

Chemical Surface Modification of Alumina and Titania Surface Additives for Charge Control of Xerographic Toners

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Abstract

Nanosize silica, titania and alumina metal oxide particles are common xerographic toner additives for control of flow, charge, development and transfer. While silica is the most common and most studied oxide, titania and alumina have a more complex surface, comprised of surface acidic, basic and neutral sites. Further, superacid sites can be created by treatment with sulphuric, phosphoric or boric acids. These treated oxides show increased negative charge and admix when used as toner surface additives. For titania the charge increases with the acidity of the acid, in the order: boric acid < phosphoric acid < sulphuric acid.

Infrared spectroscopy shows that calcining results in surface attachment of these acidic sites to the TiO₂ surface. Further, these acidic sites, which involve about 5% of the total hydroxyl sites, can form ionic salts with triethylamine, a result of proton transfer from the acid to the amine. This results in a further increase in charge, and improvement in toner admix rates and RH sensitivity.

Introduction

Metal oxides such as alumina, titania and silica are commonly used to control flow,¹ charge,^{2,3} development⁴ and transfer⁵ of xerographic toner. While metal oxides are potent charge control agents (CCA's), in contrast to "traditional" CCA's little work has been done to either understand or modify the charging of metal oxides, aside from standard hydrophobic silane treatments, which react with surface hydroxyls, or simple surface physisorption.⁶ The current work highlights a new approach that mimics that of "traditional" CCA's, resulting in higher charge, enhanced admix, and narrowed charge distributions.

Experimental

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 100% coverage⁷ (equal additive and toner surface areas). Coverage uniformity was confirmed by scanning electron microscopy. Toner (2 wt%) and carrier were conditioned

overnight at 20%, 50% or 80% RH, then roll milled for 1, 15, 30, and 60 min. Toner charge was measured by blow-off tribo⁸ and charge spectrograph.⁹ A stable saturating charge was reached within 15 min., the value quoted here. As charging conditions were constant, q/m and q/d values are proportional to A_c, representing the materials' chemical potentials.¹⁰ Admix was determined by adding 2% toner to charged developer, then roll milling until the observed two peaks collapse to a single peak.¹¹

Infrared spectra (IR) were obtained from thin oxide films and are plotted as difference spectra (the observed spectra with treatment, minus the spectrum before treatment).¹² Positive peaks represent bonds formed, while negative peaks represent bonds broken.

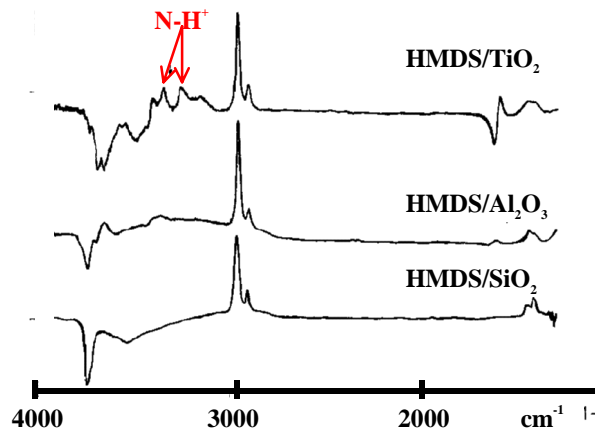


Figure 1. IR spectra of HMDS treated oxides.

Results and Discussion

Base Treated Alumina

Figure 1 shows IR spectra of Degussa A380TM silica, aluminum oxide CTM, and titanium dioxide (P25TM) after treatment with hexamethydisilazane (HMDS), a self-catalyzing hydrophobic treatment (Figure 2a). The amine H-bonds to a surface hydroxyl, activating the site to attack a trimethylsilyl moiety. This activation has been previously demonstrated by addition of triethylamine (TEA) to

catalyze silane surface reaction.¹³ For silica, the NH_3 is H-bonded to surface hydroxyls, while titania and alumina have acidic sites that react to form surface-attached salt (Figure 2b). While H-bonded NH_3 can be readily removed by heating in vacu, the salt cannot. The IR spectra in Figure 1 do show a band due to NH_3 salt on titania, and to some extent on alumina, but not on silica.

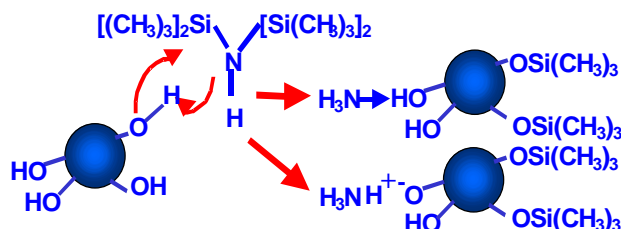


Figure 2. Reaction of HMDS with metal oxides.

Table 1. Triboelectric Charge of Base Treated Al_2O_3

Oxide	Black Styrenic Toner/Positive Charge Carrier			Xerox 1005™ Magenta Toner/ Negative Charge Carrier		
	q/m	Admix	Peak q/d 1/2-width	q/m	Admix	Peak q/d 1/2-width
none	-28	120	2.5	21	60	4
Al_2O_3 HMDS	-3	240	3	35	120	2
Al_2O_3 TEA HMDS	-7	15	2	25	15	5

All cases have 1.2 wt% additive loading.

Table 1 shows triboelectric charging with TEA treated Al_2O_3 , prepared by exposing Al_2O_3 to TEA in vacuum, followed by pumping in vacuum to remove excess. Base toner and carrier were chosen to give either negative or positive charging toner. In negative charging toner, HMDS treated alumina decreases charge and substantially increases admix time, but does narrow the charge distribution. Treatment of Al_2O_3 with TEA increases charge, with very good admix, but gives a poor charge distribution. The positive charging Al_2O_3 is better suited to negative charging carrier, with HMDS treatment of Al_2O_3 increasing charge. However, admix and charge distributions are worse. With TEA and HMDS, charge is not as high as with HMDS alone, but admix is much improved, and the best charge distributions are obtained. Overall, TEA gives a less positive charging alumina with better admix.

Base Treated Titania

Table 2 shows triboelectric charging with TEA treated titania, as negative charging toner. With untreated titania, admix of the base toner is improved, q/d and RH sensitivity are dramatically improved, and charge distributions sharpen. Note that there is an anomalous high

ratio of q/m to q/d for the base toner. This has been observed in a number of cases where the charge distribution is broad. Work is in progress to understand this. HMDS further improves distributions, but admix suffers. In contrast, TEA improves distributions and dramatically improves admix, while RH sensitivity suffers. With both TEA and HMDS, admix improves further, with higher q/d and narrower distributions, but a worse RH ratio. It would appear that proton transfer with TEA hinders successful hydrophobic treatment.

Table 2. Triboelectric Charge with Base Treated TiO_2

Oxide	Cyan Polyester Toner/Positive Charge Carrier						
	q/m 20% RH	q/m 50% RH	q/m 80% RH	q/m 20% RH	q/d 20% RH	Peak q/d 1/2-width	Admix (s)
None	-21	-5	-4	5.3	-0.39	3.0	240
TiO_2	-18	-7	-7	2.4	-0.63	3.7	120
TiO_2 /HMDS	-18	-10	-10	1.8	-0.66	4.2	240
TiO_2 /TEA	-20	-11	-5	4.0	-0.62	4.1	30
TiO_2 /TEA/HMDS	-18	-8	-5	3.3	-0.70	4.3	15

All cases have 2 wt % Degussa P25™ TiO_2

Superacid Containing Titania

Figure 3 shows the reactions to create TiO_2 sulphate sites, to convert them to surface-attached superacid sites,¹⁴ and to create ionic salts of these superacid sites with TEA.

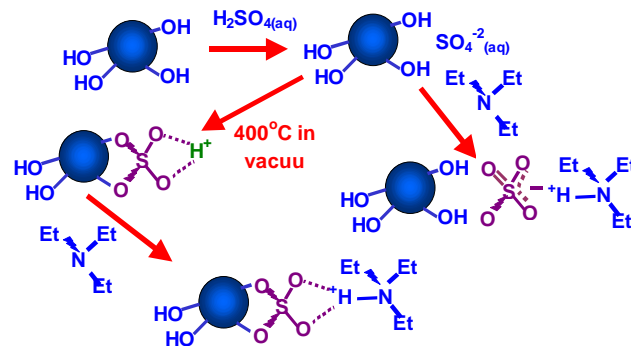


Figure 3. Treatment of titania to create superacid sites

Table 3. Toner Charge with Superacid on TiO_2

Oxide	Cyan Polyester Toner/Positive Charge Carrier						
	q/m				Peak q/d 20% RH	Peak q/d 1/2 width 20% RH	Admix 50% RH
	20% RH	50% RH	80% RH	20% 80%			
None	-21	-5	-4	5.2	-0.39	3.0	240
TiO_2	-18	-7	-7	2.6	-0.63	3.7	120
$\text{TiO}_2/\text{SO}_4^{2-}$ (24h)	-26	-11	-9	2.9	-0.45	2.1	30
$\text{TiO}_2/\text{SO}_4^{2-}$ (4 days)	-17	-5	-1.6	10	--	--	--

All cases have 2 wt% additive loading

Admix, charge and charge distributions improve with TiO_2 addition (Table 3). TiO_2 non-surface bonded sulphate sites were produced by exposure to air bubbled through sulphuric acid solution. Calcination for 4 h at 400°C forms surface-attached superacid sites (Figure 4).

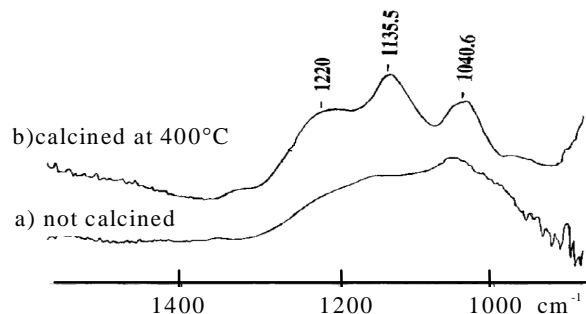


Figure 4. IR spectra of superacid formation on TiO_2 .

After TiO_2 is treated 24 h with sulphuric acid, q/d is lower, with much improved admix. Again, the q/m to q/d ratio is anomalous, due to a broad charge distribution on treatment. After 4 days of treatment charge decreases, nearly zero at 80% RH. The high superacid site loading creates a very hydrophilic titania, resulting in low charge, especially at high RH. Previous work³ has shown a linear decrease in charge with H_2O adsorbed on silica, eventually to zero with complete water surface coverage.

Table 4. Toner Charge with Superacid Salts on TiO_2

Cyan Polyester Toner on Positive Charging Carrier							
Oxide	TEAH ⁺ by IR	q/m			Peak q/d	Peak q/d 1/2 width	Admix (s)
		20% RH	50% RH	80% RH			
none	none	-21	-5	-4.0	-0.39	3.0	240
TiO_2	0	-18	-7	-7.0	-0.63	3.7	120
TiO_2 TMCS	0	-10	-10	-8.0	-0.21	1.0	240
TiO_2 TEA TMCS	<<1	-19	-8	-2.0	-0.68	2	30
TiO_2 SO_4^{2-} TEA TMCS	4	-31	-11	-7.0	-0.60	3.5	60
TiO_2 PO_4^{3-} TEA TMCS	2	-21	-9	-3	--	--	--
TiO_2 BO_4^{3-} TEA TMCS	1	-16	-9	-3	--	--	--

All cases have 2 wt% additive loading

Salts of Superacid Treated Titania

While superacid on TiO_2 increases charge and improves admix, RH sensitivity is still high. To reduce acidity, which might cause problems in xerographic subsystems, weaker acids can be used, or they can be neutralized with TEA to form an ionic salt. In all cases, trimethylchlorosilane (TMCS) was used as a hydrophobizing agent (TMCS avoids side reactions with amine, observed with HMDS). Charging and the amounts of TEAH⁺ formed are shown in Table 4. With TCMS on TiO_2 , RH sensitivity improves, but charge is lower at 20% RH, with much broader distributions, and slower admix. With TEA, IR shows the formation of a small amount of TEAH⁺ salt (Figure 5). With both TEA and TCMS, charge at 20%RH is increased, but at 80% RH is decreased. The charge distribution improves, and admix is much improved.

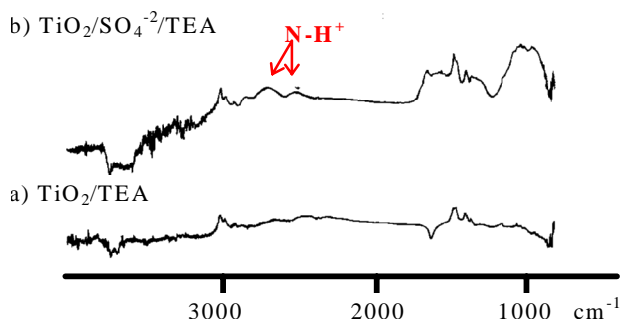


Figure 5. IR spectra of salt formation with TEA.

Table 5. Significant Effects in Full-factorial Design

Factors	Responses					
	q/m			Peak q/d	Peak q/d 1/2-width	Admix
	20%R H	50% RH	80% RH			
TiO_2 (Experiment)	-18	-7	-7	-0.63	3.7	120
Significant Factors						
Calcining	NS					
SO_4^{2-}	-10	-4	-4	NS	-0.9	-100
TEA	-4	-4.5	3	-0.25	0.8	-85
TMCS	1	NS	NS	NS	NS	NS
Significant Interactions						
SO_4^{2-} * TEA	3	NS	NS	NS	NS	-180
SO_4^{2-} * TMCS	-7	NS	NS	NS	-2.1	NS
TEA* TMCS	-7	NS	5	NS	NS	NS

NS = no significant effect (at 95% confidence level)

TiO_2 with sulphate, phosphate or borate superacid sites was prepared by treating with the respective concentrated acids (24 h), calcining, then treated with TEA and TMCS. The superacid sites donate a proton to TEA to form the salt, in the ratio of 4:2:1 for sulphate, phosphate and borate, respectively. The number of ionic sites formed, is highest

with the strongest acid, sulphuric acid, and decreases as the acid becomes weaker. Sulphate provides best charge and RH sensitivity, while phosphate and borate lost charge compared to sulphate, due to the linear relationship of charge with TEAH⁺ formed.

To study all factors in acid and TEA treatment of TiO₂, a full factorial experimental design was undertaken, as summarized in Table 5 (data not shown). Sulphate improves charge in both RH zones, TEA only at low RH, but both increase RH sensitivity. Both treatments improve admix, even more so in combination. Only TEA improves charge distributions, while sulphate and the combination of TEA and sulphate broaden distributions.

Conclusion

Bases such as triethylamine can be used to create ionic salts, much like "traditional" CCA's, on alumina and titania surfaces, a result of proton transfer from the acid to the amine. These salts improve toner admix and charge levels. Surface attached superacid sites can also be created by treatment with sulphuric, phosphoric or boric acids, followed by calcination. These sites also improve admix, and increase charge, although charge distributions broaden. The superacid sites can form TEA salts, further improving admix in a synergistic manner. However, in all cases RH sensitivity worsens as charge increases. Further, the creation of acidic or ionic salts on the titania surface appears to hinder treatment with hydrophobizing silanes.

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Biography

Rick Veregin received his B.Sc. and M.Sc. degree in Chemistry from the University of Manitoba, and in 1985 his Ph.D in Chemistry from the University of Guelph. For the last 14 years he has worked at the Xerox Research Centre of Canada. Dr. Veregin has interests in xerographic physics, surface chemistry, polymer chemistry, and magnetic resonance spectroscopy. He is the author of over 50 papers and 30 US patents, and is a recipient of the A.K. Doolittle Award from the American Chemical Society.