and p-tolyl (TTMS) groups afforded materials with close to zero negative tribocharge. Treatment with silane containing trifluoromethyl group (TFTPMS) boosts tribocharge to -30 µC/g. It is even more surprising, however, that treatments with silanes containing nitro substituted aromatic groups (DNPTMS and TESPNB) afford materials with even higher tribocharge.

Figure 1 shows tribocharge data (LL conditions) for a series of alumina samples treated with the mixtures of DNPTMS and isobutyltrimethoxysilane (IBTMS) containing different ratios of the two silanes. Data presented in Figure 1 show that tribocharge increase parallels the increase in number of DNPTMS molecules on the surface.

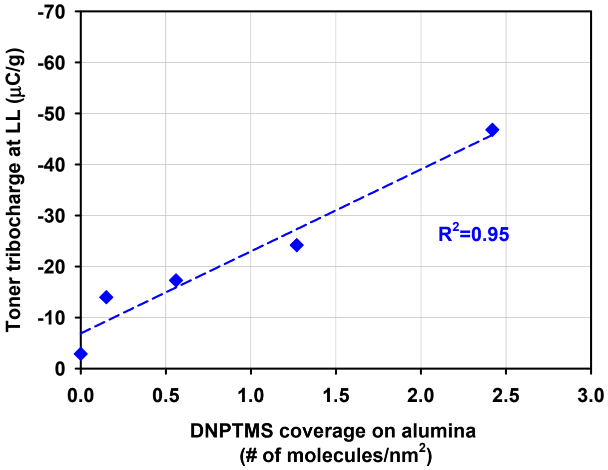


Figure 1. Relationship between tribocharge (LL) and surface coverage of fumed alumina with functional silane DNPTMS.

While IBTMS only treated alumina (DNPTMS coverage = 0) exhibited a small negative charge, DNPTMS treatment increased the negative charge up to almost -50 µC/g, which is the highest negative charge for treated fumed alumina that we were able to achieve so far.

Results of tribocharge measurements for fumed silica treated with functional silanes. Samples of CAB-O-SIL® LM-130 fumed silica treated with the mixtures of hexamethyldisalazane (HMDZ) and a fluorosilane ($CF_3CH_2CH_2Si(OCH_3)_3$ or $C_4F_9CH_2CH_2Si(OCH_3)_3$) taken at different ratios were prepared via dry treatment method and tested. Results of tribocharge measurements are shown in Figure 2.

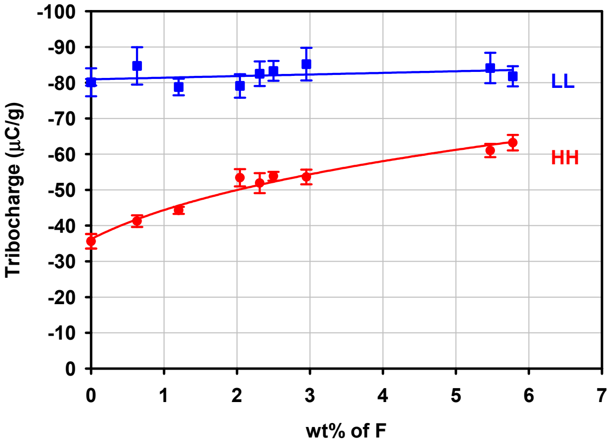


Figure 2. *Tribocharge at HH and LL conditions as a function of wt% of F for CAB-O-SIL LM-130 silica treated with fluorinated silanes.*

Interestingly, tribocharge of toner samples conditioned at low humidity and temperature (LL) shows no dependence on the amount of fluorine on the additive's surface, while tribocharge measured for samples conditioned at high humidity and temperature (HH) increases significantly with the increase of the wt% of F on additive's surface. For instance, HMDZ only treated LM-130 exhibited HH charge of -36 µC/g while sample treated with nonafluorosilane shows charge of -65 µC/g. As a result, the environmental humidity dependence of toner tribocharge is significantly reduced when highly fluorinated silica is used as an external additive.

Water adsorption measurements. Water adsorption isotherms were measured for all samples of LM-130 silica treated with mixtures of HMDZ and fluorosilane. Two limiting cases representing isotherms for samples treated only with HMDZ and only with nonafluorosilane are shown in Figure 3. These examples demonstrate that treatment with fluorosilane significantly reduces water adsorption in the range between 0 and 80% RH.

The amount of water adsorbed by treated LM-130 silicas at 20 and 80 % relative humidity verses wt% F is plotted in Figure 4. Strong linear correlations between these parameters are observed with R^2=0.97 and 0.94 for LL and HH conditions, respectively.

Discussion

Data in Table 1 show that treatment with silanes containing –Ar–NO_2 or –CF_3 groups substantially increases tribocharge of fumed alumina. Since alumina treated with alkyl silanes without specific functional groups e.g., treated with OTES, has tribocharge close to zero, observed tribocharge increase is clearly due to the presence of –Ar–NO_2 and –CF_3 groups. At the moment we do not fully understand the physics and chemistry behind this phenomenon.

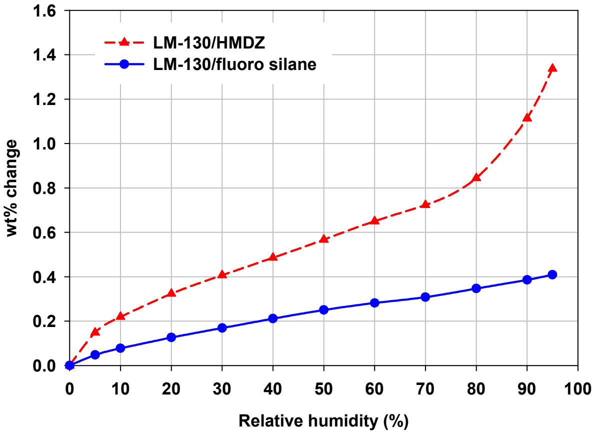


Figure 3. *Water adsorption isotherms for LM-130 fumed silica treated with HMDZ and nanofluorosilane.*

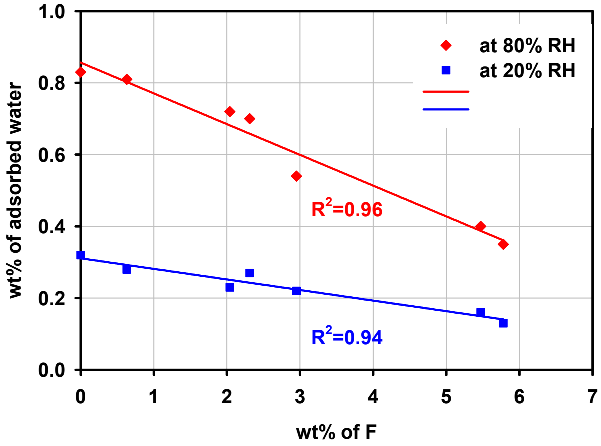


Figure 4. *Amount of water adsorbed by LM-130 silicas treated with HMDZ and fluorosilanes as a function of wt% of fluorine.*

Assuming an ion-transfer mechanism of tribocharging, several explanations could be speculated. One possibility is that the acidity of uncondensed silanols, which are always present when di- or tri-functional silanes used for surface treatment, is higher in case of fluorosilanes than in case of alkylsilanes (OTES) due to the strong electron withdrawing effect of –CF_3 or –C_4F_9 groups located two methylene carbons away from Si.

Another possibility is that surface containing –CF_2– and –CF_3 groups shows strong preference for hydroxide ion adsorption (similar to what was reported for water/fluoropolymer interface) which is the cause for negative tribocharge [1, 5].

Proton transfer mechanism also could be contemplated to explain tribocharge enhancement by –Ar–NO_2 functionalities. It is conceivable that hydrogen atoms of secondary amino groups present in both silanes, DNPTMS and TESPNB, are unusually acidic. The possibility of an electron transfer mechanism also could not be ruled out in this case because aromatic compounds substituted with nitro groups may serve as good electron traps and can contribute to or possibly even dominate the charge transfer mechanism.

It has been documented in the literature that tribocharge of metal oxides, minerals, and polymers tends to correlate with zeta potential [1, 3]. To check whether this correlation is applicable to materials prepared in this study, zeta potentials of several fumed alumina samples treated with different silanes were measured. Fumed alumina samples treated with different amounts of DNPTMS, TFPTMS, and IBTMS were tested. Since these materials are hydrophobic, powder dispersions in methanol were used.

Results of the measurements are shown in Figure 5. It turns out that there is a fairly good correlation between the magnitude of zeta potential and tribocharge of alumina particles. This result suggests that ion-transfer is likely to be the major mechanism of tribocharging for fumed aluminas investigated in this work.

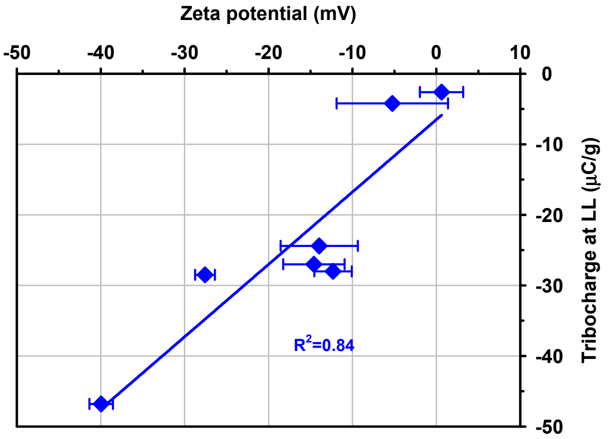


Figure 5. *Tribocharge (LL) of treated fumed alumina samples as a function of zeta potential. Samples were prepared as dispersions in methanol.*

Figure 4 showed correlation between the amount of water adsorbed by fluorosilane treated LM-130 silica and fluorine content. The data suggest that materials with higher fluorine content on the surface are more hydrophobic and adsorb less water at both high and low humidity. The effect, however, is more pronounced at high humidity than at low. This could be the reason why higher fluorosilane coverage on LM-130 silica rendered large tribocharge increase at high humidity conditions leaving tribocharge at low humidity essentially unchanged.

Combination of low water adsorption and preferential adsorption of hydroxide ions on fluorinated surface are possible reasons for high tribocharge and improved humidity resistance of fluorosilane treated LM-130. It is also should be noted that fluorosilane treated fumed silica showed excellent free flow properties when combined with toner.

Another important factor that has to be considered when attempting to correlate tribocharge dependence with water adsorption is the manner in which the water is distributed on the surface. Is the water film a continuous conducting network able to dissipate charge effectively or a series of isolated islands [1, 5]?

The following are the principal conclusions of this study.

(i) Series of samples of fumed alumina and fumed silica, treated with alkyl silanes, and silanes containing –Ar–NO_2, –CF_3 and –C_4F_9 groups were prepared and characterized.

(ii) It has been shown that tribocharge of alumina increases in parallel with the increase in the number of –Ar–NO_2 groups on the metal oxide surface.

(iii) Treatment of fumed silica with fluorosilanse affords materials adsorbing less water than materials treated with regular alkylsilanes. Fuorosilane treated silicas show higher tribocharge at high humidity and, as a consequence, have lower tribocharge humidity sensitivity.

(iv) Results of zeta potential measurements suggest that despite the big difference in the nature of –Ar–NO_2 and –R_f groups, ion transfer mechanism of tribocharging of treated metal oxides is likely to be involved in both.

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