JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 45, Number 2, March/April 2001

Chemical Surface Modification of Alumina and Titania for Improved Admix of Xerographic Toners

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Nanosize silica, titania and alumina metal oxide particles are common xerographic toner additives for control of flow, charge, development and transfer. Typically the oxides are rendered hydrophobic by reaction of the surface hydroxyl groups with organosilanes. This treatment leads to improved flow and charging properties but also typically gives unacceptably long admix charging times. It is shown that admix times on alumina and titania can be dramatically reduced by adsorption of amines such as triethylamine. The most acidic hydroxyl groups of alumina and titania undergo a proton transfer to form a salt with the triethylamine: it is this species that gives rise to improved admix. In effect, the formation of the quaternary salt on the surface mimics the performance of traditional ionic charge control agents. Alternatively, the same decrease on admix can be achieved by incorporating covalently bound sulfate species on the oxide surface. The sulfate groups increase the ionic character through an enhancement of the Bronsted acidity of the oxide. Only a relatively few hydroxyl groups need to be converted to an ionic form (either by amine addition or sulfate incorporation) to dramatically improve admix. A majority of the hydroxyl groups remain unaffected. These remaining groups can then be reacted with an organosilane to yield an oxide with increased negative charge and improved flow. The decrease in admix time with amine pretreatment is independent of the effects of subsequent hydrophobic treatments. In this case, the shorter admix times generated by the quaternary amine salt is retained.

Journal of Imaging Science and Technology 45: 174–178 (2001)

Introduction

Metal oxides such as alumina, titania and silica are commonly used to improve flow,[1] charge,[2,3] development[4] and transfer[5] of xerographic toner. These improvements in xerographic properties are obtained by dispersing the metal oxides on the surface of the toner. The net effect is that the surface properties of the toner are then controlled by the surface properties of the metal oxide particles. Because the surface properties of the metal oxide are dictated by the nature of the surface hydroxyl groups, any chemical modification of the surface hydroxyl groups is tantamount to performing a chemical modification of the surface of the toner. However, in contrast to "traditional" ionic CCA's, comparatively little work has been done to understand the role of the metal oxide surface chemistry in xerographic systems.[2,3,6]

Contact potential measurements (CPD) have shown that toner triboelectric charge depends on the work function of the metal oxide[7] with metal oxides as surface additives. The work function is correlated with the acid/base nature of the oxide surface, which, in turn, is primarily controlled by the nature of the surface hydroxyl groups. The more acidic the hydroxyl group, the more negative the triboelectric charge. The implication is that by changing the nature of the hydroxyl sites one can modify the charge control properties of metal oxides. This behavior is analogous to that observed by Hair and Fabbish[8] and Julien[9] for carbon black surfaces, where the work function, and thus the triboelectric charge, was shown to depend on the pH of the carbon black surface.

Organosilanes are by far the most common chemical agent used to modify the surface of metal oxide particles.[10] The organosilanes are bifunctional in nature containing either alkoxy or chloro groups that react with the surface hydroxyl groups, as well as organo functionalities that extend out from the surface.

$$\mathrm{MOH} + \mathrm{X}_{(4-n)}\mathrm{SiR}_n \rightarrow \mathrm{M{-}O{-}\,Si\,X}_{(3-n)}\mathrm{R}_n + \mathrm{HX} \qquad (1)$$

Here M = metal atom, X = Cl or alkoxy, and R = organo group.

Conversion of the hydroxyl groups to organosilanes typically yields hydrophobic metal oxide particles. This produces a change in the amount and distribution of adsorbed water on the surface which impacts both charge and flow and the relative humidity dependence in these properties.[3] While hydrophobic silane treatments lead to better charge and flow characteristics, it is accompanied by unacceptable increases in admix times.

Original manuscript received July 10, 2000

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Admix is a critical performance attribute for a xerographic developer. Figure 1 illustrates the charging of an ideal two component developer as a function of the developer mixing time. An initially uncharged developer shows an increase in charge (q/m) that ultimately reaches a saturated equilibrium value, determined by the difference in workfunction, or chemical potential. Following Gutman and Hartmann's Eq. 18 in Ref. 11,

$$\frac{q}{m}=\frac{b}{(C+C_0)}\left(\Phi_t-\Phi_c\right)\left(1-e^{-t/\tau}\right). \qquad (2)$$

Here Φ_t and Φ_c are the chemical potentials of toner and carrier, C is the toner concentration in the developer, C_o is a constant that depends mainly on the toner and carrier geometry, and b collects a series of terms that can be considered constant for the purposes here. Thus, toner charge initially increases from zero with a time constant, τ ,to a q/m value at longer mixing times that has saturated to a constant value determined by the toner and carrier chemical potentials.

Admix occurs when uncharged toner is added to an already charged developer. The added toner will increase in charge, while the initially charged toner in the developer will decrease in q/m to balance the overall charge. Eq. 2 requires that as the toner concentration increases, the overall q/m must decrease. At some time after addition of the uncharged toner, called the admix time, the initially charged and uncharged toner will have the same q/m, and ideally, a charge distribution that is no broader than the initial charge distribution. The q/m of the final admixed developer will be lower than the initial q/m, as the toner concentration (C in Eq. 2) has increased. The developer admix is critical to functional performance in a xerographic marking engine, as new uncharged toner is continually added to replace the toner that is developed onto the image. Insufficient admix results in low charge, uncharged, and wrong sign toner that will develop poorly, or into the background, or even cause a catastrophic emission of toner to the environment.

Gutman and co-workers[12] have analyzed the admix charging process as shown in Eq. 3:

$$\frac{dq}{dt}=\frac{a\varepsilon_0 v\Delta}{ed_s}\left(\Phi_t-\Phi_c\right)+\left(a\varepsilon_0 v\Delta\right)E \qquad (3)$$

In Eq. 3, dq/dt is the time rate of change of the charge; a is the actual contact area; d_s is the maximum separation of the toner and carrier where the two remain in equilibrium via charge tunneling; v is the rate of collision of toner and carrier; Δ is the joint density of states available for charge transfer; ε_0 is the permittivity constant; and E is the interfacial field at the toner/carrier contact. Thus, Eq. 3 shows that the charge rate is increased by an increase in density of states or collision rate. The density of states would be expected to be higher for organic molecules that have greater delocalization of the orbitals. Increasing the intensity of the mixing can increase the frequency of contacts, leading to a faster admix. Gutman and co-workers also speculate that admix may depend on toner–toner charge sharing, and thus, perhaps, on a "local" toner conductivity that can equalize the potential between two toner particles over a small local area. Thus, an increase in local toner conductivity could lead to faster admix.

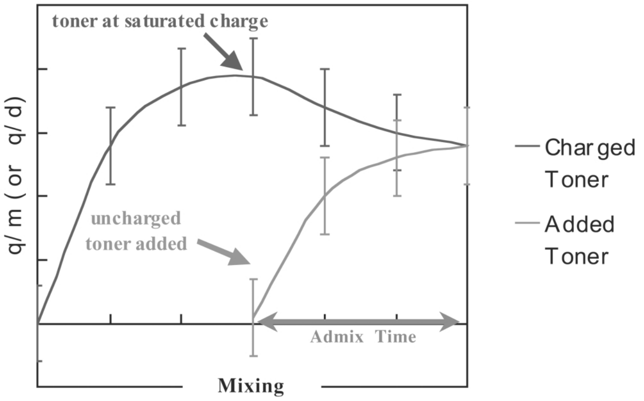

Figure 1. Charging and admix behavior of an ideal xerographic developer.

While Eq. 3 indicates some of the factors that control admix for a given toner and carrier in given mixing conditions, it is currently not possible to predict how the developer will admix, *a priori*. However, one known method to improve admix times is to add a traditional charge control agent (CCA), such as metal complex salts, to the toner. An example of typical metal complex salts are $\{ML_n^{y-}\}\,y\,N^{+}$, where y and n are integers, M is a metal, L is a ligand, and N is a positive charged counterion, as described by Law and co-workers.[13] One might speculate that the metal complex has a high density of states due to the additional states provided by the metal ion, and perhaps, delocalization across the ligands of the complex.

The current work highlights a new approach that chemically modifies a fraction of the hydroxyl groups on alumina and titania to mimic that of traditional ionic CCA's. Specifically, the most acidic hydroxyl groups on alumina and titania are converted to an ionic form by proton transfer via addition of a strong amine base such as triethylamine (TEA). A quaternary salt is produced in which surface Al–O⁻ or Ti–O⁻ sites act as the counter anion.

$$\mathrm{MOH + N(CH_2CH_3)_3 \rightarrow M{-}O^{-}\,H^{+}N(CH_2CH_3)_3} \qquad (4)$$

Alternatively, portions of the hydroxyl groups are converted to chemisorbed sulfate species.[14] Upon exposure to water the sulfate groups exhibit enhanced Bronsted acidity.[15]

The remaining hydroxyl groups on either the TEA treated or sulfated oxides are then modified using standard silane treatments to improve flow and reduce charge variance with relative humidity (RH). These dual functional metal oxide additives dramatically improve admix times, while maintaining flow and RH sensitivity comparable to that of a silane-only treated oxide. In this work, we correlate the molecular surface chemistry as determined by infrared spectroscopic analysis to the xerographic properties of charge and admix. It is noted that we purposely avoided using these new approaches with silica. While silica is by far the most common metal oxide used in xerographic applications, its chemistry differs markedly from titania and alumina. Results on silica are provided solely for comparative purposes. Adsorption of TEA on silica results in the formation of a strong hydrogen bond with the surface hydroxyl groups with few, if any undergoing a proton transfer.[16] In addition, SO_2 or H_2S do not adsorb on silica or lead to any chemisorbed sulfate products upon high temperature oxidation.[17]

Experimental

Silica (Aerosil 380™), aluminum oxide (AlonC™), and titanium dioxide (P25™) were obtained from Degussa A.G. Hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) were obtained from Huls Petrarch. All other reagents were obtained from Aldrich. Reagents were transferred to evacuated glass bulbs using standard freeze–thaw cycles.

The metal oxides (300–500 mg) were placed inside a glass reaction vessel and evacuated at room temperature for 30 minutes. HMDS, TMCS and TEA treated samples were produced by adding an excess quantity of reagent vapor to the oxide for 30 min. at room temperature followed by evacuation for 5 min. Sulfated titania was produced by exposure of the titania to air bubbled through sulfuric acid solution or by exposure to SO_2 or H_2S vapor. The sulfuric acid, or SO_2/H_2S vapor treated sample, was then calcined for 4 h at 400°C to form a surface-attached sulfate species.[14] Additional silanation of the TEA or sulfated treated oxides was done by evacuating the treated oxide at room temperature for 30 min, followed by addition of gaseous TMCS or HMDS for 30 min, and then evacuation for 5 min.

Oxides were roll milled on base toners with 10:1 wt/wt steel shot for 15 min. As charge depends on additive coverage, experiments were conducted at consistent 100% coverage[18] (as defined by equal additive and toner surface areas). Because fumed metal oxides are fractal fused aggregates of the primary spherical particles, it is not possible with any blending to produce non-aggregated primary spherical particles on the toner surface. Thus, the additives are dispersed on the surface as these fused aggregates (typically about 200 to 400 nm for the additives here), not as primary particles. Scanning electron microscopy confirmed that the coverage of additives was relatively uniform, dispersed to the expected aggregate size, but was in all cases significantly less than a perfect 100% coverage. Nevertheless, provided the coverage is uniform, this 100% coverage provides enough surface coverage of the toner (about 50% actual coverage, as judged by SEM) to ensure that the toner contact with carrier is between the toner surface additive and the carrier, and not the bare toner particle and the carrier. Thus charging performance is dependent on the additive properties, and not the parent toner properties.

Toners (2 wt%) and carriers were conditioned overnight at 20% relative humidity, then roll milled for 1, 15, 30, and 60 min. Toner charge was measured by blow-off tribo[19] and charge spectrograph.[20] A stable saturating charge was reached within 15 min. The saturated charge at 15 minutes is reported here. As charging conditions were constant, q/m and q/d values are proportional to A_t, representing the materials' chemical potentials.[11] Admix was determined by adding 2% toner to charged developer (15 min), then roll milling until the observed two peaks collapsed to a single peak.

Flow of the toner was measured using the Hosokawa Micron Powder Characteristics Tester with the standard Hosokawa screens and conditions, calculating the standard Hosokawa % cohesion. Better flow is indicated by a lower percent cohesion value.

The use of infrared spectroscopy to identify chemical reactions on metal oxide surfaces is well established.[21]

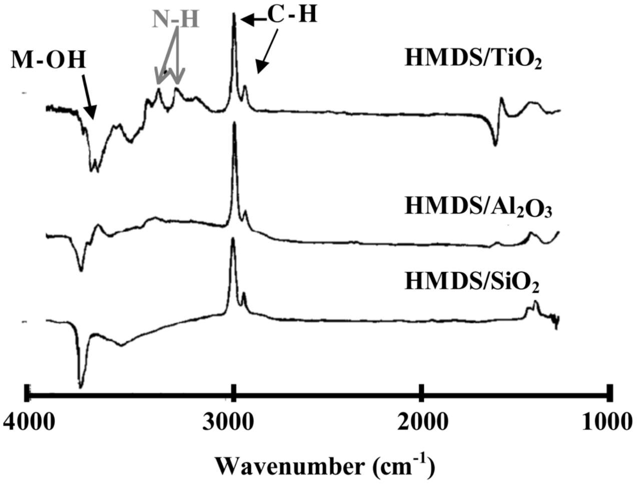

Figure 2. IR spectra of HMDS treated oxides.

TABLE I. Triboelectric Charge of Base Treated Al_2O_3

Alumina Surface Additive	Charging of Black Styrenic Toner (Electropositive Carrier)		Charging of Xerox 1005™ Magenta Toner (Electronegative Carrier)	
	q/m (μC/g)	Admix (s)	q/m (μC/g)	Admix (s)
none	–28	120	21	60
Al_2O_3	–1	>240	34	>240
Al_2O_3/HMDS	–3	>240	35	120
Al_2O_3/TEA	–2	15	23	15
Al_2O_3/TEA/HMDS	–7	15	25	15

All cases have 1.2 wt% additive loading.

Detailed procedures for the thin film experiments and in situ gas cell are given elsewhere.[22] Infrared spectra were collected on a Bomem Michelson 102 FTIR equipped with a CsI beam splitter and a DTGS detector. Typically, 100 scans were co-added at 4 cm^{-1} resolution. Each scan required approximately 6 sec. Spectra are reported as difference spectra and as such, positive bands are due to species formed on the surface and negative bands refer to bonds removed from the surface.

Results and Discussion

Triboelectric Charging of Toner with Silane treated Metal Oxide.

Hexamethyldisilazane (HMDS) is a common silating agent for metal oxide particles and reacts with the surface hydroxyl groups according to the following scheme.

$$2MOH + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow 2MO\text{–}Si(CH_3)_3 + NH_3 \quad (5)$$

Evidence supporting this reaction on silica, alumina, and titania is provided by the infrared spectra shown in Fig. 2. The negative bands in the 3750–3600 cm^{-1} are due to MO–H stretching modes and the negative bands shows that the hydroxyl groups participate in the reaction. Positive bands at 2953 and 2900 cm^{-1} (C–H stretching modes) is clear evidence of formation of M–O–$Si(CH_3)_3$ on the surface. Additional positive features appear in the region 3400–3200 cm^{-1} for both titania and alumina. The peaks have been assigned to NH_3 bonded at two different Lewis acid sites and to a molecular adsorbed NH_3.[23] There is no evidence of M–NH_2

TABLE II. Triboelectric Charge of Base Treated TiO_2

Oxide	Toner q/m at 20% RH (μC/g)	Toner Admix (s)
None	–21	>240
TiO_2	–18	120
TiO_2/HMDS	–18	>240
TiO_2/TEA	–20	30
TiO_2/TEA/HMDS	–18	15
TiO_2/TMCS	–10	>240
TiO_2/TEA/TMCS	–19	30

Toners had 2 wt% TiO_2. The base toner was a cyan polyester. The carrier was the same electropositive carrier used with aluminas as in Table I.

TABLE III. Triboelectric Charge of Base Treated SiO_2

Silica Surface Additive	Q/m 20%RH (μC/g)	Admix (s)
None	–21	>240
A380	–49	60
A380/TEA	–43	30

Toners have 0.5 wt% SiO_2 loading. The base toner was a cyan polyester. The carrier was the electropositive charge carrier used for aluminas as in Table I.

species or protonated compounds on either alumina or titania.[23] Lewis acid or base sites are not present on silica and therefore positive bands due to adsorbed NH_3 in the 3400–3200 cm^{-1} are not detected.

Table I shows triboelectric charging and admix data of toner blended with HMDS treated Al_2O_3. The base toner and carrier were chosen to give either negative or positive charging toner. In negative charging toner, alumina decreases charge. Due to the low charge on a negative charging toner, the positive charging Al_2O_3 is better suited to a positive charging toner. In this case, the Al_2O_3 increases charge. In both toners, alumina decreases the work function of the toner, making it more positive (or less negative) charging. Also in both cases the admix becomes substantially longer, which is not desirable. Treatment with HMDS shows little or no effect on charge level, but admix was improved by greater than two fold for the positive charging toner.

Table II shows triboelectric charging with HMDS and TMCS (trimethylchlorosilane) treated titania on a negative charging toner. TCMS also produces an M–O–$Si(CH_3)_3$ attached species but generates HCl instead of NH_3 as a byproduct. The untreated titania improves the admix of the base toner, but this performance is lost after HMDS or TMCS treatment. Therefore, the effects of using silane treated oxide produce similar admix results on both alumina and titania. While charge is slightly better with HMDS/Al_2O_3 and remains unchanged with HMDS/TiO_2, the admix time is worse. The results with HMDS and TMCS treated TiO_2 further show that the presence of adsorbed NH_3 species with the HMDS treatment had little effect on admix time.

Triethylamine Treated Alumina and Titania

The reaction of TEA with alumina and titania occurs at both Lewis acid sites and with the surface hydroxyl groups.[24–26] In our experiments the oxides are fully hydroxylated and under these conditions, the reaction of TEA occurs primarily with the hydroxyl groups on the surface. Figure 3 shows the spectra obtained after addition of TEA to titania, alumina and silica. In all cases, the negative MO–H bands in the 3750–3600 cm^{-1} spectral region indicate interaction with the surface hydroxyl groups. There are several bands in the 2980–2800 cm^{-1} spectral region, which are due to various C–H modes of the attached TEA molecule. The broad feature near 2690 cm^{-1} in the silica spectrum (Fig. 3c) is due to shift in the SiOH band at 3747 cm^{-1} arising from a strong H–bond with the adsorbed TEA.[13] In contrast, the spectra of TEA adsorbed on alumina and titania (Figs. 3a and 3b) show distinct bands in the 2700–2400 cm^{-1} that are due to formation of N–H^+ species. This provides clear evidence supporting formation of a quaternary species as outlined in Scheme 3. A portion of the hydroxyl groups on alumina and titania have sufficient acidity to undergo a proton transfer with the TEA. In contrast, the N–H^+ bands do not form on silica. TEA only forms a strong hydrogen bond with the silica hydroxyl groups as evidenced by the shift in frequency from 3747 cm^{-1} to 2690 cm^{-1}.

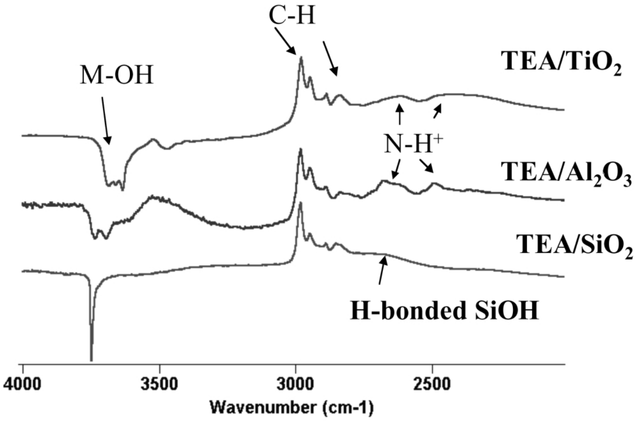

Figure 3. IR spectra of TEA treated oxides.

The impact on incorporating ionic surface attached species on admix is evident. Both alumina and titania show a marked decrease in admix time. On silica, the adsorbed TEA does not form ionic species and when blended on a toner, this additive shows little change in admix time. This need for an ionic amine surface species explains the admix results obtained with both HMDS and TMCS treated titania. Both additives show equally poor admix times despite the presence of adsorbed NH_3 in the HMDS treated surface. As with TEA treated silica, the HMDS treated alumina and titania show no spectral evidence of any protonated NH_3 species.

The data in Tables I–III show that the changes in admix with TEA addition occurs without a major change in the charge. Overall, TEA treatment gives a slightly less positive charging alumina for both the negative and positive toner charging system, whereas on titania incorporation of TEA has no appreciable effect on the charge. Moreover, improvements in admix with TEA treatment is retained when the oxides are subsequently treated with HMDS. This is in contrast to the effect on admix with HMDS treatment alone. It is noted that subsequent HMDS treatment of a TEA doped oxide can also result in improved RH sensitivity and improved flow. For example, HMDS treated alumina on the black styrenic toner of Table I has the same excellent flow cohesion, with or without TEA (2.4% measured with the Hosokawa Micron Powder Tester), compared to the untreated alumina (5.6% cohesion measured with the Hosokawa Micron Powder Tester). Similarly, titania HMDS treatment significantly improves flow cohesion, with or without TEA (6.4% cohesion for untreated tita-

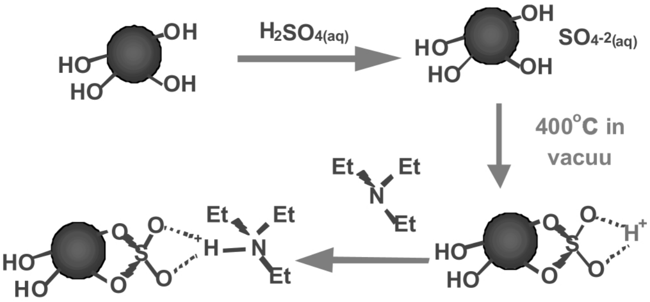

Figure 4. Treatment process for preparation of sulfated Titania.

nia, compared to 3.8% for HMDS treated titania, and only 2.4% cohesion for HMDS and TEA treated titania). Also, HMDS treatment of titania with TEA, on the negative charge toner, improves RH sensitivity (the ratio of the charge at 20% RH to the charge at 80% RH, improves from 4.0 to 3.6), although only slightly. Thus, using the two step treatment (TEA followed by HMDS) retains the fast admix due to TEA, while the subsequent HMDS treatment can improve flow and RH sensitivity. It should be noted, however, that RH sensitivity of TEA treated titania, even with subsequent HMDS treatment, is inferior to titania with HMDS treatment alone.

Sulfated Titania

Both sulfated titania[27] and alumina[28] exhibit augmented acidity that give rise to increased catalytic activity.[15] The sulfate modified oxides are known as solid superacid catalysts and are generated by initial impregnation of the oxide with H_2SO_4[26] or initial chemisorption of SO_2 or H_2S [14] followed by calcination at 400°C. The increased Brønsted acidity has been shown to arise from a reaction of the covalent sulfate with water giving rise to the formation of SOH groups.[14] As with the TEA treatment, the sulfation process leads to a protonated surface species.

Table IV shows that the incorporation of covalent sulfate species lowers the admix time. The superacid on TiO_2 increases charge and improves admix. In all cases, trimethylchlorosilane (TMCS) was used as a hydrophobizing agent (TMCS avoids side reactions with amines, as observed when using HMDS). With TMCS treated TiO_2, charge is lower with a much slower admix. With both sulfate and TCMS, charge is increased and admix is much improved.

Conclusions

The acidity of the metal oxide modulates the work function of the oxide. Both acidity and the tendency to negative tribocharging increase with acidity: silica > titania > alumina. Previous work with CPD measurements[7] suggests strongly an electron transfer, not ionic transfer, mechanism is operating. Adsorption of bases such as triethylamine on alumina and titania dramatically improves admix performance. Adsorption of these bases on titania also creates ionic salts, much like "traditional" CCA's, on titania surfaces, a result of proton transfer from the acid to the amine. These salts also improve toner admix and charge levels. Surface attached superacid sites can also be created by treatment with sulfuric acid followed by calcination and this also leads to improved admix performance. Moreover, the drastic reduction in admix time achieved by incorporating a few superacid or protonated amine sites operates independently from the properties imparted by subsequent treatment with silanating agents. These dual functional additives (i.e., first sulfation or amine treatment, then silanation) exhibit favorable charge and flow characteristics derived from the silanation step while retaining the favorable admix performance of the initial superacid or amine treatment.

TABLE IV. Toner Charge with Superacid on TiO_2

Titania Surface Additive	q/m at 20% RH (μC/g)	Admix (s)
None	–21	>240
TiO_2	–18	120
TiO_2/SO_4^{2-}	–26	30
TiO_2/ TMCS	–10	>240
TiO_2/SO_4^{2-} /TMCS	–23	60

Toners have 0.5 wt% SiO_2 loading. The base toner and the carrier are the same as in Table II.

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