Humidity Sensitivity of the Adhesion of Pigmented Polymer Particles Treated with Surface-Modified Surface Additives

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Abstract

Silicas and titanias have long been used as surface additives on pigmented toner particles for xerographic applications. These surface additives alter particle flow and particle charging ability. In addition, the additives have a strong influence on the particle adhesion to various polymeric surfaces. The silicas and titanias can be rendered hydrophilic or hydrophobic depending upon which surface treatment is performed on the additive. We have measured the adhesion of many pigmented toner particles with both hydrophilic and hydrophobic silicas and titanias on the surface and we will report on the RH sensitivity of the particle adhesions for both types of additive surface modifications.

Introduction

A toner particle for xerographic applications consists of a thermoplastic binder resin and, in the simplest formulation, a colorant. Carbon black is the common colorant for black particles and color pigments are used in color particle formulations. The particle surface is quite irregular but an equivalent spherical diameter of 10 microns is applicable for most current formulations. The control of the adhesion of the toner particle to various surfaces within a photocopier (other toner particles, carrier beads, photoconductor, paper) is of utmost importance for proper clog-free and dust-free operation of the copier. Image quality and clarity on the output document is controlled by the particle adhesion and electrostatic charge. The toner charge, obtained by triboelectric charging against a carrier bead, will be affected by the toner's ability to release from the carrier bead for additional contacts. Since copiers must function year round in a variety of environmental conditions, toner flow, adhesion and triboelectric charging properties must be as insensitive to temperature and humidity changes as possible. Silicas and titanias have been shown to greatly improve toner flow through small orifices.[1,2,3] This is important for controlled toner dispense in copiers as well as controlled toner mobility in the development zone. The additives also minimize caking and clumping[4,5] which is important during product delivery and storage before use in a copier. The benefits of additives on toner performance in a copier are well known.[6] We have previously shown[7] a common improvement in toner transfer efficiency by 40-50% for toners with additives relative to toners without additives, resulting from an additive induced decrease in toner adhesion to the photoconductor by 100-200% as a function of voltage on the photoconductor. The aim of the current research is to measure the effectiveness of additives on tailoring toner adhesion as a function of RH and determine the RH sensitivity of the beneficial attributes of the additives.

Experimental

We use a Park Scientific Instruments Atomic Force Microscope for toner adhesion measurements. The toner particle is attached to the cantilever and brought into contact with an organic photoconductor surface. From a loading curve,[7] the topography of the underlying surface and the adhesion of the toner to that surface are measured simultaneously. For this series of experiments, the AFM was positioned in a temperature and RH controlled enclosure.

The silicas under investigation in this study are an untreated 14 nm hydrophilic silica and two hexamethyl disilazane (HMDS) treated hydrophobic silicas—a 40 nm silica with BET surface area = 50 m^2/gm and a 40 nm silica with BET surface area = 200 m^2/ gm . The titanias under investigation in this study are an untreated hydrophilic titania, 30 nm in size, and two silane treated hydrophobic titanias, 30 nm and 15 nm in size. Toner particles were coated at 50% and 100% additive surface coverage and subsequent toner adhesion measurements were made under various RH conditions. We chose typical humid operating conditions -70°F, 50% RH, normal office operating conditions - 70° F, 20% RH, and ideal dry operating conditions -70° F and 6% RH. Toner adhesion measurements were also made as a function of toner contact time under these various RH conditions.

Results and Discussion

Figure 1 shows adhesion in nanonewtons of a toner particle coated with 50% surface coverage of the low BET HMDS treated hydrophobic silica to the photoconductor at 70° F, 50% RH as a function of position on the photoconductor. Each adhesion data point represents an average adhesion from 32 measurements made over an 80 micron scan to capture representative microscopic behavior. Distances between positions on the photoconductor are macroscopic- on the order of millimeters. For data graphs 1-6 and 10, the average adhesion values are plotted as solid circles, while the accompanying standard deviations for each average are plotted as solid triangles. The lines connecting data points are intended as guides to the eye and are used to help distinguish adhesion populations. No fit is intended. The adhesion of the hydrophobic silica coated toner is high with an overall average near 586 nN. Standard deviations fluctuate around 60 nN. At positions 2, 4, and 15-19 however, the adhesion populations are distinctly different, with the average adhesion near 197 nN. In comparison, figure 2 shows adhesion measurements for a toner with the silica surface coverage increased to 100%. Now adhesions are very uniform around a high average of 559 nN with standard deviations consistently around 59 nN. Lower adhesion values at lower surface additive coverages may be due to less uniform additive distribution at the lower coverages. We have previously shown[7] that additives decrease toner adhesion by reducing the effective contact area of the toner to the photoconductor. The very high adhesions visible at 50% additive coverage (600 nN, 950 nN) suggest contacts to a location on the toner with a very low concentration of additive. If, however, contacts were made by the toner to the photoconductor at a point on the toner surface with a high concentration of hydrophobic additive, the moisture on the photoconductor at the point of contact may have been driven away from the contact point by the presence of the additive, thus lowering the toner adhesion to values near 197 nN. With a more uniform additive distribution at 100% surface coverage, there would be less likelihood of a large accumulation of additive at a contact point to drive the moisture away, thus leading to the more uniform adhesion of 559 nN at 100% surface coverage.

Figures 3 and 4 show the measured values of adhesion of a toner particle with 100% surface coverage of the hydrophilic silica at two different levels of RH- 50% and 20% respectively. At 50% RH, the adhesions are fairly consistent with an average of 423 nN (with standard deviations around 40 nN), with two positions on the photoconductor showing lower adhesion values at 120 nN. Again, this may be attributable to a slightly uneven distribution of additive on the surface of the particle, or, more likely, to variability in the amount of adsorbed moisture on the photoconductor at 50% RH. When the adhesion measurements were repeated at 20% RH (figure 4), the average adhesion dropped significantly to 202 nN (standard deviations dropped to 12 nN). This indicates a sensitivity of the hydrophilic additive to adsorbed moisture on the photoconductor. As the RH decreases and adsorbed moisture on the additive and photoconductor decreases, we expect the toner adhesion to correspondingly decrease as the moisture interlayer between the toner and the photoconductor diminishes. Position 3 on the photoconductor showed a bimodal distribution of adhesion values at 20% RH. In the 80 micron scan, a third of the adhesion population was considerably higher than 202 nN, averaging 575 nN. This would suggest that the additive is very sensitive to small changes in surface moisture content and responding to microscopic variability in adsorbed moisture on the photoconductor surface.

Figures 5 and 6 show the measured values of adhesion of a toner particle with 50% and 100% coverage respectively of the high BET hydrophobic silica. Adhesion measurements were made at 70° F and 20% RH. For the 50% surface coverage, bimodal adhesion distributions were observed at 4 of 8 positions on the photoconductor with high averages around 375 nN and low averages around 214 nN. The low averages represent 1/3 of the populations at each position. The behavior is reversed at 100% surface coverage. Once again, bimodal distributions are observed at 2 of 6 positions, with 1/3 of the population now at the higher value of adhesion (367 nN) compared to a low average of 158 nN. Lower adhesion at higher surface additive concentration is to be expected since a higher concentration of hydrophobic surface additive would tend to expel moisture from the contact area. Bimodal adhesion distributions at one photoconductor "position" must be attributable to variability in adsorbed moisture content of the photoconductor. Recall that each "position" on the photoconductor is actually an 80 micron scan. During an 80 micron scan the same spot on a toner contacts each photoconductor point. The toner point of contact can only vary from "position" to "position" as the cantilever is repositioned over the substrate, possibly exposing a slightly different toner area for contact, thus allowing variability in the additive surface coverage to contribute to adhesion variation. That is not the case within a scan.

Comparing hydrophobic silica toner adhesions at high (50%) and low (20%) RH, it is seen that adhesions are significantly reduced as RH is reduced, from values in the high 500 nN's at 50% RH to 375 nN for 50% surface coverage at 20% RH and 158 nN for 100% surface coverage at 20% RH. This same behavior of adhesion decrease with RH decrease is also observed in the presence of a hydrophilic silica. Adhesions drop by 100% from 400 nN to 200 nN as RH drops from 50% to 20%. Since the triboelectric charge on a toner particle depends on its ability to make and break contacts to carrier beads, one would expect adhesion differences with RH to have a large impact on toner particle triboelectric charging with varying RH. This is seen experimentally. For toner particles with a hydrophobic silica as a surface additive, typical magnitudes of equilibrium triboelectric charge after a 30 minute paint shake with carrier beads are 32.5 μcoul/gm at 60° F/ 20% temperature/RH. These values are depressed to 17.5 μcoul/gm at 80° F /80% temperature/RH after an identical paint shake. This is in part attributable to the toner's hindered ability to break contacts to carrier bead surfaces at higher RH levels due to higher adhesions. Similar triboelectric charge depressions are seen for toners with a hydrophilic silica. Triboelectric charge magnitudes of 30 μcoul/gm are achieved after 30 minute paint shakes at 60° F /20% temperature/RH. These values are depressed to 7.5 μcoul/ gm at 80° F /80% temperature/RH. Again, this is in keeping with the toner's hindered ability to break contacts to carrier beads at higher humidity. We must not overlook other sources for changes in triboelectric charge. In the Gutman-Hartmann model of triboelectric charging,[8] contact area and surface chemical potentials of the toner and carrier also come into play in determining equilibrium triboelectric charge values. Both contact area and chemical potentials will also be affected by RH changes. The main point here is to include the role that adhesion changes will play in the tribocharging mechanism.

The adhesion behaviors of the toners with titanias as surface additives are in marked contrast to the behaviors of the toners with silica external additives. Figure 7 shows the adhesion of a toner with 100% surface coverage of the 15 nm hydrophobic titania at 70° F, 50% RH as a function of contact number for sub-second contacts, 4 second contacts and 8 second contacts. Here each data point represents a single contact at a single location. Each subsequent contact is made at the same location on the photoconductor. For sub-second contacts, the adhesion starts very high (880 nN) and exponentially decays to an equilibrium value of 175 nN. The curve is drawn to aid the eye. An exponential decay fit to the data has an R^2 value of .998. Similar behavior was observed for the 30 nm titania. When the toner contact time is increased to 4 seconds, the exponential decay is no longer observed and adhesions are stable at 715 nN. When the contact time is increased further to 8 seconds, adhesions remain stable at an even higher value of 760 nN. We hypothesize that during the sequence of sub-second contacts, moisture is forced out of the contact region between the titania and the photoconductor surface with each successive contact, thus lowering the toner adhesion with each hit. When the contact time is increased to 4 seconds, however, the moisture interlayer, rather than being forced out of the contact zone, has time to conform to the contact area and form a uniform titania-water-photoconductor bond, thus increasing the adhesion considerably. This effect is enhanced with increased contact time as evidenced by the adhesion increase which accompanies increasing contact time to 8 seconds. Figure 8 shows that this effect of increased adhesion with increased contact time is common to both hydrophobic titanias. For both the 15 nm and the 30 nm silane treated titanias, adhesion is seen to increase with contact time. Since the BET surface areas of the titanias differ and the silane treatments differ, I will not speculate on any one reason for the adhesion of the toner with the smaller titania being higher. It is consistent with van der Waals theory which predicts the adhesion to vary with the inverse of the distance between the sphere and the plane. Here the sphere is the toner and the plane is the photoconductor. The titanias are the spacers so the distance between toner and photoconductor is halved with the smaller titania thus allowing adhesion to increase. Figure 9 shows that the adhesion decay phenomenon for hydrophobic titania coverage is highly RH sensitive. At lower RH values (6%), the decay phenomenon is not observed and the adhesion is constant with contact number. Presumably, the water interlayer has diminished with decreased RH and is not pushed out of the contact zone with successive contacts.

The behavior of the toner with 100% surface coverage of hydrophilic titania is in marked contrast to the hydrophobic titania behavior. Figure 10 shows titania adhesion behavior similar to the high RH hydrophobic silica case with adhesion being very high (734 nN average) and constant with contact number. Here again each data point is an average of 32 contacts made over an 80 micron area. No adhesion decay with contact number was observed. The standard deviations, however, are higher than the silica case. This is not surprising for the hydrophilic titania. According to additive product literature[4], the weight percent adsorption of moisture by the titania at 50% RH is 3%. This is in contrast to values of 0.9% adsorption of moisture by hydrophobic titania, and hydrophobic and hydrophilic silicas at 50% RH. Thus, regardless of the number of contacts made by the toner with hydrophilic titania additive, the moisture layer at the interface cannot be displaced and the adhesion remains at a high value.

Conclusions

We have measured the adhesion of toners, with various hydrophobic and hydrophilic titanias and silicas as surface additives, to photoconductor surfaces, under a variety of RH conditions and at a variety of additive surface coverages. Hydrophobic silicas at low surface coverages and high RH give erratic adhesion values due to uneven surface coverage of the additive on the toner. Toners coated with both hydrophobic and hydrophilic silicas show an increase in adhesion to the photoconductor with increasing RH. This observation also explains the toner's inability to generate triboelectric charge as effectively in high RH as in low RH due to a higher degree of difficulty in breaking toner-carrier contacts at high RH. RH dependent surface chemical potentials will also play a role in determining the triboelectric charge.

Adhesion behaviors of titania coated toners are in marked contrast to behaviors of toners with silica coatings. Toners coated with hydrophobic titanias show an adhesion decay to an equilibrium value with successive contacts, along with an increase in adhesion with increased contact time. These phenomena are caused by the shifting of the water interlayer at the titaniaphotoconductor surface. For the case of hydrophilic titania, the amount of water present in the interlayer is too high to be removed by successive contacts, and the adhesion behavior mimics the silica case-namely, constant with contact number. The adhesion magnitudes are considerably higher than the silica case because of the increased amount of water at the toner-photoconductor junction.

Acknowledgments

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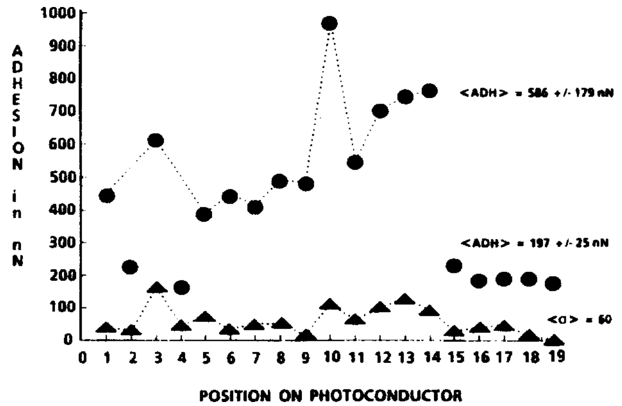

Figure 1. Adhesion of toner with 50% surface coverage of low BET (50 m²/g*) hydrophobic silica at 70°, 50% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.*

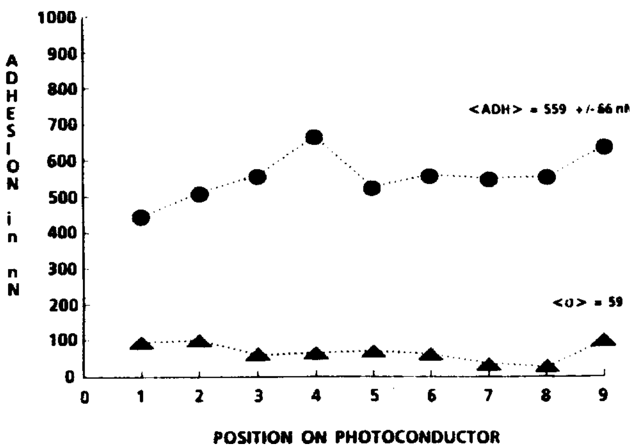

Figure 2. Adhesion of toner with 100% surface coverage of low BET (50 m²/g*) hydrophobic silica at 70°, 50% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.*

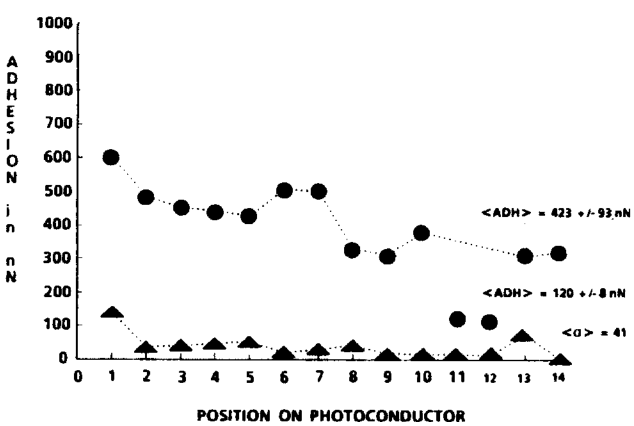

Figure 3. Adhesion of toner with 100% surface coverage of hydrophilica slica at 70°, 50% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.

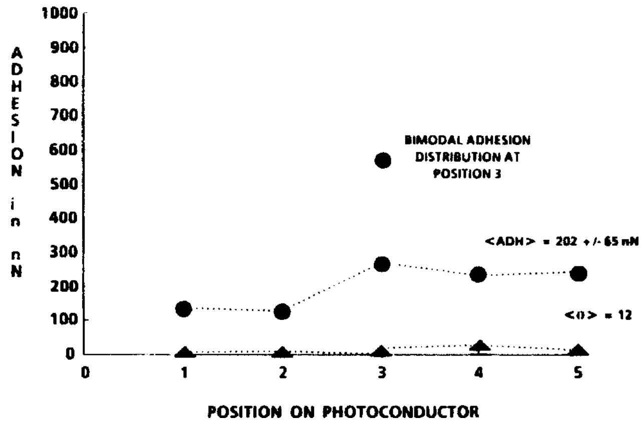

Figure 4. Adhesion of toner with 100% surface coverage of hydrophilic silica at 70°, 20% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.

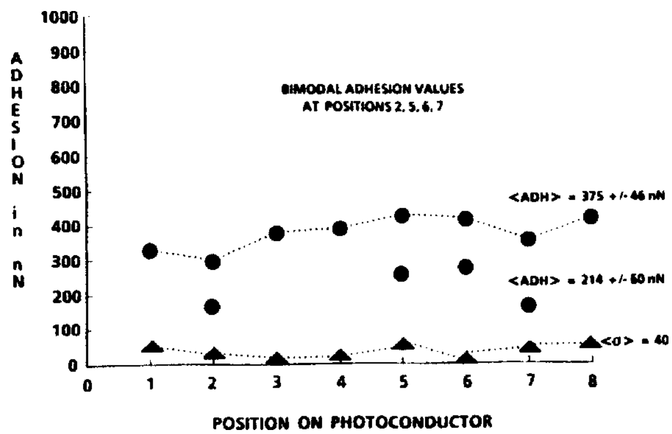

Figure 5. Adhesion of toner with 50% surface coverage of high BET (200 m²/g*) hydrophobic silica at 70°, 20% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.*

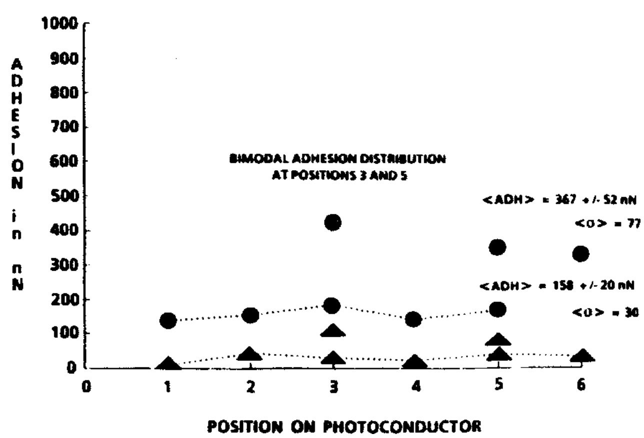

Figure 6. Adhesion of toner with 100% surface coverage of high BET (200 m²/g) hydrophobic silica at 70°, 20% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.

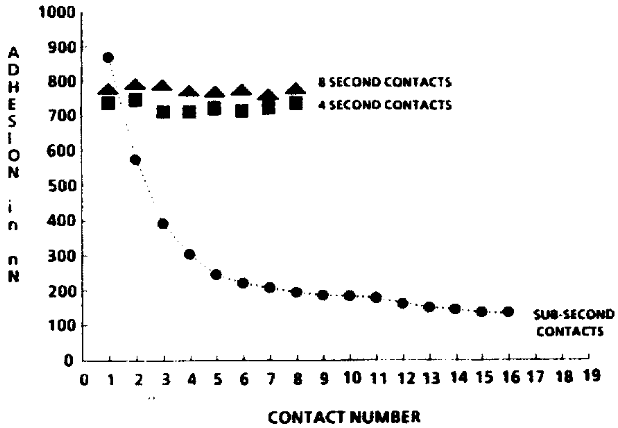

Figure 7. Adhesion of toner with 100% surface coverage of high BET 15 nm titania at 70°, 50% RH.

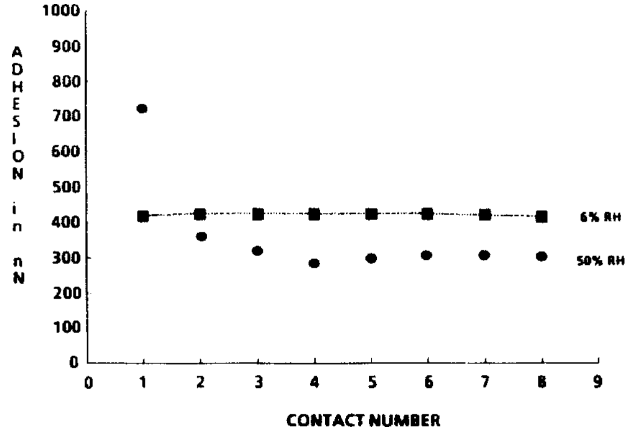

Figure 9. RH response of adhesion of toner with 100% surface coverage of 30 nm hydrophobic titania.

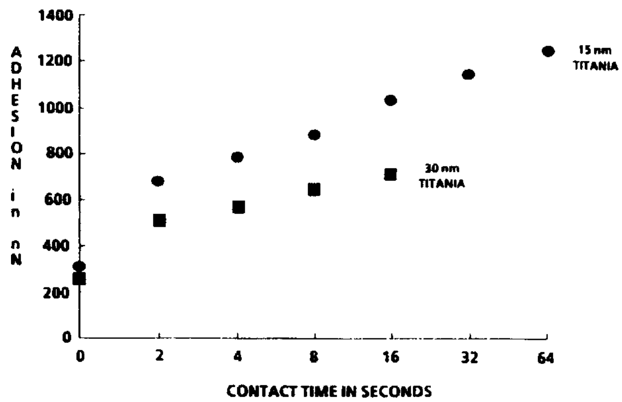

Figure 8. Adhesion increase as function of contact time at 70°, 50% RH for toners coated with 100% surface coverage of 15 nm and 30 nm hydrophobic titanias.

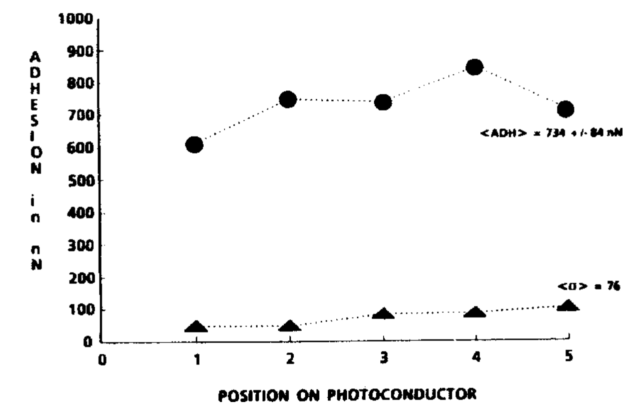

Figure 10. Adhesion of toner with 100% surface coverage of hydrophilic titania at 70°, 50% RH. Average adhesion values in solid circles. Standard deviations in solid triangles.