

The Effect of Water on the Triboelectric Charging of Metal Oxide Particles in Xerographic Toners

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Abstract

In xerography, submicron particles of metal oxides, such as silicon dioxide, are commonly added to the surface of toner particles. A series of hydrophobically modified silicon dioxide samples have been prepared, and characterized by Infrared Spectroscopy (IR). The charging of toner particles coated with the untreated hydrophilic and hydrophobically modified silicon dioxide surface additives was measured from 5% to 80% relative humidity. The charging behavior was also measured as a function of toner concentration in the xerographic developers. Infrared Spectroscopy was used to measure the surface water content on the silicon dioxide, as it changed due to relative humidity and the surface hydrophobic treatment of the metal oxide. There is a strong correlation of the toner charge and its toner concentration dependence, with the surface water content on the silicon dioxide. The effect of surface water on the xerographic charging behavior will be discussed in light of the current models of toner charging.

Introduction

In xerography, fumed silica particles are blended onto the surface of the toner particle to improve toner flow,¹ to control triboelectric charge,²⁻⁵ and to reduce the adhesion of the toner particles.⁶ Since the surface of the toner essentially becomes a silica surface, in principle, it should be possible to control the properties of the toner by controlled modification of the silica surface. Alkylsilane treatment is commonly used, producing hydrophobic silicas. Hydrophobic silicas are preferred over hydrophilic silicas for their better flow, as we have previously shown.³ However, hydrophobic silicas typically give triboelectric charge that is sensitivity to relative humidity (RH).^{3,5}

In previous work we have shown the importance of surface attachment of the silane to the silica, and how it affects the triboelectric charging properties of the silica particles.^{3,4} We have also shown that the water on the surface of the silica controls the toner charge.⁵ The current work makes use of these well-characterized silicas, with surface attached alkylsilanes, to study the role of water in the triboelectric charging. Infrared (IR) spectroscopy is used to quantitate the amount of water on the silica surface, while the toner concentration dependence of the charging is followed to study the mechanism by which water controls the triboelectric charge.

Experimental

A fully hydroxylated silica, A380 ($380 \text{ m}^2\text{g}^{-1}$), was used as the base particle. $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiCl}_3$ (FTS) and $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ (OTS) hydrophobic treatments of the silica were done as described previously.^{3,4} These silanes were attached to the silica by way of surface Si_2OSi bonds. For OTS this requires the use of a base, triethylamine (TEA), in a two-step process.^{3,4} The amounts of FTS and OTS were equivalent to the hydroxyl density on the silica (about 3.0 OH/nm^2).

The silicas were blended on Xerox Corporation 1075 toner by roll milling with steel shot for 35 minutes. Since triboelectric charge depends on silica coverage, all samples were at 100% coverage⁷ (based on silica and toner surface areas). Uniformity in coverage between samples was confirmed by scanning electron microscopy. Xerox Corporation 1075 toner with surface additives and a Xerox Corporation 9200 carrier were conditioned overnight at the desired RH, before charging in a sealed bottle for 15 minutes on a roll mill. The toner charge was determined using the standard total blow-off tribo.⁸ Charging was determined with varying weight% toner concentration (TC) with the carrier.

The amount of surface water was determined by using IR spectroscopy as previously described.^{3,4,5}

Results and Discussion

Toners containing silica charge negatively, and the triboelectric charge may be sensitive to relative humidity (RH) and thus surface water.^{1,3-5} Typically, the triboelectric charge measured at low RH is higher than that measured at high RH. The decrease in toner charge with RH is reasonably ascribed to the increase in water content of the silica with RH. The water adsorption curves of the parent A380 silica, and the treated A380/TEA/OTS and A380/FTS treated silicas, are shown in Figure 1.

The triboelectric charge (q/m) of the toners with silica additives is plotted against the silica surface water content in Figure 2. The charge of a Xerox Corporation 1075 toner alone is $-7 \mu\text{C/g}$ at 20% RH and $0 \mu\text{C/g}$ at 80% RH. Thus the toner itself contributes little to the charging. Looking first at the toner with A380/FTS, the charge initially increases linearly with increasing RH from 5% to 20% (and increasing water content), then passes through an inflection point beyond which charge decreases linearly as RH increases.

A linear extrapolation of the latter decrease to zero charge, gives a water content of $2.4 \text{ H}_2\text{O}/\text{nm}^2$, close to the value of $3.0 \text{ OH groups}/\text{nm}^2$ for the A380 silica. That is, there is no charge on the toner with silica when the silica has one water molecule per silanol group. It is also interesting that the change from increasing charge with water content, to decreasing charge with water content (denoted by the arrow in Figure 2), occurs near the inflection point of the water adsorption curve (see Figure 1).

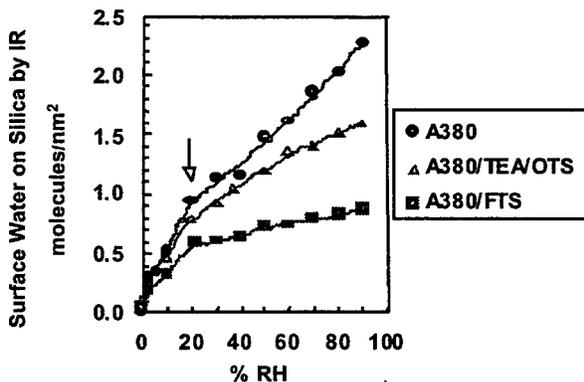


Figure 1. Water content of silica surface as a function of RH, as determined by IR spectroscopy.

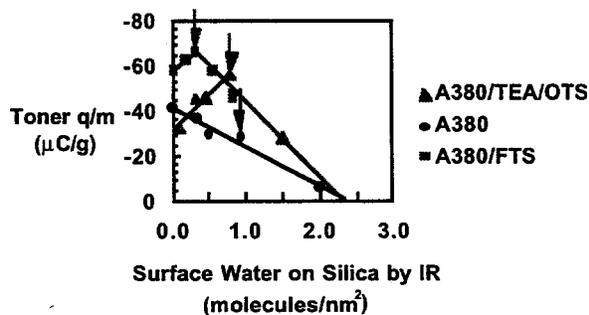


Figure 2. Triboelectric charging of a 1075 toner with different silica surface additives and a 9200 carrier, at 2% TC, as a function of water content of the silica.

The trend for A380/TEA/OTS is very similar to that for A380/FTS. Again the charge initially increases linearly with increasing water content, then passes through an inflection point beyond which the charge drops linearly with further increases in water content. Again, this inflection point is nearly the same as the inflection point in the water versus RH curve. However, below the inflection point, the charge with the A380/TEA/OTS is lower than with A380/FTS at the same water content. In this low water content regime, the chemistry of the surface affects the charge, with the fluorinated surface giving the higher charge. This difference is clearly due to the fluorination, since the silane chain is longer with the OTS, than with the FTS, yet the FTS gives the higher charge with respect to the silica with no treatment. Above their inflection points, the charge of both FTS and OTS treated silicas is identical at the same water content. Thus, above about 20% RH, the charge and its drop with water content, are not controlled by the chemistry of the surface, only by the water content. Finally, both treated silicas show the same water content of $2.4 \pm 0.4 \text{ H}_2\text{O}/\text{nm}^2$ at zero charge at high RH (by linear extrapolation).

The A380 silica q/m appears to drop linearly with water content, even below the inflection point of the water curve in Figure 1. The extrapolation to zero charge is identical to that for the two treated silicas.

Since the charge of the toner with silica correlates well with the water content of the silica alone, it is clear that the charging of the toner with silica is controlled solely by the silica. Without any treatment, the charge of the silica drops with RH. There are two obvious possibilities to explain this behavior, as discussed previously.⁵ Briefly, one possibility is that water makes the surface of the silica conductive. Thus, as the water content increases, the surface becomes more conductive, as contiguous conductive paths of water are present on the silica, which can dissipate charge. This can be called a leaky dielectric model. While there may be charge transfer when the toner and carrier contact, the charge can leak away, either by ion transport (^-OH , ^+H) or by electronic charge transport. It appears that the silica charge arises from the silanol groups of the silica. When each of these sites adsorbs a water molecule, charge dissipation is unavoidable. In the treated silicas, the hydrophobic chains disrupt the conductive paths on the surface of the silica, at least at low water contents. The fact that charge initially increases with water content suggests that some water is needed for charging to occur. It may be that the inflection point of the water versus RH curve is the point at which a contiguous water layer is formed on the surface, resulting in the loss of toner charge.

Alternatively, the adsorbed water blocks a charging site. The assumption with this mechanism is that water covers the silica charging sites, preventing their charge exchange with the carrier (assuming water cannot accept or donate charge to carrier). Again, it is necessary to assume that some water is necessary to charge exchange, to explain the initial increase charge with water content. The weakness of this model is that it does not explain why there is an inflection point in the water curve with RH. However, if the silanol groups of the silica are the charging sites, then this explains why there is no charge if all silanol groups have a water molecule associated with them.

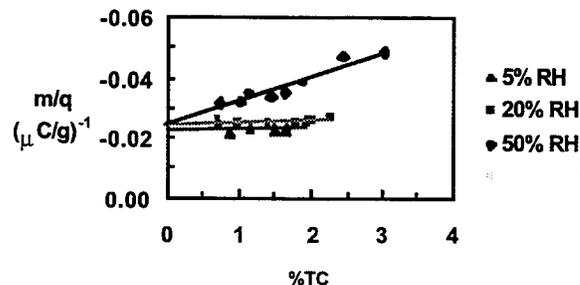


Figure 3. Toner m/q is plotted as a function of toner concentration at different RH conditions for 1075 toner with A380 hydrophilic silica and 9200 carrier.

In order to shed some light on the mechanism of the charging with water content, and in particular, the loss of charge with increasing water content, the charge of each of these toners with silica was measured as a function of toner concentration, at 5% RH, 20% RH, 50% RH and 80% RH. Data for hydrophilic A380 silica is shown in Figure 3, and

typical data for the hydrophobic FTS treated A380 silica is shown in Figure 4, plotting the usual inverse charge, m/q as a function of TC.⁹⁻¹² For untreated A380 silica no data was obtained at 80% RH, as charge was too low to obtain reliable TC dependence. The data obtained for A380/TEA/OTS is not shown.

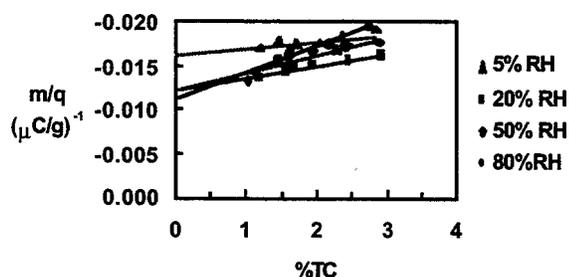


Figure 4. Toner m/q plotted as a function of TC at different RH conditions for 1075 toner with A380/FTS silica and 9200 carrier.

Two parameters were measured from the m/q versus TC plots for the three toners with silica, the slope of the line, S , and the slope to y-intercept ratio, S/I . For the A380 silica, Figure 3 shows an increase in the slope, but a constant S/I ratio, as RH increases. For A380/FTS, the behavior is similar, except that 5% RH shows a larger intercept (lower charge). For A380/TEA/OTS all data follows the same trend as the untreated A380. Thus, the intercepts give a charge of $-42 \pm 5 \mu\text{C/g}$ for A380, $-59 \pm 5 \mu\text{C/g}$ for A380/TEA/OTS and $-83 \pm 5 \mu\text{C/g}$ for A380/FTS (ignoring 5% RH). Thus, the charge at the intercept increases in the above order. Since this charge is essentially independent of RH, this is some intrinsic charging property of the surface, not due to water content. The lower charge at the intercept with A380/FTS at 5% RH is in correspondence with the lower charge observed at 5% RH in Figure 2, except that a similar deviation is not seen for the A380/TEA/OTS, which showed an even large deviation at low RH in Figure 2. The suggestion, since A30/FTS has the lowest water content, is again that some water is needed for charging. Below that level of water, the possible charge obtainable is reduced.

If the plots in Figure 3 and Figure 4 are compared with that expected based on either the low or high density limit models of charging, then the data at low RH data does not fit the expectations: the slope should depend on TC under all conditions, yet these Figure 4 shows that q/m can be essentially independent of charge at low RH. The predicted dependence on TC depends on the model chosen.⁹⁻¹² For example, using the model of Gutman and Hartmann⁹ predicts an intercept on the negative TC axis of 5% TC. For A380 in Figure 3 at 50% RH the extrapolated intercept is -3%, reasonably close to the predicted value. However, at 5% RH the extrapolated intercept is approximately -40% TC. For A380/FTS the observed intercept goes from -4% at 80% RH to approximately -20% at 5% RH. Thus, at low RH the agreement with the model is very poor. Work is in progress to rationalize these models in terms of the possible effect of water content: to date there has been no work done on the effect of water on these charging models.

The slope, S , is plotted in Figure 5 as a function of silica surface water content for all three toners with silica, while the slope/intercept ratio is plotted in Figure 6 as a

function of the silica surface water content. Within the limits of error in Figure 5, the slope of the m/q versus TC is proportional to the water content, independent of the surface treatment of the silica. Thus the dependence of m/q on TC is only dependent on water, not on the chemistry of the surface. The A380/TEA/OTS data now does seem to be an exception at 5% RH, while the A380/FTS silica does fit the common relationship, although there is perhaps a small deviation at 5% RH as well.

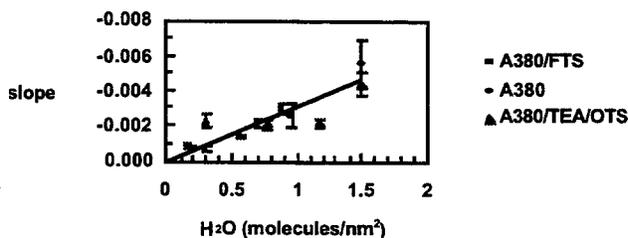


Figure 5. The slope from m/q versus toner concentration graphs is plotted versus the water content of the silica surface.

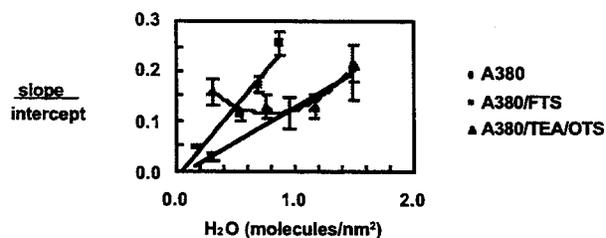


Figure 6. The slope-to-intercept ratio from m/q versus TC graphs is plotted with the water content of the silica surface.

Figure 6 shows many features that are similar to Figure 5, in that S/I is linearly related to water content for A380/FTS and A380 alone, and shows a deviation from linearity for A380/TEA/OTS at the lowest water content (5% RH). However, A380/FTS gives a greater dependence on water content than do the other two silicas, clearly falling along a different line. This suggests that there is a charging difference due to FTS at all relative humidities that is due to the specific chemistry, not just water content. This supports and extends the difference noted in the charging at low RH in Figure 2 for A380/FTS. In Figure 2, A380/TEA/OTS shows an even larger deviation to low charge at low RH, than does A380/FTS. In Figures 2, 5 and 6 the A380/TEA/OTS shows deviations to lower charge at low RH, compared to the other silicas, but does not appear to show significant deviations above 20% RH. Only in Figure 6 does A380/FTS show the largest deviation, and that deviation is at all RH values. Clearly, the chemistry of FTS and OTS are affecting the slope and intercept of the m/q vs. TC plots in different ways, independent of the effect of these treatments on the water content. Unfortunately, to this date the effect of RH on the various charging models has been ignored.⁹⁻¹² Again, we are in progress of attempting to rationalize these differences in terms of the current charging models.

Conclusions

The charging of the toners in this study, with 100% coverage of hydrophilic untreated silica, or hydrophobic modified silica, is primarily controlled by the water content of the silica. At low relative humidities, water adsorption is very rapid, and the charge on the silica depends both on the chemistry of the silica surface, and on the water content. Charge in this region actually increases with increasing water content, indicating that water is necessary for the silica charging. Above about 20% RH, the adsorption of water on the silica occurs at a much less rapid rate, and the charge decreases linearly with increasing water content. Linear extrapolation of the charge with all of the silicas, leads to a common point at high relative humidity where all toners with silica show zero charge. The common point of zero charge corresponds to about $2.4 \text{ H}_2\text{O}/\text{nm}^2$, very close to the $3.0 \text{ OH}/\text{nm}^2$ of the silica surface. This suggests that the silica charging sites are the surface silanol groups, and that when each silanol group has a water molecule associated with it there is no charging possible. There are two basic models proposed to explain these observations. In both models, some water is necessary to develop optimal charge on the silica surface. As the water content increases, the drop in charge can be explained by two different mechanisms. In one, the drop in charge is described by a leaky dielectric model, where charge is dissipated by the presence of contiguous conductive paths of water on the silica surface. The transition to the contiguous water layer would coincide to the inflection point in the rate of water adsorption: a surface monolayer of water does not allow charge to accumulate. In the second model, water simply acts to block the silanol charging site, preventing the contact of the toner and carrier to develop a potential difference. This latter model does not explicitly explain the change in water adsorption, or why the drop in silica charge with water content coincides with the change in water adsorption.

The slope of m/q with toner concentration is proportional to the water content of the silica, again essentially independent of the chemistry of the silica surface. Indeed, the relationship of the slope to the water content is nearly the same for all of the silicas. In nearly all cases, however,

the y-intercept of these plots is constant with RH. The end result is that as RH decreases, the extrapolation of m/q with toner concentration intercepts the negative toner concentration axis at ever increasing values, which are far above those predicted by current charging models.

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