Small Particle Adhesion: Measurement and Control

M. Ott, E. Eklund, H. Mizes and D. Hays
Xerox Corporation, Webster, New York

Abstract

The adhesion of toner particles charged by triboelectricity plays an important role in the electrophotographic process. In spite of the importance of this phenomenon to electrophotography, the physics of toner adhesion is not well understood. Toner adhesion measurements reveal adhesion forces 5 to 50 times larger than the predictions of an electrostatic image force model. To better understand the root causes of these discrepancies, we have used three different techniques to investigate small particle adhesion. We will discuss these techniques as well as their advantages and disadvantages.

Introduction

In high quality electrophotographic printing, toner must be moved in a controllable manner through the printing engine so that it ends up in the desired place on the paper.[1] Toners, generally irregularly shaped polymer particles approximately 10 microns in diameter, can have various internal and external additives and pigments. Toner particles are triboelectrically charged and are moved by electric fields. If the electric fields are unable to move the toner due to strong adhesion forces then insufficient toner will be deposited on the final print. The results are low image density in solid areas, decreased operating latitudes and color shifts in color systems.

We have developed three techniques to measure particle adhesion: atomic force microscopy, electric field detachment and centrifugal detachment. These techniques have been used to determine the effects of particle charge, shape and substrate morphology on particle-surface adhesion. Atomic force microscopy and computer modeling are used to investigate the effects of surface roughness, external additives and applied electric fields on the adhesion of single particles. Electric field detachment has enabled rapid characterizations of the adhesion of particle layers, providing insight into the roles of particle-surface contact area and nonuniform particle charging on the adhesion of ensembles of particles. Centrifugal detachment is used to measure the adhesion force distribution of several hundred particles simultaneously and to determine its sensitivity to particle charge and size. The addition of digital photography to the detachment techniques has allowed in-situ visualization of particle detachment, enabling us to probe interparticle effects on adhesion.

Techniques

Atomic force microscopy (AFM) is frequently used in colloidal science to measure the interaction forces between a particle and a surface.[2] We apply the same technique in air, as others have done.[3-5] A single toner particle is attached to a weak cantilever. A surface is brought into contact with the toner in the AFM using piezoelectric transducers. When the surface is retracted, the particle will adhere to it and bend the cantilever. A laser is used to monitor cantilever motion, which is proportional to the force pulling the particle back from the surface. The maximum displacement of the cantilever before it springs back with the particle is a direct measure of the removal force.

The electric field detachment transfer cell consists of two transparent, conducting electrodes, each possessing a sensor to detect the presence of toner.[6] The electrodes are held apart by an insulating spacer. The detection system operates on the principle of frustrated total internal reflection. A prism mounted to the back of each electrode allows an infrared light beam (λ = 940 nm) to enter and reflect from the front face of the plate. The light undergoes total internal reflection, creating an evanescent electromagnetic field just outside the surface of each electrode. Toner particles deposited on this surface allow some of the light to be transmitted into the gap, thus reducing the internally reflected intensity in proportion to the toner contact area. By monitoring the intensity of the totally internally reflected beam, it is possible to obtain a direct measure of the average contact area of the toner particles on each electrode as they are transferred across the gap by the applied electric field.

In centrifugal detachment, particles are deposited at submonolayer coverage on a substrate that does not necessarily have to be transparent. The substrate is placed in an ultracentrifuge which provides a centrifugal force on the particles acting normal to the substrate surface. The substrate is photographed before the spin and after a series of spins going from slow to the maximum spin velocity of the centrifuge. After each spin, more particles are seen to have left the substrate, and from the spin velocity the force required to remove them can be inferred.

Each technique has its strengths and weaknesses. By applying all three we can gain a better understanding of the forces involved. AFM can rapidly explore the dependence of adhesion on loading force, contact time, and electric field. However, since only a single particle can be measured at a time, the statistics of the technique make it difficult to infer the average behavior of a collection of irregularly shaped particles. Also, uncharged particles must be used. Electric field detachment measures the adhesion of tens of thousands of charged particles simultaneously. It therefore provides a technique to characterize toner in an environment representative of the xerographic development and transfer zones. Centrifugal detachment can remove both charged and uncharged particles from a wide variety of surfaces. Also, because the surface is photographed after each spin, we know the exact spatial location of the removed particles. By virtue of being ensemble measurement techniques, electric field and centrifugal detachment allow us to examine the effect of neighboring particles on charged particle adhesion.

AFM Results

Silicas, titanias and similar nanometer sized particles have often been used as surface additives on toner particles.[7] These surface additives, while altering particle flow and charging ability, also have a strong influence on the particle adhesion to various surfaces. The additive's ability to modify particle adhesion varies with additive size, additive surface treatment and impaction level of the additive into the particle surface. Humidity also alters toner adhesion, with toners exhibiting higher adhesion at higher humidity regardless of the hydrophilic or hydrophobic nature of the surface additives.[8] Additive burial into the toner surface through normal use of a copier significantly increases toner-toner adhesion, i.e. cohesion. We will focus our discussion on AFM measurement of toner-toner cohesion since this is the only technique available to measure this property on a *particle-to-particle* level.

Toner cohesion is a very important property. As we strive for increased image quality with smaller and smaller toners, it becomes increasingly important to be able to produce and control single particle motion. In the AFM toner cohesion measurement, toner is mounted on the AFM cantilever as in the adhesion measurements. The contacted surface, however, is replaced by toner held in place on a glass slide with Temp-Fix epoxy. Temp-Fix softens below the softening point of toner so the toner surface is not altered in the mounting process and it remains epoxy-free as well.

It is well known in xerography that toner surface additives may become buried into the toner surface by continued mixing with carrier beads in a development housing.[9] This aging process has a significant effect on toner cohesion and toner adhesion.

Figure 1 shows the cohesion of 5 minute and 60 minute aged toner with small silicas and titanias on the toner surface. Aging is accomplished by running the toners in an actual development housing for the times specified. Each bar in Figure 1 represents an average of 16 measurements of a single toner-toner contact. Adjacent bars indicate an intentional slight shift in topography of the contact for the same pair of toners to investigate the effect of topography on cohesion. Widely spaced bars indicate cohesion measurements for different toner-toner pairs. There are wide variations in cohesion for aged toners. Cohesions of five minute aged toners range from an almost unmeasurable 5 nN to 550 nN. Cohesions of 60 minute aged toners vary from 400 nN to 900 nN, roughly 3.5 times the values for 5 minute aging. This is a definite signal of additive burial. Reference 7 contains scanning electron micrographs of aging induced additive impaction.

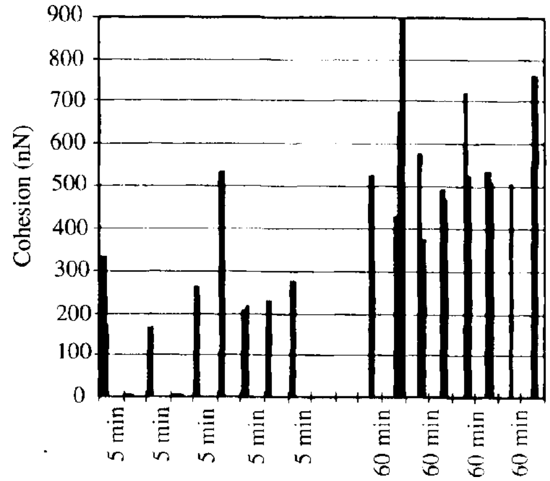

Figure 1. Cohesion measurements in nN for toner-toner pairs of 5 minute aged toners (167 nN average) and 60 minute aged toners (570 nN average) with small silicas and small titanias as surface additives.

Figure 2 shows toner cohesion values as a function of aging time for toners with large silicas and titanias on the surface. Corresponding Hosokawa Powder Tester[10] cohesion values for the toners are 16%, 20%, 40% and 50%. This set of toners with large additives still suffers from the aging process which increases toner cohesion by burying surface additives. AFM cohesivities generally follow the Hosokawa trend—increasing cohesivity with aging time. In the limited data set, however, a particularly cohesive 30 minute aged pair was sampled which increased the 30 minute aged average cohesion slightly above the 60 minute aged average cohesion. Presumably with larger sample sets, the AFM cohesions would track the Hosokawa cohesivities exactly. An added feature of AFM cohesivity measurements is the distribution information possible. One can track not only cohesion means with aging time, but cohesion ranges as well.

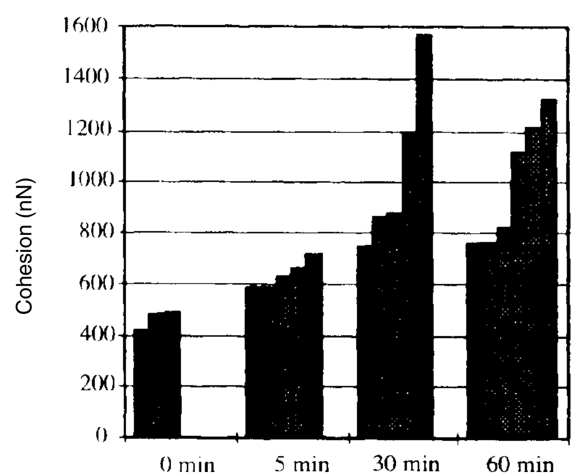

Figure 2. Cohesion in nN for aged toner-toner contacts for toners with large silicas and large titanias as surface additives. Unaged (0 min) average = 462 nN, 5 min aged average = 632 nN, 30 min aged average = 1050 nN and 60 min aged average = 1000 nN.

Figure 3 illustrates another unique feature of AFM measurements of toner cohesion. Aged toner cohesion is plotted as a function of force of contact for 5 minute aged toner. Cohesion increases with increased contact force. The toner shows an irreversible plastic surface deformation as evidenced by the inability to return to low values of cohesion as the contact force is decreased after a monotomic increase. The load force which produces plastic deformation is an important property to keep in mind when designing developer housing aggressiveness of mixing. AFM is the only technique capable of providing this information.

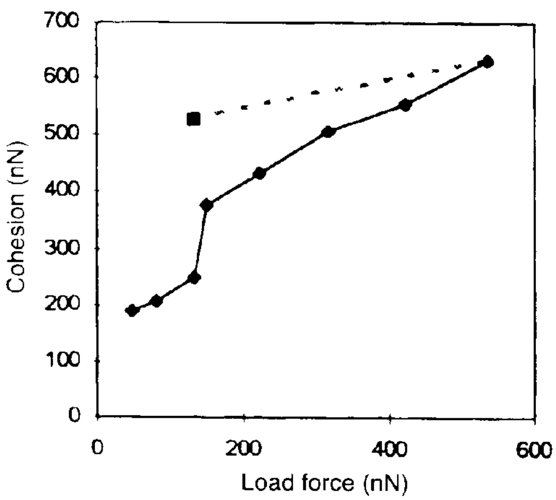

Figure 3. Cohesion of 5 minute aged toner as a function of load force. Diamonds—increasing load force. Squares—decreasing load force.

Electric Field Detachment Results

In xerographic subsystems, it is important to understand the behavior of an ensemble of toner particles (i. e., a toner layer). In particular, the adhesion of a toner particle can be affected by its neighbors. Our work is divided into two major thrusts: performing analytical calculations to determine the predicted detachment conditions for uniformly and non-uniformly charged particles in various configurations, and experimentally determining the adhesion of toner layers with electric field detachment. The comparison of experimental detachment data with calculated behavior has provided a more detailed understanding of electrostatic adhesion, particularly for the case of irregularly shaped, triboelectrically charged toner particles.

To understand the effects of neighboring particles on charged particle adhesion, one must consider the influence of the particle structure on electrostatics. We will consider two cases when calculating the adhesion of isolated and neighboring particles: (1) charged particles with uniform distributions of surface charge and (2) charged particles with nonuniform distributions of surface charge.

For the case of a uniformly charged, spherical particle, the electrostatic adhesion to a conductive surface is given by the electrostatic image force model,

$$F_i = -\alpha \frac{Q^2}{16\pi\varepsilon_o \ R^2} \tag{1}$$

where Q is the particle charge, R is the particle radius and ε_o is the permittivity of free space. For a toner particle dielectric constant of $\kappa = 4$, the polarization correction factor α is 1.9.[11] When an electric field is applied to detach the particle, the applied force due to the field E is

$$F_a = \beta QE - \gamma\pi\varepsilon_o \ R^2E^2 \tag{2}$$

where β and γ are correction factors due to the polarization of the particle. For a dielectric constant $\kappa = 4$, $\beta = 1.6$ and $\gamma = 0.063$. For sufficiently low detachment fields, the second term in Equation (2) can be neglected. When the sum of the forces from Equations (1) and (2) is zero, particle detachment will occur at a field E_d of

$$E_d = \alpha \frac{Q}{\beta 16\pi\varepsilon_o \ R^2}. \tag{3}$$

For $Q = 20$ fC and $R = 10$ µm, $E_d = 0.55$ V/µm. The observed detachment field for typical toner particles used in xerography is 5 to 50 times this value.

Neighboring uniformly charged, spherical particles produce an increase in the adhesion and detachment field, as described fully in reference 12. Table 1 shows a summary of the results of model calculations based on a multipole expansion method.[12] The particles have total charge $Q = 20$ fC and radius $R = 10$ µm. The increase in detachment field with increasing number of neighbors is attributed to modifications to the local electric field due to the adjacent charged particles. These values for detachment field are still significantly smaller than those seen experimentally for typical triboelectrically charged toner layers.

Table 1.

Particle Configuration	E_d (V/µm)	Field Ratio, to Single
Single	0.55	1
Double	0.74	1.34
Triple	0.92	1.66
Line	1.05	1.89
Hexagonal Close Packed	2.99	5.44

Nonuniform charging can also increase particle adhesion. To calculate the adhesion force and detachment field for a nonuniformly charged dielectric sphere, one can expand the surface charge distribution in a series of spherical harmonics.[13] For an axisymmetric charge distribution, such as charge arranged in "polar caps", the electric field outside the sphere is equivalent to a series of linear multipoles placed at the center of the sphere. The multipoles depend on the expansion coefficients for the charge distribution. The additional source multipoles augment the other multipoles which take into account the polarization of the particle by the applied electric field and the multipoles of neighboring particles, as well as their image multipoles induced in the conductive substrate. The force acting on the nonuniformly charged particle has been calculated in reference 13. The detachment field is obtained by setting the force equation to zero. Table 2 displays values of the detachment electric field for particles which have the same charge and size as the uniformly charged spheres, except that the charge is concentrated at the axisymmetric polar caps. One of the polar caps contacts the substrate.

Table 2.

Particle Configuration	E_d (V/µm)	Field Ratio (to Single)
Single	2.56	1.00
Double	2.75	1.07
Triple	2.94	1.15
Line	3.12	1.22
Hexagonal	5.42	2.12

As expected, the detachment electric fields are higher than for the uniform charged particle case due to the proximity of the nonuniform charge distribution to the substrate. Also as expected, the detachment field ratios are lower due to the dominance of the particle's own field over neighboring fringe fields.

As mentioned above, typical toner particles are highly irregular in shape. Triboelectric charging adds an "electrostatic texture" to the particles by distributing the toner charge over the surface in patches, thought to be primarily at surface asperities. The adhesion and electric field detachment characteristics of isolated, triboelectrically charged particles are described quite well by a charge patch model,[6,11] which indicates that a patchy distribution of charge enhances the *single* particle adhesion over the value predicted by Equation (1) by about a factor of ten. Taking neighboring particles into effect, fringe electric fields will exist that modify the adhesion of nearby particles. When considering toner layers, one would expect the neighboring particle fringe field effect on adhesion and the detachment electric field to be much less for patchy charged particles than for uniformly charged particles. This is because the electric fields associated with charge patches near the substrate are much higher than the fields from neighboring particles. Electric field detachment is the appropriate tool to investigate the adhesion of ensembles of uniformly charged and nonuniformly charged particles.

To test these predictions, a series of toner transfers was performed in a parallel plate electric field detachment cell, in which the initial sub-monolayer toner coverage on the donor electrode was varied systematically from 0.1 to 0.9 mg/cm^2.[6] Each electrode of this cell is equipped with an optical sensor to detect the contact area of the toner layer present as the detachment field is increased. These contact area signals can also be converted to give the mass of toner present on each electrode as a function of detachment field. The data from this series of measurements is summarized in Figure 4 by plotting the field required for 50% detachment of the initial toner layer as a function of toner coverage. A convenient metric of toner adhesion, this median detachment field, ranged from 15 V/µm at the lowest coverage (0.14 mg/cm^2) to 6.9 V/µm for a coverage of 0.81 mg/cm^2. These values are significantly higher than calculated detachment fields shown in Tables 1 & 2, revealing the unique adhesion behavior of particles with highly irregular shapes and nonuniform charge patches. In addition, the median detachment field dropped monotonically by more than a factor of two over the initial coverages investigated.

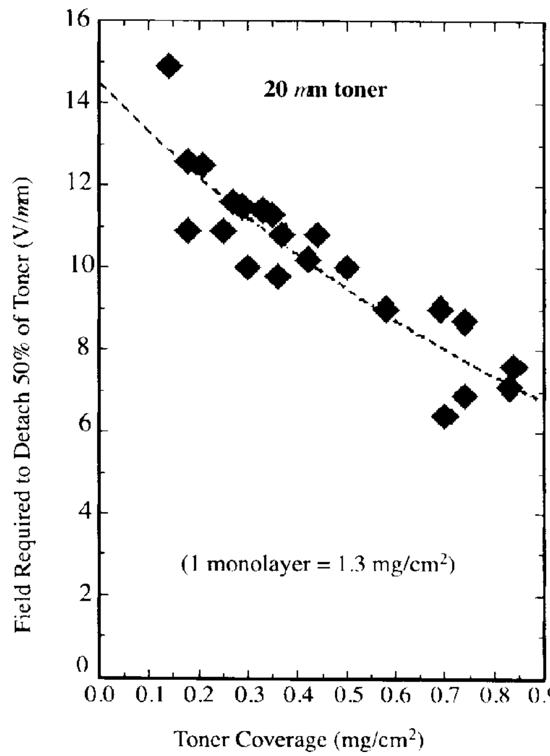

Figure 4. Median detachment field vs. initial toner coverage on donor electrode. Note that all initial coverages are well below a monolayer.

The data shown in Figure 5 suggests that the reduced adhesion for higher coverages is due to a decrease in the average contact area per particle as the initial toner coverage on the donor is increased. For light coverages, the particles are isolated and able to optimize their contact area solely on the basis of their shape and orientation as they are initially deposited on the donor electrode. As more particles are deposited in the initial loading, some are prevented from assuming their optimal orientations (maximizing their contact area) by other neighboring particles. This effect produces more low contact area particles for heavier depositions, particles which will be removed more easily during detachment. It is important to note that all coverages investigated in this study were significantly below a monolayer, so the effects of second layer particles are minimized.[6,11]

Centrifugal Detachment Results

Centrifugal detachment has been used to study particle-surface adhesion over the past 30 years.[14-18] In these studies, the measurements explored three general aspects of the problem: the dependence of adhesion on the properties of the surface, the properties of the particle, and the conditions under which the particles are being removed.

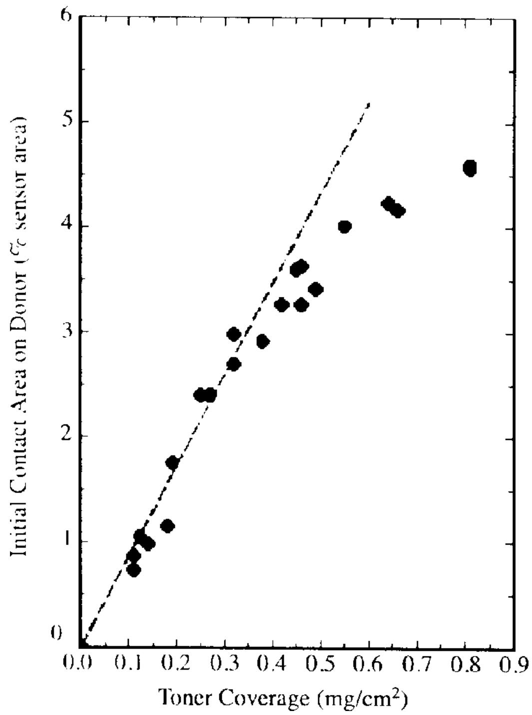

Figure 5. Initial toner contact area vs. toner coverage on donor. Deviation from initial linear behavior indicates a decrease in the average contact area per particle for heavier depositions.

We describe a novel modification of centrifugal detachment which allows one to gather more information from a single experiment.[19] After each spin with the centrifuge, a small area of the toner bearing surface is imaged with a CCD camera. The magnification of the image is approximately 200X, high enough to size individual particles. The particle sizing is performed with Image-Pro® software. By monitoring the substrate in this way, one can determine for every particle its size and the rotational velocity required to remove it.

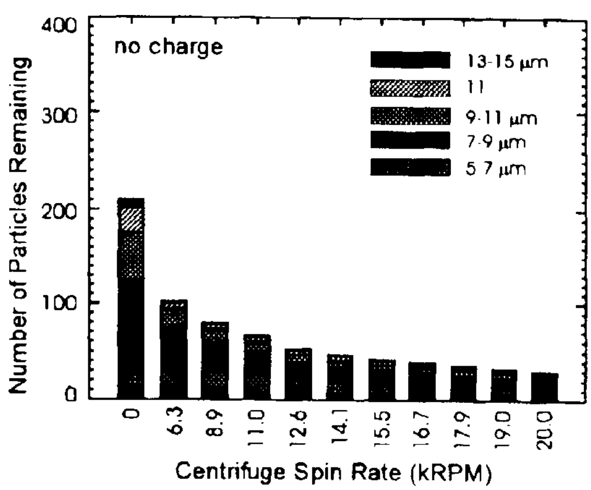

Figure 6a. Number of particles remaining at each centrifuge spin rate for no toner charge.

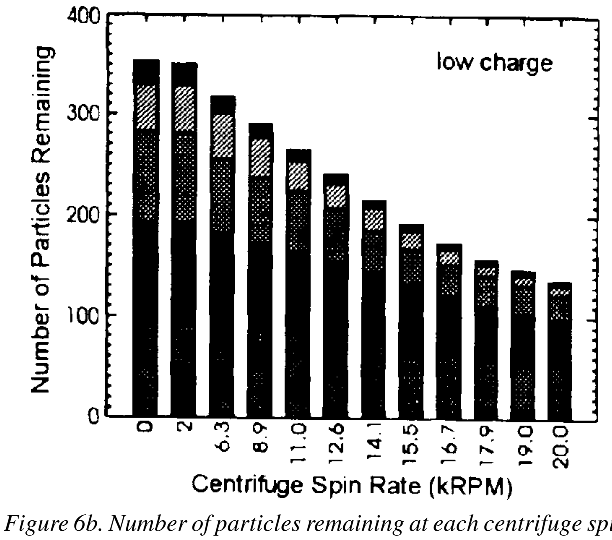

Figure 6b. Number of particles remaining at each centrifuge spin rate for low toner charge.

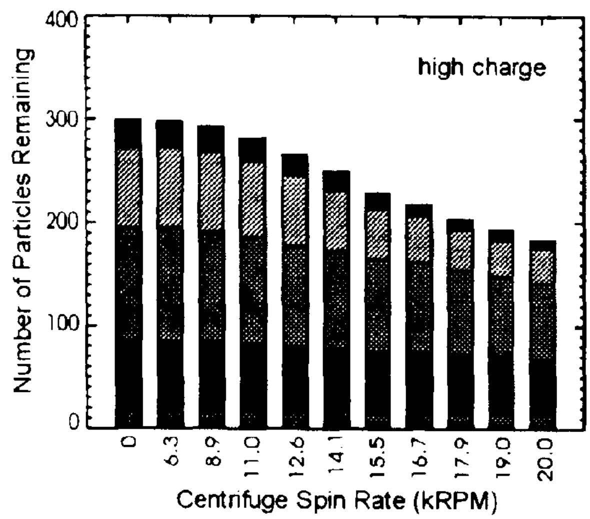

Figure 6c. Number of particles remaining at each centrifuge spin rate for high toner charge.

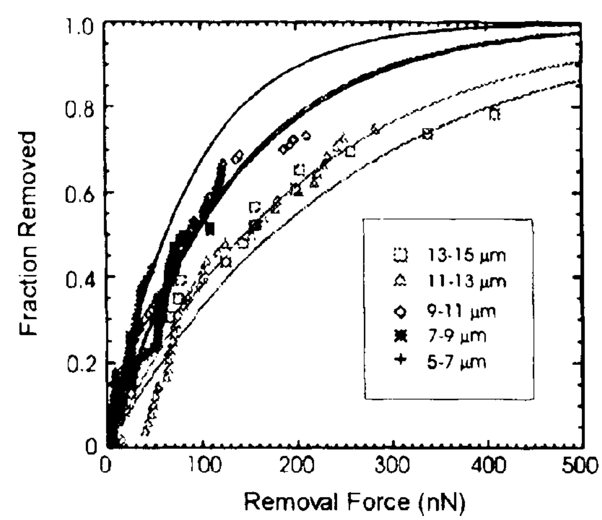

Figure 6d. Fraction of toner removed as a function of removal force for low toner charge.

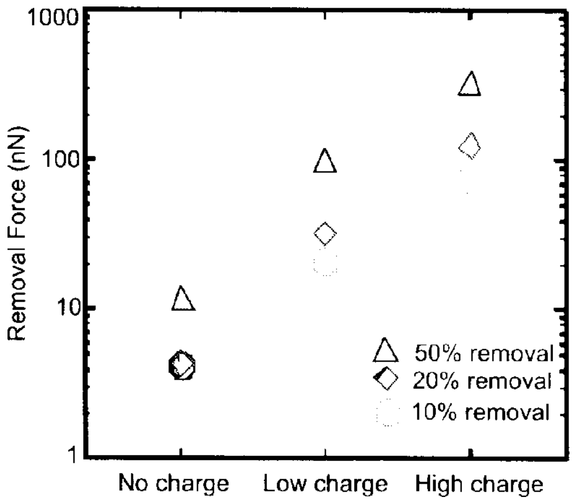

Figure 6e. Removal force in nN as a function of toner charge state for 10%, 20% and 50% removal of 10 μm particles.

We illustrate the analysis process for a xerographic toner of polydisperse particles with an average size of 9 μm and three charge states—no charge, low charge and high charge. The sample was spun in 18 increments to 19 kRPM. The number of particles remaining on the substrate after each spin is given by the height of the bars in Figures 6a, b and c. The bars have been subdivided to indicate how the different sizes of particles contribute to the total count.

For all charge states, one can observe that the decrease in the total particle count comes primarily from the large particles (>11 μm). This occurs because the removal force is proportional to the particle mass, or the cube of the particle diameter. At a given rotational speed, the force acting on a 13-15 μm diameter toner is over an order of magnitude larger than the force acting on a 5-7 μm diameter toner. A plot of the fraction of particles removed vs. applied force has been generated from centrifuge data for each of the size bins for each toner charge state. Representative data for low toner charge is presented in Figure 6d. The symbols correspond to the centrifuge data. Each symbol is plotted along the x axis at the force a particular particle is removed. The y axis shows the ratio of the count of that particle and all particles removed at smaller forces to the initial number of particles in that size bin. One can clearly see from the plot how the size of the particle corresponds to the maximum force that can be probed The squares (13-15 μm) extend out to 500 nN while the +'s (5-7 μm) extend out to less than 50 nN. The solid lines are best fits of the function $1\text{-}\exp(-aF_R)$ to the data, where a is a least squares fit to the data and F_R is the fraction removed. Overplotting this function allows an extrapolation of the data to larger forces. For these particular toners, the electrostatic attraction to the surface was found to dominate the nonelectrostatic forces of particle adhesion. This is shown graphically in Figure 6e where removal force for 10%, 20% and 50% removal of particles is plotted for a 10 μm particle for no toner charge, low toner charge and high toner charge. The dependence of adhesion on particle size and charge is in agreement with other centrifuge and particle adhesion studies.[14-18]

Centrifuge measurements were also used to look for an adhesion enhancement from neighboring particles. The adhesion of charged particles to a substrate depends not only on the particle and substrate properties, but may also be influenced by neighboring particles. This is because if neighboring particles are charged, fringe electric fields may exist that modify the adhesion of adjacent toners. In centrifuge detachment experiments, we typically deposit toner so that 20% of the substrate is covered. Goel and Spencer[17] calculate that if these particles were uniformly distributed over the substrate, their adhesion would be enhanced roughly by a factor of 2. When the particles are not uniformly distributed over the surface, one would expect that the particles that happened to have a larger number of neighbors would have a higher adhesion and those that have a smaller number of neighbors would have a lower adhesion, if any enhancement was happening at all.

The electric field detachment data showed that steric hindrance effects dominated neighboring particle fringe field effects.[12] The CCD images of the centrifugally detached particles allow us to eliminate steric effects from the data analysis. If toners are touching each other, they appear as a cluster and are eliminated from the analysis.

With a simple algorithm, the degree of isolation of a particle can be quantified. A 52 μm diameter circle was drawn around the center of each particle. Inside the circle, the number of pixels that consisted of a particle was counted and divided by the number of pixels in the circle. We call this number the fraction of surrounding particles f_s. This fraction becomes large when a given toner has more neighbors.

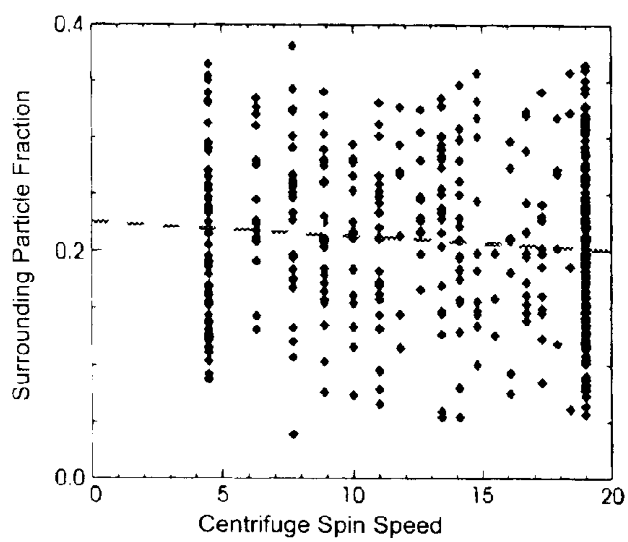

Figure 7. Centrifuge data shows that the removal force is independent of the number of neighboring particles.

In Figure 7, the fraction of surrounding particles for each particle is plotted against the centrifuge speed at which that particular toner last appears on the substrate. If neighboring particles enhance adhesion, then one would expect to see a positive slope to the data; that is, particles with a large number of surrounding particles should tend to be removed at higher centrifuge speeds. If neighboring particles decrease adhesion (steric hindrance), a negative slope would be seen. We see that f_s is distributed uniformly, independent of spin speed, indicating that there is no relationship between the fraction of surrounding particles and the toner adhesion. This observation supports the idea that toner charge is distributed nonuniformly and the particles own electrostatic adhesion from charge patches dominates fringe field effects from neighbors.

Conclusions

Atomic force microscopy, electric field detachment and centrifugal detachment are three highly complementary techniques for studying particle adhesion. We have applied these methods as useful tools in characterizing materials and in understanding the forces that drive toner particle adhesion.

References

1. D. M. Pai and B. E. Springett, *Rev. Modern Phys.*, **65**, 163 (1993).
2. W. A. Ducker, T. J. Senden, and R. M. Pashley, *Nature* **353**, 239 (1991).
3. H. A. Mizes, *J. Adhesion* **51**, 155 (1995).
4. H. A. Mizes, *J. Adhesion Sci. Technol.* **8**, 937 (1994).
5. H. A. Mizes, K.-G. Loh, R. J. D. Miller, S. K. Ahuja and E. F. Grabowski, *Appl. Phys. Lett*. **59**, 2901 (1991).
6. E. A. Eklund, W. H. Wayman, L. J. Brillson and D. A. Hays, *Proc. of IS&T 10th Int. Congress on Advances in Non-Impact Printing Tech.*, 142, (1994); (see page 1, this publication).
7. M. L. Ott and H. A. Mizes, *Colloids and Surfaces A,* **87**, 245 (1994).
8. M. L. Ott, *Proc. of the 19th Annual Meeting of the Adh. Soc*, **1**, 70 (1996).
9. R. Nash, S. Silence and D. Muller, *Proc. of IS&T 10th Int. Congress on Advances in Non-Impact Printing Tech*., **1**, 95 (1994); (see page 169, this publication).
10. Data supplied by S. M. Silence from a Hosokawa Powder Characteristics Tester Model PT-N by Hosokawa Micron Corporation.
11. D. A. Hays, *Particles on Surfaces 1: Detection, Adhesion and Removal*, 351-360, ed. K. L. Mittal (Plenum Press, NY, 1988).
12. D. A. Hays, *J. Adhesion*, **51**, 41 (1995).
13. E. A. Eklund, W. H. Wayman, L. J. Brillson and D. A. Hays, *Electrostatics* '95, ed. S. Cunningham (The Institute of Physics, Bristol, to be published).
14. H. Krupp, *Advan. Colloid Interface Sci.* **1**, 111 (1967); W. Kottler, H. Krupp and H. Rabenhorst, *Z. Angew. Phys*. **24**, 219 (1968).
15. D. K. Donald, *J. Appl. Phys*. **40**, 3013 (1969); D. K. Donald, *J. Adhesion* **4**, 233 (1972).
16. D. F. St. John and D. J. Montgomery, *J. Appl. Phys.* **42**, 663 (1971).
17. N. Goel and P.R. Spencer, edited by L. H. Lee, Plenum Press, New York, 1975.
18. J. C. Mastrangelo, *Photographic Science and Engineering* **26**, 195 (1982).
19. H. Mizes, *Proc. of the 19th Annual Meeting of the Adh. Soc*., **1**, 318 (1996).