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Why Does the Tribo Value Appear to be Independent of Toner Concentration in Some Two–Component Electrophotographic Developers?

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Abstract

Recent data for some toners and carriers have shown that the tribo value is independent of the toner concentration. This is contrary to the conventional response in which the tribo value decreases as the toner concentration is increased. Since conventional models seemingly do not predict this behavior, new models have often been proposed to explain this effect. In this work we examine a toner:carrier pair for which the tribo value is independent of toner concentration. This result is obtained when separate developers are made at different toner concentrations. By changing the toner concentration using a technique which preserves the surface properties of the toner and carrier, we show that the conventional tribo-value:toner-concentration dependence is obtained and is consistent with the conventional models. The unusual behavior in which the tribo value is independent of the toner concentration is a result of changes in the toner and carrier surface composition when developers are prepared and mixed at different toner concentrations. Surface measurements of toner and carrier show toner-concentration-dependent surface modifications.

Introduction

In commercial xerographic equipment employing two component developers, the mass of toner particles developed on the photoreceptor depends on the quantity of charge on the toner particles. The charge on the toner particles is controlled by the triboelectric properties of the toner particles and carrier beads in the developer. The triboelectric properties can be assessed by measuring the toner charge-to-mass ratio, q/m, using the blow-off technique. For many toner:carrier pairs, the mass-to-charge ratio, m/q, is found to vary approximately linearly with toner concentration, TC. The slope of the line is related to the compositions of the toner particles and carrier beads; the intercept on the toner concentration axis is dependent on the sizes of the toner particles and carrier beads.

To interpret the relationships governing the triboelectric charging of toners and carriers, Gutman and Hartmann (G-H)[1,2] have proposed a physical model that assumes field-dependent contact electrification as the basic contact charge exchange mechanism. The electric field in the gap in the region of contact between a toner particle and carrier bead, E_g, is the contact charge density exchanged during the contact plus the "external field" from charges outside the region of contact. They named the "external field" the toner-carrier interfacial field; it is due to charges from previous contacts distributed on the carrier bead, the toner particle and neighboring toner particles. The dependence of m/q on TC is a consequence of the toner-carrier interfacial field. From their physical model, the slope of the line is A_0^{-1}, where

$$A_0 = \frac{a}{s}\frac{4\pi R^2}{M}\frac{\varepsilon_0}{ed}\left(\sum_j^{TS} P_j\mu_j - \sum_i^{CS} P_i\mu_i\right) = \frac{a}{s}\frac{4\pi R^2}{M}\frac{\varepsilon_0}{ed}\left(\Phi_t - \Phi_C\right) \quad (1)$$

and, where a is the microscopic area of contact of asperities between toner and carrier, s is the area of localized conductivity on the surface of the toner particle, R is the radius of the carrier bead, M is the mass of the carrier bead, e is the electronic charge, d is the electronic tunneling length, $P_{i,j}$ are contact probabilities for the constituent materials, $\mu_{i,j}$ are characteristic energy levels for the constituent materials, TS and CS are sums over the constituent materials on the toner and carrier surfaces, respectively, and $\Phi_{t,C}$ are the weighted chemical potentials of the toner or carrier. G-H assumed the density of states for the toner and carrier materials can be approximated by unity, the high density of states limit. Nash and co-workers have investigated the effect of systematic changes in the constituent materials of toners and carriers on their triboelectric properties. They show that it is necessary to understand the time dependence of the P's (the surface area coverage) in order to compare experimental results with theory.[5]

Recently, results have been reported that the q/m of the toner particles can be independent of the toner concentration.[3,4] Since these results are not in agreement with the G-H and other similar surface state models, the authors[3,4] have proposed new models to explain the results. The new models consider the density of states on the carrier beads and toner particles and whether the density of states on the carrier beads is greater then, less than, or approximately equal to the density of states on the toner particles. For the first case, m/q is independent of TC; for the second case, m/q is linearly dependent on TC; and, for the third case a combination of the first two cases.

In this paper we study a toner:carrier pair which exhibits q/m independent of toner concentration. This result is obtained when individual developers are prepared at different toner concentrations. However, if the toner concentration is varied in a manner which does not change the surfaces of the toner and carrier, then the usual dependence of the m/q on TC is obtained. We will show that mixing individual developer samples prepared at different toner concentrations changes the surfaces of the toner and carrier. Consequently, the observation of q/m independent of toner concentration is a result of different surface composition for the toner and carrier. The data from such an experiment are not a proper test of any model which assumes the surfaces do not change when the TC is varied.

Experiment

Materials

Carrier: Atomized iron-grit powder with volume median diameter of 158 µm and powder coated with about 0.2% polyvinylidene fluoride (PVF). The carrier was conditioned by mixing 1% of the toner described below with the carrier for 30 minutes. The toner was removed from the carrier.

Toner: Styrene/n-butyl methacrylate copolymer melt-mixed with 5 wt.% carbon black and with 2 wt.% of a long-chain alkyl pyridinium salt to produce a positive polarity toner when mixed with the above carrier. The toner was micronized and classified to a volume median diameter of 11 µm.

Developer Preparation

Developers were prepared by blending the appropriate amount of toner with 200 g of carrier in a glass jar to obtain toner concentrations of approximately 1, 2, 3, 4 and 5%. Two sets of developers were prepared: one set with the conditioned carrier and one set with the non-conditioned carrier. The developers were then mixed on a roll mill for 300 min. Toner concentration and q/m measurements were made on approximately one gram samples taken from the developer at 5, 10, 15, 30, 60, 120, 240 and 300 min. The 1, 2 and 5% developers were “detoned” to 0.5, 1 and 2% respectively using the procedure described below. Toner concentration and q/m samples were taken at 1, 2, 5, 10 and 30 min.

Three other developers were prepared at 1, 2 and 5% toner concentration as above and mixed on the roll mill for 300 min. For these developers, the toner concentration and q/m were only determined at 300 min to verify the developers were the same as above. Then the toner concentration of each of the three developers was decreased using a three step “detoning” procedure. First, a developer was split into two portions. Second, the toner was completely removed from one portion by a large scale analogue of the blow-off procedure used for the tribo measurement. Third, the carrier recovered from this “detoned” portion was added back to the other “toned” portion. The developer-carrier mixture was then hand tumbled to distribute the carrier beads in the developer beads and then put on the roll mill to mix. Toner concentration and q/m samples were taken after 1, 2, and 5 min of mixing. The three step procedure was repeated as necessary to obtain the desired lower toner concentrations.

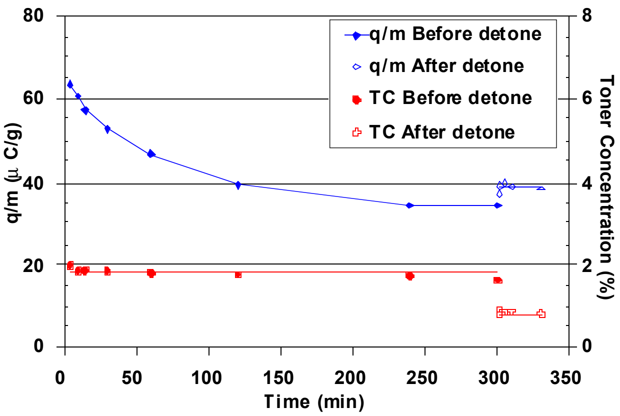

Figure 1. Toner concentration and q/m as a function of mixing time for the 2% developer. After 300 minutes, the developer was partially detoned to a lower TC; the q/m increased.

Results

Figures 1 and 2 show the q/m and toner concentration as a function of the roll mill mixing time for the 2 and 5% developers made with the conditioned carrier, respectively. For both developers, the q/m ratios have the largest values at the shortest mixing times and then decrease to steady values. The q/m for both developers are about equal. At the end of the 300 min of mixing, the developers were detoned to 1 and 2% as described above and mixed for another 30 minutes. As a result of the detoning procedure, the toner concentration is lower; the q/m values increase rapidly indicating the toner particles are quickly re-distributing themselves on all the carrier beads and gaining charge. These data indicate that the q/m does respond to the toner concentration.

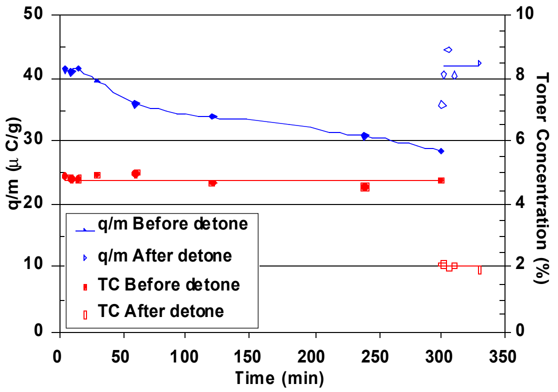

Figure 2. Toner concentration and q/m as a function of mixing time for the 5% developer. After 300 minutes, the developer was partially detoned to a lower TC; the q/m increased.

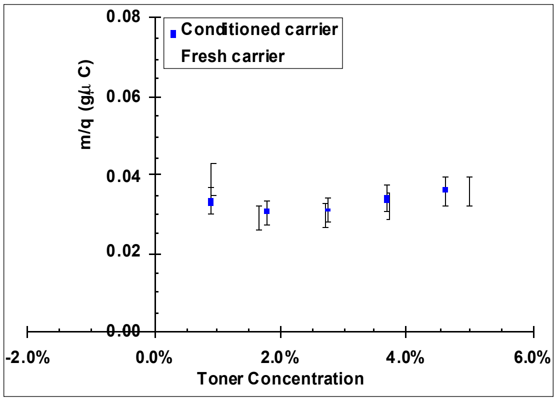

Figure 3. m/q as a function of toner concentration for the individual developers after 300 minutes of mixing. The carrier conditioning does not have a significant effect

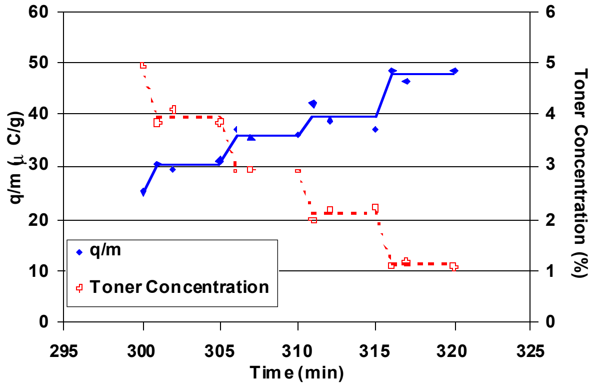

Figure 4. Toner concentration and q/m as a function of mixing time for the 5% developer detoned in steps. As the toner concentration is reduced, the q/m increases.

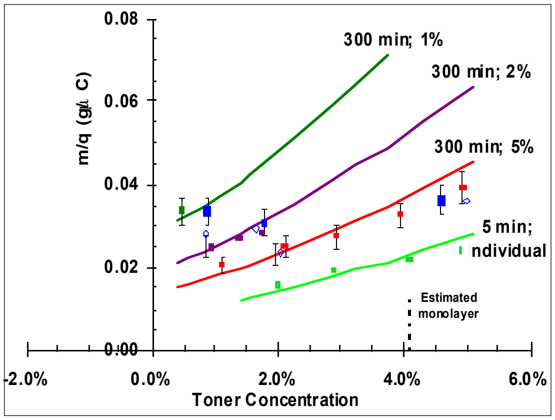

Figure 5. m/q as a function of toner concentration for the 1,2,5% developers detoned in steps and the 5minute points for the individual developers. The lines are the G-H model with one parameter, A_0, adjusted for each data set. The developers initially have a common A_0 value; but, mixing for 300 minutes at different toner concentrations changes the A_0 value

The m/q:TC data for the set of five developers, made with either the conditioned or fresh carriers, after 300 minutes of mixing are shown in Figure 3. The m/q values are independent of toner concentration. Although the conditioning process shows a small trend at the lower TC's, also reported by Nash and Muller[3], there is not a significant effect due to the conditioning process. Subsequent experiments were done with the conditioned carrier.

Toner concentration and q/m values are shown as a function of mixing time in Figure 4 for the 5% developer which was detoned in steps. The q/m quickly reaches a steady value for each toner concentration.

The m/q:TC data for the 1, 2 and 5% detoned developers are shown in Figure 5. Also shown in this figure are the m/q:TC data for the five individual developers after 5 min of mixing when the q/m values are near their maximum. The error bars in this figure (and Fig. 3) are for a measurement error of 10%. The lines through each set of data points are calculated from the G-H continuous charge model with one adjustable parameter, A_0, chosen for each data set. These data show that these developers exhibit the usual m/q:TC behavior. The five developers start with a common A_0 value; but, after 300 minutes of mixing, each developer has a different A_0 value. The observation, that m/q appears to be independent of toner concentration, Figure 3, is an artifact of the different A_0 values for the developers prepared at different toner concentrations. The different A_0 values are a result of the surfaces of the toner and/or carrier being modified by mixing at different toner concentrations. In Figure 5, we also indicate an estimate of a monolayer coverage of the grit carrier beads.[6]

Discussion

The toner:carrier pair used in these experiments is noteworthy for the time dependence of the q/m values, largest at short mixing times decreasing to about the same value at long mixing times. The long time steady state values are independent of the toner concentration of the individual developers. However, by decreasing the toner concentration in steps following the detoning procedure, we observe the usual m/q:TC dependence. The purpose of the detoning procedure is to change the toner concentration and toner charge rapidly without changing the surface properties of either the toner particles or carrier beads. The 300 minute mixing time was chosen because the slopes of the q/m values for all the developers were approximately zero and further mixing in the detone process would not change the surfaces of the toner particles and/or carrier beads. In the detoning process, the toners rapidly redistribute themselves among all the carrier beads and gain charge due to fewer toner particles per carrier bead. If the toners did not redistribute themselves on all the carrier beads, the q/m would not increase with the lower toner concentrations, and might even decrease extending the time track to longer mixing times.

The lines in Figure 5 are calculated by the G-H continuous charge model using one adjustable parameter, A_0, for each data set. The values of the parameters used for the toner-carrier interfacial field calculation are, R/r=14.2, carrier density=7.7 g/cc and carrier dielectric constant = 50 (the results are not different for values greater than 30). This calculation need only be done once for this experiment. The toner-carrier interfacial field calculation determines the shape of a line in Figure 5; the adjustable parameter, A_0, then shifts a line in the m/q:TC space. The values for the adjustable parameter, A_0, were chosen for each set of data to make the line fit the data.

The different A_0 values indicate that the surfaces of the toner and/or carrier are dependent on the toner concentration at which the developers were initially prepared. To investigate changes in the surfaces of the toner particles and/or carrier beads, small quantities of toner and carrier were recovered from the fresh, 1, 2 and 5% developers and analyzed by x-ray photoelectron spectroscopy (XPS). The XPS technique determines the elements present in approximately the top 4 nm of the surface of the sample. The results show 1) fluorine on the toner particles; 2) a loss of fluorine on the carrier beads; and, 3) an increase in iron on the carrier beads. We suspect the fluorine signal on the toner is due to transfer of some of the small PVF particles from the carrier beads to the toner particles. Since PVF is a very electronegative material, its presence on the toner particles and loss from the carrier beads would have a large impact on the charging properties of the positive toner particles and negative carrier beads. The XPS data for the F signal from toner particles and carrier beads and the Fe signal from the carrier beads are listed in Table I. From these data, we conclude that mixing at different toner concentrations changes the surfaces of both the toner particles and carrier beads.

Table 1. XPS data for the F signal from toner particles and carrier beads.

Sample	F signal on toner (At%)	Loss of F signal on the carrier (At%)	Increase of Fe on the carrier (At%)
Fresh (5 min)	0	0	0
Detone-5% TC	1.5	12.2	1.6
Detone-2% TC	2.8	12.9	0.6
Detone-1% TC	4.9	14.7	0

The G-H model can be used to relate the XPS data to the q/m data. Recalling Eq. 1, the weighted chemical potential for the toner particles, Φ_t, is

$$\begin{gathered}\Phi_t = P_R\mu_R + P_{CB}\mu_{CB} + P_{CCA}\mu_{CCA} + P^t_{PVF}\mu_{PVF} = P_t\Phi'_t + P^t_{PVF}\mu_{PVF} \\ P_t + P^t_{PVF} = 1 \quad and \quad P^t_{PVF} = \alpha XPS^t_F \\ \Phi_t = \Phi'_t + \alpha XPS^t_F\left(\mu_{PVF} - \Phi'_t\right)\end{gathered} \tag{2}$$

where P_t is the fraction of the toner surface not covered with PVF, α is a proportionality constant, XPS^t_F is the XPS F signal on the toner particles, and, Φ_t' is the potential of the fresh toner.

For the carrier beads, the weighted chemical potential is

$$\begin{gathered}\Phi_C = P_{ox}\mu_{ox} + P_{PVF}\mu_{PVF} \\ P_{PVF} = P'_{PVF} - \gamma\Delta XPS^C_F \quad \text{and} \quad P_{ox} = P'_{ox} + \beta\Delta XPS_{Fe} \\ \Phi_C = \Phi'_C + \beta\Delta XPS_{Fe}\mu_{ox} - \gamma\Delta XPS^C_F\mu_{PVF}\end{gathered} \tag{3}$$

where β and γ are proportionality constants, $\Delta XPS_F{}^C$ is the change in the XPS F signal on the carrier, and ΔXPS_{Fe} is the change in the XPS Fe signal due to PVF loss from the carrier beads. The difference of the toner and carrier weighted potentials is

$$_t - \Phi_C = \Phi_t - \Phi_C + \alpha(\mu_{PVF} - \Phi_t)XPS^t_F - \beta\Delta XPS_{Fe}\mu_{ox} + \gamma\Delta XPS^C_F\mu_{PVF} \tag{4}$$

where the primes denote the fresh surfaces.

One chemical potential term can be chosen as a reference; it is convenient to choose the fresh toner potential as the reference. With this choice,

$$\Phi_t - \Phi_C = -\Phi'_C + \alpha XPS^t_F\mu_{PVF} - \beta\Delta XPS_{Fe}\mu_{ox} + \gamma\Delta XPS^C_F\mu_{PV} \tag{5}$$

If we assume that the tribo charge is dominated by the very electronegative PVF, and ignore the change in the Fe signal on the carrier surface, then, Eq.5 can be used with Eq. 1 to partition A_0 into contributions from the transfer of PVF from the carrier surface to the toner surface and the loss of PVF on the carrier surface. The contributions of these two factors to the change in A_0 are shown in Figure 6. The transfer of PVF from the carrier surface to the toner surface appears to be a major factor for the change in A_0 due to mixing developers at different toner concentrations.

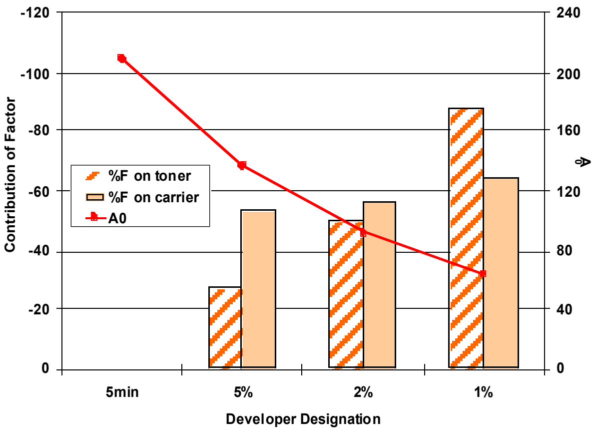

Figure 6. The contribution of F on the toner and loss of F from the carrier on the change in A_0. The A_0 values for the developers are also shown.

From the collective work of several authors,[5,7-10] it would seem that mass transfer is a "common" occurrence in triboelectric charging. Nash and co-workers[5,7] have investigated the dependence of q/m on mixing time for developers prepared at different toner concentrations. The toners used in their work contained internal or external additives. Their experiments demonstrated the importance of changes in toner and carrier surface chemistry as a function of mixing conditions. By assuming kinetics for additive transfer, they were able to determine a form for the P's in Eq. 1 to model the time dependence of the q/m ratio. They showed that kinetic changes can confound the interpretation of q/m:TC data and their comparison to simple models.

Gutierrez et al[8] have also reported that the silica on toners contributes to time dependent carrier surface contamination. They also note that the q/m time dependence for toners with silica is similar to the time dependence observed with toners with internal charge control agents.

K-Y. Law and co-workers[9,10] have investigated ion transfer as a mechanism of charge exchange. They have related the charge generated on the toner to the amount of ions transferred to the carrier.

Mass transfer modifies the composition of the toner and carrier surface. Using the G-H model, we have related the XPS data to the change in the triboelectric properties of the toner and carrier surfaces; thereby, quantifying the effect of mass transfer on triboelectric charging. The expected linear m/q:TC dependence is only observed if care is taken to assure that the surfaces of the toner particles and carrier beads remain constant during the experiment.

Summary

We have shown that mixing developers at different toner concentrations can cause surface modifications to the toner particles and carrier beads. This can lead to the observation that m/q is independent of TC. If the toner concentration is varied by the partial detoning procedure which preserves the surface composition of the toner and carrier, then the conventional m/q:TC dependence is observed. The modification of the surfaces was confirmed with XPS analysis which showed 1) transfer of the polyvinylidine fluoride from the carrier beads to the toner particles; and, 2) loss of active polyvinylidine fluoride on the carrier surface due to adhering toner particles. The transfer of polyvinylidine fluoride is the major contributor to the decrease in the A_0 value after mixing the developers for 300 minutes. While the toner:carrier pair selected for this work can exhibit m/q independent of TC, that behavior can be understood within the framework of the Gutman-Hartmann model and does not require a new model.

Acknowledgement

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Biography

Edward Gutman received the B.S. and M.S. degrees from John Carroll University in 1965 and 1967. After receiving a Ph.D. in solid state physics from Iowa State University in 1970, he was a post-doctoral research associate at the University of Illinois. In 1972, he joined Xerox Corporation where his research interests have focused on the physics of the xerographic development process and the science of xerographic developer materials Dr. Gutman received the Xerox President's Achievement Award for his contributions to the design of xerographic developer materials. He holds several patents for xerographic developer materials or devices. Currently he is a Research Fellow in Xerox Supplies Development and Manufacturing Services. He is a member of the Society for Imaging Science and Technology and the American Physical Society.