Surface Characterization of Xerographic Developers by Inverse Gas Chromatography: Influence of Surface Acid and Base Properties on Work Functions and Triboelectric Charging

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Abstract

Inverse Gas Chromatography (IGC) has been applied to study the surface properties of developer materials, measuring acid, base and dispersion interactions. Model carrier and toner particles were prepared, where the toner was blended with various nano-particulate metal oxide surface additives: silica, titania and alumina. Toner charging was determined with these surface additive formulations. IGC was used to characterize carrier and additive surface chemistry. Results from IGC were evaluated with respect to toner charge and to metal oxide work functions. A correlation was found between IGC-determined surface acid-base interaction parameters of the developer materials, and their work functions and triboelectric charge. Together, the IGC, work function and charging results strongly support a work function model for developer charging, where the work function is determined by the acid and base properties of the developer components. Thus, as the ratio of the acid to base interaction parameters of the metal oxide surface additive increased, toner charge became more negative. A charging model incorporating all these results has been proposed and integrated with the current understanding of triboelectric charging in xerographic developers.

Introduction

Toner charging with metal oxide surface additives, such as SiO_2, TiO_2, and Al_2O_3, has been shown to be controlled by the oxide work function, as measured by Kelvin potentials.[1] But, what controls the oxide work function? In this paper, Inverse Gas Chromatography (IGC), a powerful method to measure surface properties, has been used to study metal oxide additives and carrier. IGC measured acid and base constants represent the ability of materials to accept or donate electrons, respectively.[2,3] These properties will be shown to be critical to determine both material work functions and triboelectric charge.

Experimental

Contact potential differences (CPD) were measured previously at 20% and 80% RH, using a non-contact, electrostatic voltmeter.[1] The surface additives studied by CPD were Degussa A300™ SiO_2, P25™ TiO_2 and Al_2O_3 C™. CPD values were extrapolated from 20% to 15% RH to enable comparison to charge and IGC data collected at 15% RH (a small correction). CPD values were converted to work functions using a CPD of +0.1 eV for the reference carbon black relative to Au,[4] and an Au work function of 4.46 eV (also measured by CPD).[5]

For triboelectric charge evaluation, all oxides were dry-blended on 4.6 μm PMMA model toner particles for 30 s at 15 krpm, with 100% toner surface coverage.[6] Also included in the charging studies were Degussa R812™ and Wacker H2050™ silica. The carrier was a 65 μm irregular iron core powder-coated with 1 wt% of the same PMMA toner particles. The fused PMMA coating on the carrier surface covered more than 95% of the carrier core, as measured by SEM. Developers were prepared at 4% toner concentration (TC), equilibrated overnight at the desired RH, and then paint shaken for 15 min to reach equilibrium charge. Charge was measured by standard total blow-off tribo.[7]

Acid and base interaction constants, K_a and K_b respectively, were obtained from IGC measurements, following well established procedures.[3,8,9] The metal oxide and carrier stationary phases were packed in stainless steel columns, housed in a Varian 3400 gas chromatograph.

Substrate temperatures ranged from room temperature to about 80°C. RH was controlled by sweeping the columns with He carrier gas, which first passed through a dead space volume where RH was established with salt solutions of specific concentrations. The dispersive interaction capacity of the stationary phases was obtained from retention volumes of n-alkane probes, injected at extreme dilution. Polar vapors, selected from Gutmann's tabulations,[2] then led to evaluations of K_a and K_b. Retention volumes were collected in at least triplicate, with experimental uncertanties ±4%. The experimental uncertainty in acid-base parameters is about ± 8%.

Results and Discussion

An Acid-Base Charge Model

In the high density surface-state charge model,[10] toner charge can be described by:

$$Toner\ q/m = A\ [\phi_c - \phi_t)] \qquad (1)$$

Here ϕ_t and ϕ_c are toner and carrier work functions, respectively. The factor *A* is a composite of a number of terms that have been defined elsewhere.[10] Under the conditions of this study, fixed toner/carrier geometry and TC at equilibrium charge, *A* is a constant. Note that the work functions are defined here as positive numbers, so that a larger number represents lower energy. Thus, a more positive work function for toner compared to carrier gives a negative toner charge. Previous work has shown that this model is consistent with toner charging with metal oxide surface additives.[1,11] In the current work, the toner charge is completely controlled by the surface metal oxide, as the base toner particle and carrier particle surfaces are identical (both are PMMA). Thus, $\phi_t = \phi_{oxide}$, verified by confirming that base toner particle charge with the carrier was zero.

Vide infra, toner charge is related to both acid and base properties of the oxide and carrier. Thus, both toner and carrier have acceptor and donor sites that are active in charge exchange, which collectively determine an *effective* work function. This model recognizes that bidirectional charge exchange is important, with two electron exchange interactions that occur essentially simultaneously:

1) transfer from toner donor (basic) sites to carrier acceptor (acidic) sites, which results in positive toner charge, and;
2) transfer from carrier donor sites to toner acceptor sites, which results in negative toner charge.

The effective work function is the average of the work function of acid and base sites. Thus, Eq. (1) becomes:

$$Toner\ q/m = (A/2)\ [(\phi_{ac} + \phi_{bc}) - (\phi_{at} + \phi_{bt})] \qquad (2)$$

Here the work functions are: ϕ_{at} for acidic toner sites, ϕ_{bc} for basic carrier sites, ϕ_{bt} for basic toner sites, and ϕ_{ac} for acidic carrier sites. Note that this implies that the average work function for a *pure* material does not actually correspond to an existing physical state. The work functions for individual acid sites and the basic sites correspond to actual states. The observed work function is thus only a global average over the work functions of the individual acid and base sites. Eq. (2) is shown schematically in Fig. 1.

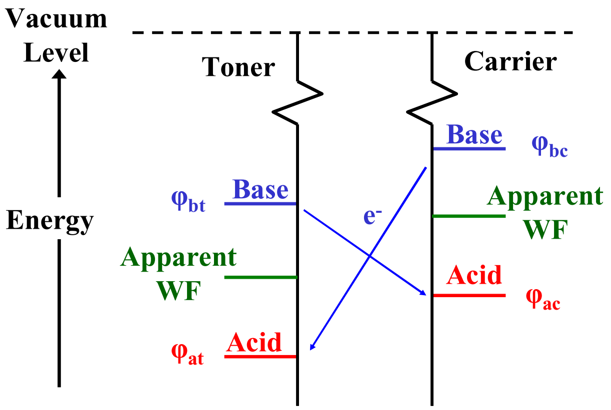

Figure 1. Toner-carrier charge exchange interactions. Arrows show the direction of the electron flow.

We can relate the acid constants, K_a, to the corresponding chemical potentials, the more acidic the site, the lower the energy, and the higher the work function:

$$\phi_a = RT\ ln\ K_a \qquad (3)$$

Similarly, we can relate the acid constants, K_b, to corresponding chemical potentials, the more basic the site, the higher the energy and the lower the work function:

$$\phi_b = -\ RT\ ln\ K_b \qquad (4)$$

Substituting Eq. (3) and Eq. (4) into Eq. (2) gives:

$$Toner\ q/m = -(A/2)\ RT\ [(ln\ K_{at} - ln\ K_{bt}) - (ln\ K_{ac} - ln\ K_{bc})] \qquad (5)$$

Rearranging Eq. (5) gives:

$$Toner\ q/m = -(A/2)RT\ [ln\ (K_{at}/K_{bt}) - ln\ (K_{ac}/K_{bc})] \qquad (6)$$

Eq. (6) predicts that a plot of toner *q/m* vs $ln\ (K_{at}/K_{bt})$ for a fixed carrier, will be linear with a slope of *–ART*. That is, negative toner charge increases with the increasing ratio of toner acid to toner base constants. Eq. (6) also predicts that toner q/m is zero if $K_{at}/K_{bt} = K_{ac}/K_{bc}$, when toner and carrier acid/base ratios are equal. This is a key confirmation for the proposed model. Also, comparing Eq. (2) and Eq. (6) for a fixed carrier, gives:

$$\phi_t = RT\ ln\ (K_{at}/K_{bt}) \qquad (7)$$

Thus, the apparent toner work function is directly related to the ratio of the K_a to K_b values for acid and base sites of the toner.

Work Functions and Acid-Base Equilibria for Metal Oxide Particles

Work functions of hydrophilic oxides, SiO_2, TiO_2, and Al_2O_3, were previously shown to correlate well with toner charge, where the oxides were toner surfaces additives.[1] Thus, electron-accepting oxides increased negative toner charge, while electron-donating oxides decreased negative charge, as expected for the proposed model here. In the current study, the oxide surface acid and base constants, K_a and K_b, were determined by IGC. The oxide work functions determined by CPD are shown in the semi-log plot in Fig. 2, plotted with the corresponding oxide K_d/K_b values. The plot shows the expected linear correlation of oxide work function with the *ln* (K_d/K_b) for the oxide, as predicted by Eq. (7). Also expected from the proposed model, the more negative charging the oxide, the larger the work function, and the larger the K_a/K_b ratio. Thus all aspects of the proposed model are confirmed by the plot in Fig. 2.

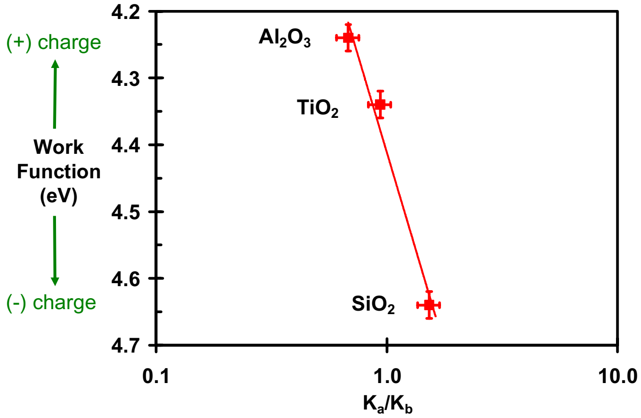

Figure 2. Work functions of untreated oxides plotted with the oxide (K_a/K_b) values as predicted by Eq. (7).

Toner Charging and Acid-Base Equilibria Metal Oxide Particles and Carrier Particles

Eq. (6) predicts that toner charge with fixed carrier will be zero when *ln* (K_a/K_{bt}) = *ln* (K_{ac}/K_{bc}). That is, net charge exchange will be zero when the toner and carrier acid/base ratios match. From that zero point, negative toner charge will increase linearly with the toner (oxide) *ln* (K_d/K_b) values.

Figure 3 shows the semi-log plot of charge for toners with the untreated hydrophilic SiO_2, TiO_2, and Al_2O_3 surface additives plotted against the oxides' respective K_d/K_b values. The point of zero charge for the toner with oxide additives, as extrapolated from the oxide K_d/K_b values, is 0.69 (the 95% confidence limits are 0.57 and 0.82). As predicted by Eq. (6), the carrier K_d/K_b value of 0.45±0.10 matches the point of zero toner charge, within the 95% confidence levels. Thus, the data plotted in Fig. 3 matches the predictions from Eq. (6), showing both the expected linear trend of negative toner charge with increasing *ln* (K_d/K_b), and the zero charge intercept of the toner with respect to the carrier. Thus, for the three hydrophilic metal oxides, all aspects of the proposed model have been confirmed. The acid/base chemistry of the metal oxides, as determined by IGC, defines the apparent work function of the oxides (and toner), and thus determines the oxide (and toner) charging.

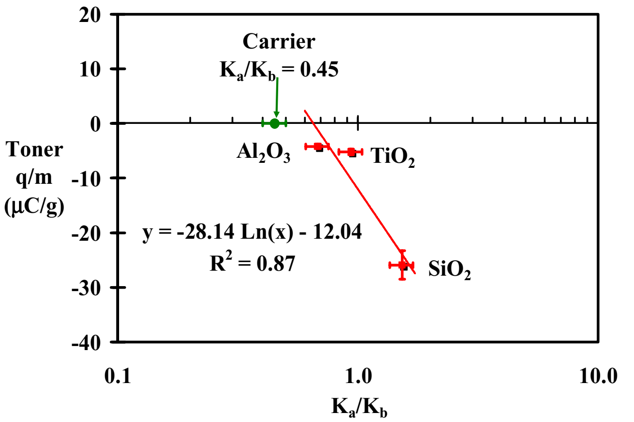

Figure 3. Toner charge with untreated oxide additives plotted with oxide K_a/K_b values, as predicted by Eq. (6).

While the data plotted in Fig. 3 is compelling, further work was done to extend the range of charge and K_d/K_b values, by studying two more silica surface additives: Wacker H2050™ SiO_2 and Degussa R812™ SiO_2. Unlike the three previous oxides studied, these oxides are not native untreated oxides, but rather are surface treated with silane coupling agents to render them more hydrophobic and to control their charging. The toner charge and the acid/base parameters were measured for these two additional oxides.

Toner q/m with *ln* (K_a/K_b) for all five oxides is shown in the semi-log plot in Fig. 4. The plot is linear, and the additional data follows closely that of the initial three hydrophilic oxides shown in Fig. 3. Again, negative toner charge increases with oxide acid-base ratio, as predicted. The point of zero toner charge shown in Fig. 4 is a K_a/K_b *of 0.73* (95% confidence limits are 0.55 and 0.96), compared to the carrier K_a/K_b of *0.45±0.10.* Within 95% confidence levels, zero charge is observed at the predicted K_d/K_{bt} = K_{ac}/K_{bc}. Thus, again no electron transfer occurs if carrier and toner acid-base ratios match, while charge increases linearly with the difference in *log* (K_d/K_b) between carrier and toner.

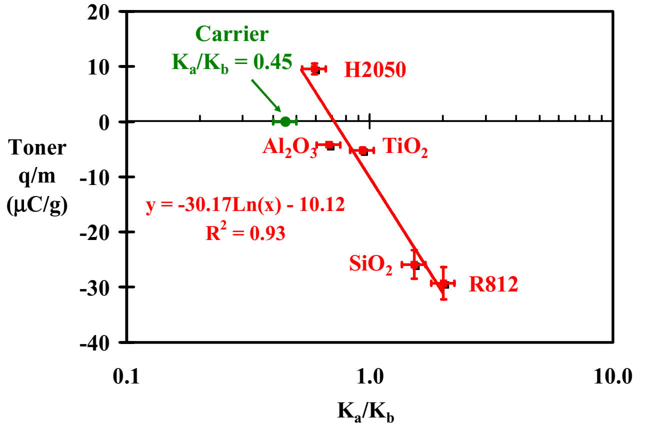

Figure 4. Toner charge with surface oxide additives plotted against log (K_a/K_b), including both untreated native oxides and treated hydrophobic oxide additives.

Conclusions

Xerographic carrier and toner surface additives have been evaluated for surface acid/base properties using IGC, and for developer charging. Based on the results of this analysis, a model for charging of xerographic developer materials has been developed, which proposes bidirectional electron transfer from toner basic sites to carrier acidic sites, and from carrier basic sites to toner acidic sites. The result is an observed "effective" work function that is the average of the work functions of the acid and base sites of each material in the charge exchange. Thus, the observed work function and toner charge are determined by the relative amounts of these two electron exchange processes. This also implies that the electron donor and acceptor sites in developer materials, which are responsible for developer triboelectric charging, are the Lewis base and acid functional groups, respectively, in the materials. As predicted by the model, the metal oxide measured work function increases with the logarithm of the ratio of surface acid to base constants for the oxide, as determined by IGC. Also, as predicted by the model, negative toner charge increases linearly with the logarithm of the ratio of the toner acid-to-base constants. The toner charge is zero when the toner and carrier acid-to-base ratios are identical.

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Biography

Rick Veregin holds a B.Sc., and an M.Sc. and Ph.D in Chemistry. He has worked at the Xerox Research Centre of Canada for the last 19 years, where he currently manages the Developer Physics group. His interests focus on the interface of chemistry, physics and surfaces, especially in xerographic materials. Rick is a member of the IS&T, the American Chemical Society and the ACS Polymer Division, and is an author of 55 publications, an inventor of 59 US patents, and a recipient of the American Chemical Society A.K. Doolittle Award.