Treated Fumed Alumina Particles for Toners

Dmitry Fomitchev, Casey Whicher, Adam MacKay, Larry Flowers and William Williams
Cabot Corporation, Business and Technology Center, 157 Concord Road, Billerica, MA 01821

Abstract

Surface modified fumed metal oxide particles are used as external additives on toners in order to improve the free flow, tribo-electrostatic charging and other performance characteristics of the toner. The type of base metal oxide, particle morphology, surface area, and surface chemistry affect the properties of the additive. The type of the base metal oxide also puts certain limitations on possible chemical treatments, for instance, not all treatments used for fumed silica particles could be applied for titania and alumina.

Untreated fumed alumina particles usually show low absolute level of tribo-electrostatic charging and relatively small variation of tribo-electrostatic charge due to changes of temperature and relative humidity. In this paper we will discuss the treatments of fumed alumina particles (i.e., Cabot grades SpectrAl® 51, SpectrAl® 81, and SpectrAl® 100) with different silicone fluids and different alkoxy silanes and the effect of these treatments on the properties of the additive. In particular, the effect of surface treatments on the absolute level of tribo-electrostatic charging, tribo-electrostatic charge humidity sensitivity, and free flow will be addressed.

Introduction

Chemically treated particles of fumed silica are widely used in toner formulations. The primary functions of these particles are to enable free flow and to enhance tribocharging of toner. It is well known that the tribocharging of fumed silica depends on the temperature and relative humidity of the environment. It is often the case that tribocharge of toner formulated with fumed silica is too high at low humidity and too low at high humidity. This affects the toner transfer efficiency in the machine and, ultimately, image quality.

External additives based on metal oxides other than silica (i.e., titania and alumina) have been under development with the goal to improve humidity resistance of toner formulations. It has been shown that hydrophobically treated fumed alumina and, especially, titania [1, 2] are viable alternatives to fumed silica.

In this paper we describe some performance characteristics of fumed alumina treated with silicon oil and alkyl silane. We report that tribocharge properties of the treated fumed alumina can be different depending on treatment chemistry and conditions. Absolute level of tribocharge and tribocharge humidity dependence of treated fumed alumina could be manipulated in a wide range and, in principal, tuned for the particular formulation.

Experimental

Sample preparation. Fumed alumina SpectrAl® 81 (BET=80 m^2/g, primary particle size ~21 nm) and SpectrAl® 100 (BET=95 m^2/g, primary particle size ~18 nm) available from Cabot Corporation were used in this work.

Fumed alumina powders were treated with polydimethylsiloxane oil (PDMS), octyltriethoxy silane (OTES) and octyltrichlorosilane (OTCS). To achieve chemical attachment of PDMS to the particle surface, the treatment was done at elevated temperature. Silane treatments were performed using minimal amounts of organic solvent (e.g. acetone) at room temperature. After treatment with the silane, the materials were cured at elevated temperature to maximize the degree of condensation of silanol groups.

PDMS and OTES treatments have been carried in a variety of batch sizes from lab to pilot to commercial prototype scale. Most results reported here are for materials synthesized in a 5 gallon Parr reactor (~1 kg) although results from different scales are similar.

Sample characterization. Carbon content in treated samples was measured using LECO C-200 analyzer. The amount of chemically attached treating reagent was estimated by measuring carbon content of samples extracted with organic solvent.

Methanol wettability (hydrophobicity) of the treated samples was evaluated using the methanol wettability test developed by Cabot Analytical Laboratory.

Titration with lithium aluminum hydride (LAH) was done for selected samples to determine the number of unreacted OH groups on alumina surface [3].

^{29}Si and ^{1}H CP MAS NMR spectra of treated samples were recorded. The spectra provided information about types and relative amounts of chemical species present on the surface.

Performance evaluation. Pulverized additive-free toners (polyester and styrene acrylic) were formulated with treated fumed alumina (0.5-1.5 wt%). Developers were prepared by mixing 2 wt% of formulated toner and 98 wt% of Cu-Zn ferrite carrier (purchased from PowderTech Co.) coated with silicone resin. The developers were exposed to high temperature (30 °C) high humidity (80 %RH) and low temperature (18 °C) low humidity (15 %RH) conditions abbreviated as HH and LL, respectively, and were charged by rolling them in glass jars for 2h.

The standard blow-off type method using a Vertex T-150 instrument was used for tribocharge (Q/m) measurements.

Free flow measurements were done using an in-house apparatus, consisting of a horizontally mounted steel tube with a set of aligned holes. The tube is rotated for a set number of revolutions around its horizontal axis by a step motor. The amount of toner lost through the holes is determined by measuring the weight loss. It is assumed that the weight loss is larger in case of better free flowing toner formulation.

Results

Thermal degradation of PDMS on alumina surface. There are two primary chemical reactions taking place on the surface of alumina at high temperature. One is the depolymerization of PDMS oil into fragments of smaller molecular weight. Another is the oxidation of PDMS oil.

Thermal depolymerization of PDMS was the subject of several investigations [4, 5, 6] and several mechanisms for this process have been suggested. This reaction affords mixture of low molecular weight cyclic siloxanes. Non-cyclic siloxanes of lower molecular weight than the original polymer are also produced. It has been demonstrated that water and hydroxyl ions, which are present on alumina surface, effectively accelerate the depolymerization [4].

Thermal oxidation of PDMS takes place at high temperatures in the presence of oxygen. The oxidation occurs through the formation of side-chain peroxide groups, which decompose with formation of formaldehyde [4]. As a result of this reaction, some of the PDMS methyl groups are transformed into hydroxy groups, which can form Si-O-Al and Si-O-Si linkages with the particle surface. If the reaction continued for long enough, silica would form on the surface of alumina.

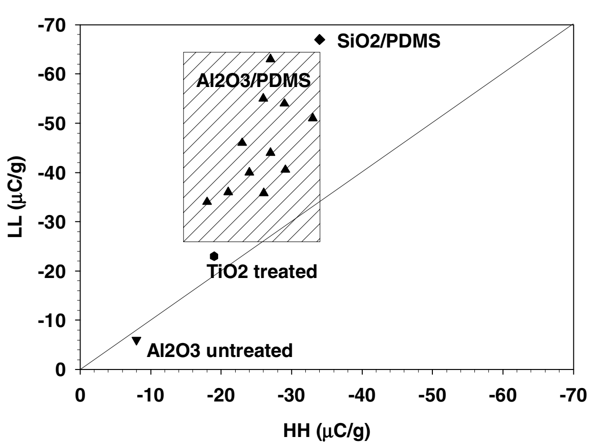
Solid state ^{29}Si NMR spectra recorded after PDMS treatment at different reaction conditions show the presence of silica and fragments of PDMS attached to the surface in different proportions.

Results of LAH titration indicate that before treatment approximately 12-16 reactive hydroxy groups per nm^2 are present on the surface of fumed alumina. PDMS treatment brings this number down to 2-3 or even 1 hydroxy group per nm^2.

Prepared samples have carbon content between 0.5 and 6.5 wt% and become fully wetted in water/methanol solution at methanol concentrations greater than 70 vol%.

Performance of PDMS treated fumed alumina in toner formulations. Results of the tribocharge measurements for formulations with polyester and styrene acrylic toners are summarized in Figure 1 and 2, respectively.

Figure 1. Tribocharge data for PDMS treated SpectrAl® 81 and SpectrAl® 100 together with the data for untreated SpectrAl® 100, octyltriethoxysilane

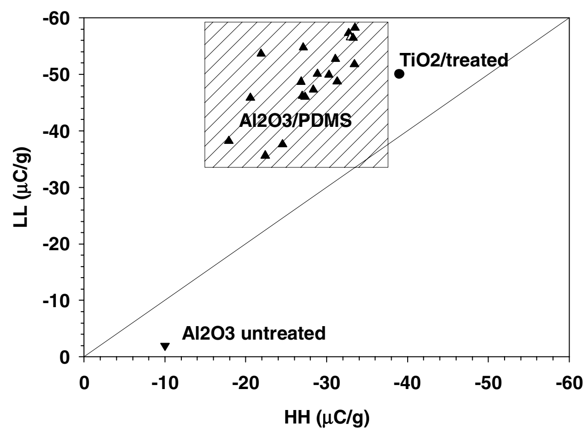


treated titanium oxide, and PDMS treated fumed silica (Cab-o-Sil® TG308F grade, BET=200 m2/g). All additives except Cab-o-Sil® TG308F were used at 1.5 wt% level in formulation with polyester toner. Loading of Cab-o-Sil® TG308F was adjusted for surface area.

Data in Figures 1 and 2 indicate that in formulations with either type of toner untreated fumed alumina shows tribocharge close to zero at HH and LL. Low absolute values and small variation of tribocharge with temperature and humidity for untreated alumina powders are not new and have been reported earlier [7, 8, 9].

Data shown in Figures 1 and 2 illustrate that the tribocharge of fumed alumina can be increased significantly by treatment with PDMS oil. As a result of high temperature PDMS treatment, some silica is formed on the alumina surface and also low molecular weight products of PDMS depolymerization become attached to the surface making it hydrophobic. The extent of these transformations can be controlled by changing either the amount of PDMS on the surface or by changing the treatment conditions.

Figure 2. Tribocharge data for PDMS treated SpectrAl® 81 and SpectrAl® 100 together with the data for untreated SpectrAl® 81 and



octyltriethoxysilane treated titanium oxide. All additives were used at 1.5 wt% level in formulation with styrene acrylic toner.

As can be seen from the graphs, tribocharge of PDMS treated alumina is significantly higher than tribocharge of untreated alumina and can be close to tribocharge of PDMS treated silica. Many of the prepared samples also show significant improvement in humidity resistance (HH/LL) vs. PDMS treated silica. In fact, some of the prepared samples show humidity resistance on par with treated titanium oxide.

Tribocharge data as a function of loading of treated SpectrAl® 100 on the polyester toner are shown in Figure 3. A slight decrease in tribocharge at HH and LL is observed upon increased loading. Humidity resistance improved from 0.66 at 0.5 wt% to 0.75 at 1.2 wt%.

Results of free flow measurements of PDMS treated SpectrAl® 81 and SpectrAl® 100 together with the data for Cabot's commercial fumed silica grades Cab-o-Sil® TG810G and TG308F and treated titanium oxide are summarized in Figure 4. Cab-o-Sil® TG810G and TG308F are 325 m^2/g HMDZ treated and 200 m2/g PDMS treated fumed silicas, which are currently used as free flow aids in several commercial toner formulations.

The data show that the free flow of PDMS treated alumina samples is comparable to that obtained by using conventional treated fumed silica grades. OTES treated alumina shows free flow similar to OTES treated titania. However, we observed that in case of alumina slightly longer induction time is required to reach that free flow level.

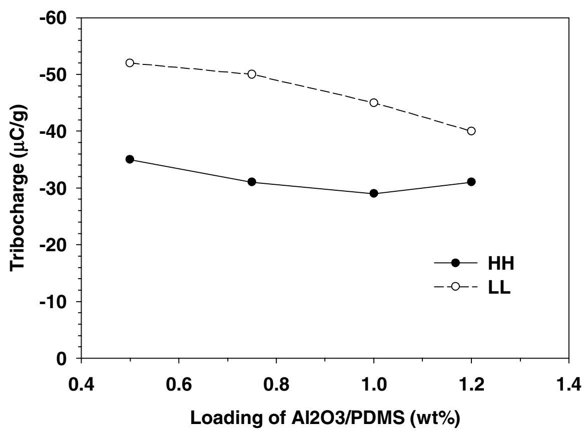


Figure 3. Tribocharge of PDMS treated SpectrAl® 100 sample as a function of loading on the polyester toner.

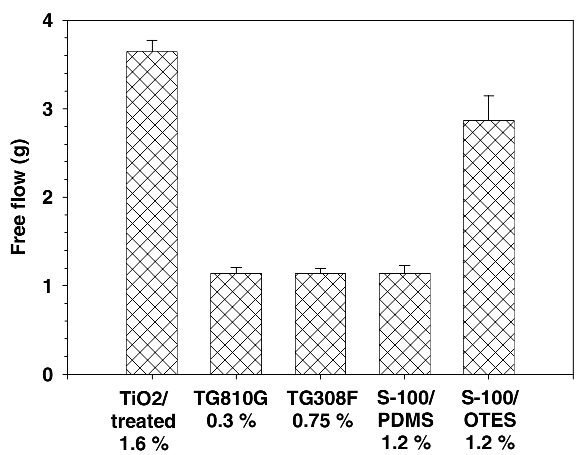


Figure 4. Free flow data for PDMS treated SpectrAl® 81 and SpectrAl® 100 in comparison with the free flow data for Cab-o-Sil® TG810G (325 m^2/g) and Cab-o-Sil® TG308F (200m^2/g) fumed silica grades. Loadings of additive (wt%) in toner formulation are also shown.

Performance of alkyl silane treated fumed alumina. Treatment of fumed alumina with octyltrichloro or triethoxysilanes affords samples that tribocharge lower than PDMS treated. Data for two octyltrichlorosilane treated SpectrAl® 100 samples are shown in Figure 5.

This treatment, as opposed to PDMS, does not produce a silica-like surface and therefore the absolute value of tribocharge for these samples is lower and closer to untreated alumina than to treated silica.

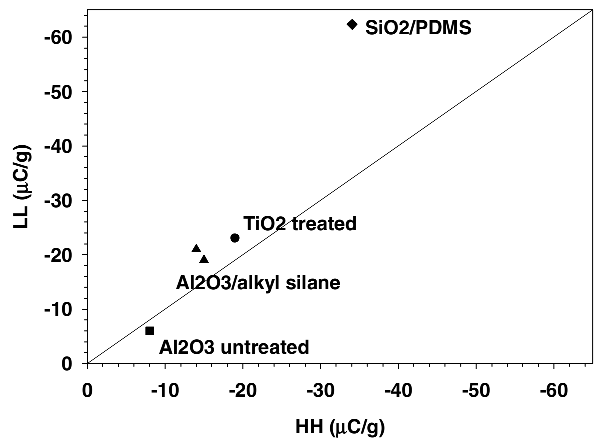


Figure 5. Tribocharge data for octyltrichlorosilane treated SpectrAl® 81 and SpectrAl® 100 together with the data for untreated SpectrAl® 100, octyltriethoxysilane treated titanium oxide, and PDMS treated silica in formulation with polyester toner.

Tribocharge data with different loadings of SpectrAl® 100 treated with OTES and formulated with polyester toner are shown in Figure 6. The data show a larger decrease of tribocharge at LL than HH with increased loading. This leads to the improvement in humidity resistance, and in fact, by adjusting the loading, one can attain perfect HH/LL = 1.

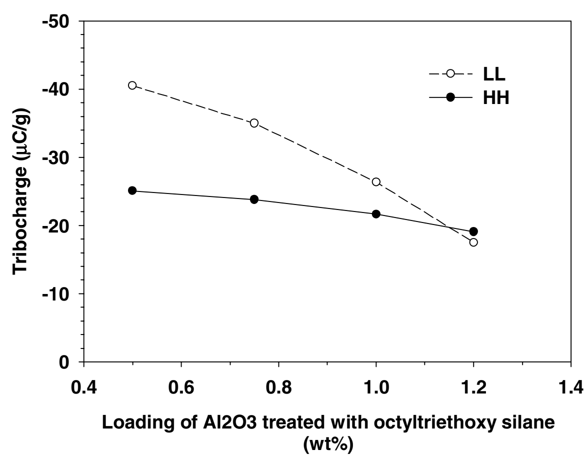


Figure 6. Tribocharge for OTES treated SpectrAl® 100 as a function of additive loading on the polyester toner.

Finally, we should point out that we have also experimented with a number of other treatments on both silica and alumina. In Figure 7 we see the summary of this work with comparisons to the reference titania material. Figure 7 illustrates two important features of humidity resistance of treated fumed oxide additives. First, by plotting the absolute (negative) LL tribocharging versus the ratio of HH/LL, we can clearly see that there is a trade-off. As absolute tribocharging is increased, HH/LL becomes lower (i.e. poorer humidity stability).

This trade-off seems to occur for all metal oxides we tested over a variety of treatments. Second, although the trade-off still exists for alumina, alumina provides flexibility not observed with silica. By changing treatments, one can manipulate the tribocharging over a wider range than one can with silica.

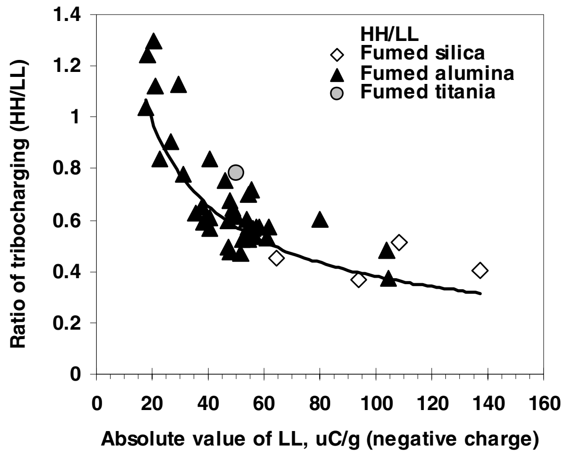


Figure 7. *All available treated alumina tribocharging data on a styrene acrylic toner base compared with treated silica and treated titania data.*

Conclusions

Alumina has been shown to be a versatile base particle for control of tribocharging and humidity resistance. By manipulating surface treatment and additive loading on the compounded toner, a wide span of tribocharging strengths can be attained. We believe this is due to alumina's low tribocharging behavior in untreated form. Thus, the surface treatment determines the tribocharging behavior. Conversely, because silica has innately high tribocharging, the base oxide dominates the tribocharging behavior, and manipulating tribocharging with surface treatment is difficult.

Specifically, treated SpectrAl® 81 and SpectrAl® 100 fumed alumina with PDMS and alkoxy provide a good balance between high tribocharging and good humidity resistance. Additionally, they have good free flow properties and thus could easily be used as external additives in toner formulations along with or instead of the more traditional fumed silica and fumed titania-based additives.

Tribocharge properties of PDMS treated fumed alumina are a function of treatment conditions and can be varied in a wide range. Humidity resistance better than that of PDMS treated silica and equal to alkoxysilane treated titanium oxide was attained for PDMS treated fumed alumina samples.

Treatment of fumed alumina with octyltriethoxy- and octyltrichlorosilanes affords materials that tribocharge lower than PDMS treated. These materials also show high humidity resistance and free flow similar to octyltriethoxysilane treated titania.

Treated alumina offers the added advantage that it does not interfere with the color characteristics of the toner as much as titania.

In summary, treated fumed alumina is an attractive alternative to other fumed metal oxides, and it can provide additional versatility in formulating toners.

References

[1] US 5,707,770

[2] EP 0 498 942 A1

[3] Colson, A.F. *Analyst*, **1957**, *82*, 358-362.

[4] Dvornic, P.R. "*Thermal Properties of Polysiloxanes*", in "*Silicon-Containing Polymers*", Jones, R.G.; Ando, W.; Chojnowski, J., Eds., Kluwer Academic Publishers, Dordrecht, the Netherlands, 2000, pp. 185-212.

[5] Grassie, N.; Macfarlane, I.G., *Euro.Polym. J.*, **1978**, *14*, 875-884.

[6] Adrianov, K.A.; Papkov, V.S.; Slonimskii, G.L.; Zhdanov, A.A.; Yakushina, S.Ye., *Vysokomol. Soedin., Sar. A*, **1969**, *11*, 2030-2042.

[7] Veregin, R.P.N.; Powell, D.; Tripp, C.P.; McDougall, M.N.V.; Mahon, M., *J. Imaging Sci. Technol.* **1997**, *41(2)*, 192-195.

[8] Veregin, R.P.N.; McDougall, M.N.V.; Tripp, C.P., *J. Imaging Sci. Technol.* **2001**, *45(2)*, 174-178.

[9] Oguchi, T.; Tamatani, M. *J. Electrochem. Soc.*, **1986**, *133(4)*, 841-847.

Author Biography

Dmitry Fomitchev received his MS in chemistry from Moscow State University, Moscow, Russia and his PhD in chemistry from SUNY at Buffalo, Buffalo, NY. Since 2005 he is working in Fumed Metal Oxide R&D at Cabot Corporation in Billerica, MA. His work is focused on the development of external additives for toners.