

Toner to Photoconductor Adhesion

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The forces needed to remove monodisperse spherical toner particles from an organic photoconductor were determined using electrostatic detachment for a series of particles having diameters between 2 μm and 12 μm . It was found that the removal force varied linearly with particle radius, as predicted by JKR (Johnson, Kendall and Roberts, Ref. 19). This result is inconsistent with the predictions of models that assume that the detachment forces are dominated by either a uniform charge distribution over the surface of the particle or localized charged patches. Moreover, reasonable works of adhesion are obtained if one assumes that the removal forces are dominated by surface, rather than electrostatic, forces. These results seem to suggest that, for spherical toner particles in this size range, adhesion may be dominated by van der Waals interactions.

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Introduction

The adhesion of toner to photoconductors in dry electrophotographic processes has long been a topic of interest and whose importance is growing with decreasing toner size. Indeed, a fundamental understanding of toner adhesion is important, not only for controlling transfer of toned images from the photoconductor to a receiver, but also in terms of cleaning and image quality. More specifically, it has been long known that the process of transferring toner electrostatically becomes more difficult as the size of the toner decreases. This can result in a decrease, rather than an increase in image quality, with decreasing toner diameter, as evidenced by the occurrence of mottle and hollow character (the failure to transfer the centers of fine lines).

As transfer efficiency decreases, it is necessary that more toner be removed from the photoconductor by the cleaning system. Moreover, the smaller toner tends to be more difficult to remove than the larger toner.¹ Both of these effects can stress the cleaning system. Moreover, inefficient transfer can lead to increased operating costs because more toner needs to be deposited on

the photoconductor to compensate for the toner that does not wind up on the receiver.

It is commonly believed that toner to photoconductor adhesion is dominated by either electrostatic forces, due to the charge on the particle interacting with an induced image charge in the photoconductor, or electrodynamic forces, such as those giving rise to van der Waals interactions. Indeed, much of the research in this area that has been conducted over the past two decades has been aimed at determining the nature of the interactions.

Despite all the interest in toner to photoconductor adhesion, the experimental results appear to be contradictory. Goel and Spencer² measured the forces needed to separate Xerox E and K toners, having diameters between approximately 3 and 50 μm , from selenium photoconductors using electrostatic and centrifugal detachment techniques. They concluded that both electrostatic and surface forces played significant roles in toner adhesion. They also reported that adhesion increased over time.

Hays³ studied the detachment of spherical 13 μm diameter toner particles from carrier and concluded that, assuming that the charge was uniformly distributed over the toner particle, electrostatic forces could account for only about 1/4 of the total detachment force. He also discussed the possibility that nonuniformly charged patches might increase the electrostatic contribution to the total adhesion force.

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Hays and Wayman⁴ measured the adhesion forces of 12 μm spherical toner particles by bouncing the particles between a pair of electrodes and concluded that surface and electrostatic forces contribute roughly equally to the total adhesion force. Subsequently, Hays and Wayman⁵ used similar techniques and concluded that nonuniform charge distributions were the dominant contributor to the adhesion of 99 μm diameter dielectric particles. Eklund and co-workers⁶ also concluded that nonuniformly charged patches dominate adhesion for 20 μm diameter toners.

Mastrangelo⁷ used an ultracentrifuge to measure the separation of toner particles having diameters between approximately 6.5 μm and 20 μm . He concluded that van der Waals interactions dominate over electrostatic contributions to toner adhesion. Moreover, he found that irregularly shaped toner was less adhesive than spherical toner. Finally, he reported that increasing the toner charge from 1 to 40 esu/cm² only increased the separation force from 400 to 650 nN on an IBM toner. Similarly, Nebenzahl and co-workers⁸ reported only a weak dependence of cleaning efficiency on toner charge for similar toners. These results would seem to argue against the electrostatic charged patch model, as non-uniform charge distributions should be more pronounced with irregularly shaped toner than with spheres.⁹

In a recent study, Gady and co-workers¹⁰ distinguished between electrostatic and van der Waals contributions to particle adhesion by attaching spherical polystyrene particles between approximately 6 μm and 12 μm to an atomic force microscope (AFM) cantilever and measuring the attractive force and force gradient, as well as the separation force between the particle and a variety of substrates. They reported that the van der Waals forces become more dominant at separation distances less than approximately 10 nm. However, there was an observable increase in the attractive and separation forces with the number of times the particle was allowed to contact a triboelectrically dissimilar substrate. Moreover, washing the particle with methanol decreased these forces, suggesting that localized charged patches can play a role in determining the separation forces.

In contrast to the results obtained in the aforementioned studies, Donald¹¹ determined that electrostatic forces dominate the adhesion of a variety of beads approximately 1/2 mm in diameter. Donald and Watson¹² used an ultracentrifuge to detach toner from carrier. They then measured the charge on the detached toner as a function of centrifuge speed and concluded that the toner to carrier adhesion was dominated by electrostatic forces.

Lee and Jaffe¹³ also determined toner to photoconductor and toner to carrier separation forces. The toner diameter in this study was 20 μm . The former force was determined using an ultracentrifuge, whereas the latter was determined using an air-jet and assuming that the air impinging on a carrier is proportional to the applied air pressure. They concluded that, although the measured forces seemed to agree with the values predicted assuming the dominance of van der Waals interactions, such a model could not possibly be correct for two reasons. First, the van der Waals force model overestimates the force of attraction because of the irregular shape of toner and second, electrostatically charged patches actually cause the electrostatic forces to be substantially larger than one would estimate assuming a spherical particle. It should be noted that this same article shows scanning electron micrographs of toner particles in contact with the photoconductor. These par-

ticles appear to be relatively smooth, although irregular, in shape and seem to be resting on flat surfaces of the particles. As discussed by Bowling¹⁴ in the same reference, such a contact may actually increase the effect of van der Waals forces.

Finally, Gady and co-workers¹⁵ recently reported measurements of 8 μm toner to photoconductor adhesion as a function of submicrometer-size silica concentration on the surface of the toner. They concluded that, for silica concentrations less than 2% by weight of toner, the separation force was dominated by van der Waals interactions. It was only when the silica concentration reached about 2% were the effects of van der Waals and electrostatic forces comparable. Moreover, they also concluded that, for the electrostatic charge patch model to successfully explain the measured separation force, the fields generated by the localized charges would be so high as to result in electrical discharges.

There are several reasons for the diversity of proposed toner adhesion mechanisms. Certainly, the variations in toner size—from about 3 μm to 99 μm —obviously can be responsible for much of the apparently contradictory results. In addition there appears to be a theme in the literature that leans to an either-or scenario, i.e., the interactions are either electrostatic or van der Waals. Indeed, many authors categorically state that because they have observed a charge dependence to the applied forces needed to effect separation, adhesion must be dominated by electrostatic forces. In fact, both forces are probably present and additive. However, a large part of the discrepancy arises from experimental difficulties. Specifically, polydispersity in toner size and shape complicate attempts to analyze data. Moreover, individual investigators tend to focus on one size of toner. Often, the dependence of the separation force on toner size may shed more light on the mechanisms controlling toner adhesion than measurements on individual batches of toner. Finally, as is often reported in the literature, there is a temporal dependence to the toner adhesion, with toner generally becoming more tightly bound to the photoconductor over time. However, separation force measurements, including centrifugation and electrostatic detachment, are generally quite time intensive.

In this article we report real time separation force measurements of a series of monodisperse spherical toners, having diameters between 2 μm and 12 μm , from a commercially available organic photoconductor.

Experiment

The force needed to separate monodisperse, spherical, polystyrene toner particles from an organic photoconductor was measured using electrostatic detachment in real time, using an electrostatic transfer station.

A series of black, polystyrene, monodisperse toner particles having diameters between approximately 2 μm and 12 μm were made using the method of Ugelstad,¹⁶ as modified by Hoskyns.¹⁷ A typical sampling of such particles is shown in Fig. 1. In addition, classified spherical polyester toners were formed by dissolving the toner material in dichloromethane and spray drying (rather than the more traditional grinding processes).

Developers were prepared by mixing a predominance of once size toner with a few percent by weight of the next larger size particle. For example, a developer comprising principally 2 μm toner would also comprise a few percent by weight of a 5 μm toner. For the largest size toner particles studied (12 μm diameter), 30 μm diameter particles were used to establish the gap. Together, these toners

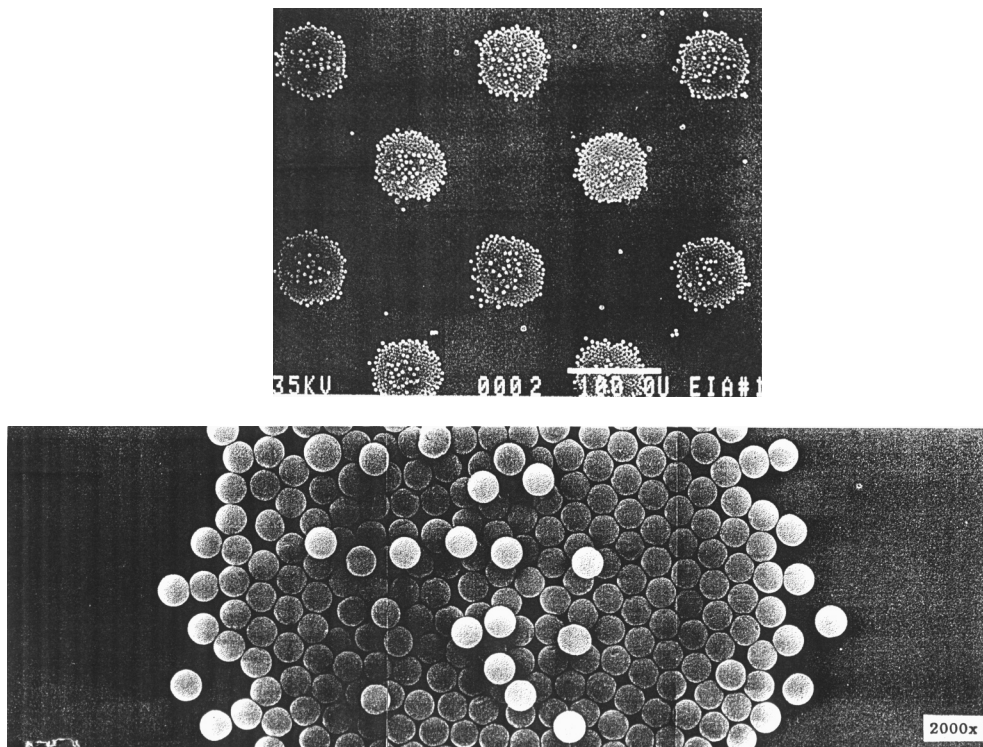


Figure 1. Scanning electron micrographs of a typical sample of toner particles used in this study.

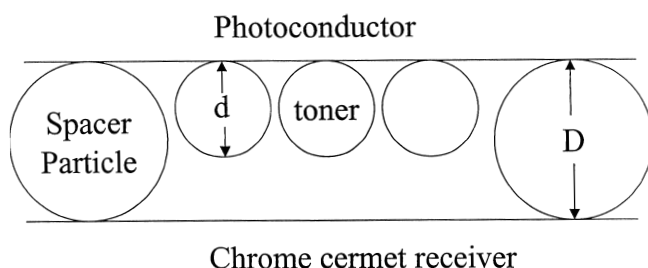


Figure 2. Schematic illustration of experimental setup. The larger toner particles fix the size of the air gap while the applied electric field cause the smaller particle to transfer from the photoconductor (top) to the receiver (bottom).

would be mixed with a magnetic carrier to impart a suitable positive charge on the toner. Typical toner concentrations were of the order of 5 – 10% by weight of developer. In addition, the toner charge was measured from a similar developer comprising only one size of toner, assuming that the addition of the small amounts of the larger-size toner particles did not significantly alter the charge on the smaller. Toner charge was measured with a Faraday cage using samples of the toner that had been deposited on a photoconductor during the development process. Figure 2 shows a schematic of the experimental layout.

Images were formed and transferred on an electrophotographic device referred to as a “linear breadboard”. In essence, this device produces an electrophotographic image by physically transporting a sample of a photoconductor through the appropriate stations. In this instance, the photoconductor was first charged to a suitable positive potential using a grid controlled, 3-wire DC corona charger. The initial voltage on the photoconductor was about +500 V.

A submonolayer of toner was deposited on a polyester-based, commercially available photoconductor by initially charging the photoconductor positively, and then optically discharging it to an appropriate potential. This technique was chosen so that the actual toner deposition process most closely resembles that encountered in an actual electrophotographic engine. It is not anticipated that altering the deposition process, such as might be done by grounding the photoconductor and biasing the development station accordingly, would dramatically affect the results. However, there might be some difference due to the presence of ions on the surface of the photoconductor. This would be a suitable topic for further research. The photoconductor was then brought into proximity with a magnetic brush development station and a uniform, submonolayer of toner was deposited using the charged area development mode.

The photoconductor was then illuminated to ensure that it was in its “conducting” mode. The receiver comprised a 4 mil thick Estar support over which was evaporated a coating of clear, electrically conducting material referred to as “chrome cermet” (chromium silicate). The receiver was gently pressed against the photoconductor during the transfer process using a roller. A DC electrical bias was directly applied to the chrome cermet layer to urge the toner to transfer. This bias was increased and the fraction of smaller toner that traversed the air gap was determined by statistically counting toner particles in representative areas of both the receiver and the photoconductor after transfer. Typically, the transfer bias would be determined by first estimating the bias and then converging on the actual bias needed. Typically, the transfer efficiency would be measured at between 6 and 12 bias levels. The fraction of particles that transferred was determined by first making a mask that allowed counting in 5 areas. Photomicrographs of both

TABLE I. Toner Diameter, Charge-To-Mass Ratio, and Average Individual Particle Charge

Toner Material	Toner Diameter (μm)	q/m ($\mu\text{Coul/g}$)	charge per particle (Coul)
polystyrene	2	100	4.0×10^{-16}
polystyrene	5	110.7	7.25×10^{-15}
polystyrene	8	33.1	8.85×10^{-15}
polystyrene	12.5	23.1	2.36×10^{-14}
polyester	8.6	43.5	1.66×10^{-14}
polyester	9.3	23.9	1.15×10^{-14}
polyester	13.5	29.7	4.38×10^{-14}

the photoconductor and the receiver were then made and the mask superimposed over the micrographs. The number of transferred and residual particles were then counted in each area. In general the counts were consistent to within a few percent. Presumably, this was due to the monodisperse, spherical nature of the particles. Toner coverage on the photoconductor was deliberately chosen to be sufficiently low so that the formation of a second layer or toner agglomeration was not a problem.

It is well known that, by coating the photoconductor with various “release agents” such as Teflon, zinc stearate, and various silicones, transfer and cleaning can be improved. In order to determine if the use of these agents decreased the toner-to-photoconductor adhesion, the force of detachment was also measured for these same toners from such photoconductors. In these cases, the release agent was generally rubbed onto the photoconductor with a cloth pad and as much as possible removed. This generally left about a monolayer-thick coating, as determined using ESCA.

Process speeds were approximately 5 cm/s. At this rate, the entire process from charging to transfer could be completed in less than 1 min, thereby closely simulating the toner transfer process in both forces applied to the toner and time periods during which the toner resided on the photoconductor.

Results

Table I lists the toner diameters and ratios of charge-to-mass. The charge per particle was calculated using a mass density for polystyrene of 1.0 g/cm^3 . The density of the polyester was 1.2 g/cm^3 .

The applied field was calculated by assuming that the transfer nip was a parallel plate capacitor and dividing the applied voltage by the separation gap. Because the applied pressure was the minimum required to press the receiver into contact with the photoconductor, all materials have relatively high Young’s moduli (greater than 3 GPa), and the photoconductor was illuminated it can be further assumed that the separation distance between capacitor plates is approximately the same as the diameter of the larger particles.

In general, when the adhesion of particles to surfaces is measured, there is a large distribution about the mean force needed to effect detachment. This is due to the variations in particle shape and size, differing particle to substrate contacts, and variations in the particle charge and charge distribution. In this study however, the use of monodisperse spherical toner particles narrowed the voltage window between transfer efficiencies of less than 10% to transfer efficiencies of more than 90% of the smaller toner particles transfer to $\pm 10 - 15 \text{ V}$. Considering that the applied voltage was typically in

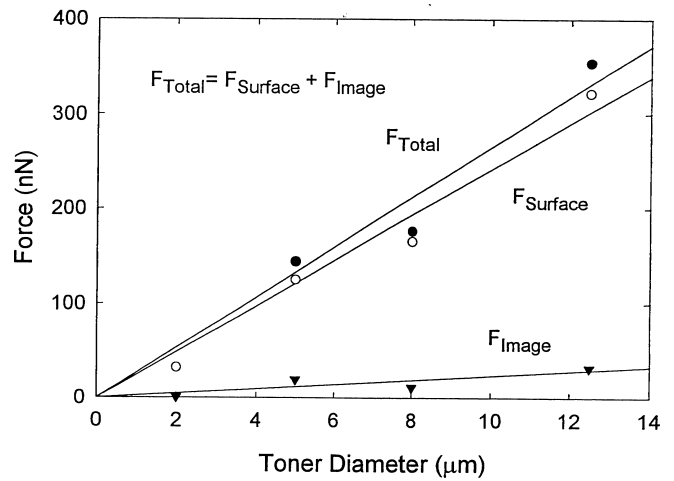


Figure 3. Total removal force and the surface and electrostatic contributions to the removal force as a function of toner diameter.

the range of 300 – 350 V, this measurement allowed a high degree of accuracy. Again, it should be noted that this accuracy is the direct result of using monodisperse spherical toner particles. In subsequent experiments that used more conventional ground toner, the transition was much more gradual. The force needed to separate the particles from the substrate was taken as that whereby half the smaller toner particles were electrostatically detached from the photoconductor.

The force F_E exerted on a particle with charge q , dielectric constant ϵ_p and radius R in contact with a substrate of dielectric constant ϵ_s by an applied electric field E acting through a medium of dielectric constant ϵ_m is given by¹⁸

$$F_E = -\beta q E \quad (1)$$

where

$$\beta \approx 1 + \frac{1}{2} \left(\frac{\epsilon_s - \epsilon_m}{\epsilon_s + \epsilon_m} \right) \left(\frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right). \quad (2)$$

For typical polymeric materials in air, β is approximately unity. Therefore, the electrostatic detachment force applied to the smaller toner particles is simply

$$F_E \approx q \frac{V}{D} \quad (3)$$

where V is the applied voltage and D is the diameter of the larger, spacer particles.

The charge per particle q was calculated from the charge-to-mass ratio, the particle radius, and the mass density (1.0 g/cm^3 for polystyrene). It was assumed that variations in particle charge were small because of the regular nature and narrow size distribution of the toner particles. This assumption is supported by the narrow voltage window between the regions where few and most of the smaller toner particles transfer.

Figure 3 shows the applied electrostatic force F_E^s needed to separate a toner particle from the photoconductor as a function of the toner diameter. This force, by definition, must equal the total force F_{Total} that needs to be applied to the toner in order to effect separation

from the photoconductor. In the area of dry electrophotography, it is frequently assumed that this force is comprised of principally of two terms and is given by⁹

$$F_E^S = \beta q E_S = \gamma \pi \epsilon_0 d^2 E_S^2 + \alpha \frac{q^2}{4 \pi \epsilon_0 d^2} \quad (4)$$

where E_S is the applied electric field needed to effect separation, d is the toner diameter, ϵ_0 is the permittivity of free space, and α and γ are constants and are equal to 1.9 and 0.063 for a particle with a relative dielectric constant of 4 in proximity to, but not contacting, a conducting substrate.⁹ The terms on the right hand side of Eq. 4 arise from the polarization of the particle by the applied field and the field arising from the charge on the particle. Moreover, the first term on the right hand side of Eq. 4 is often assumed to be negligible.⁹

Unfortunately, the analysis leading to Eq. 4 being the criterion for electrostatic detachment of toner from a photoconductor is not consistent with experimental observations. There are several reasons for this discrepancy. The applied transfer fields are typically of the order of 10^7 V/m. These are not small and, accordingly, the first term on the right hand side of Eq. 4 should not be neglected. There are even more significant problems. The constants α , β , and γ each depend on the differences between the dielectric constants of the particle and those of the substrate and/or surrounding medium. However, for real materials with finite Young's moduli and yield strengths, the stresses associated with the forces of adhesion cause the particles and/or substrates to deform, resulting in finite contact regions that effectively exclude any intervening medium in the regions of intimate contact where polarization effects should most significant. In the limit of large contacts, when the dielectric constants are equal (as would be the case of toner particles in contact with organic photoconductors), $\gamma = 0$ and $\alpha = 1$.

Another problem with the assumptions leading to Eq. 4 is that surface forces are neglected. However, these forces can be considerable¹⁹ and must, in general, be included in the analysis.

Finally, and most seriously, the assumption that separation occurs when the applied force equals the sum of the attractive forces is fundamentally incorrect. As mentioned, the forces adhering the toner particles to the photoconductor cause the contacting materials to deform. Energy is expended on creating these deformations. In order to determine the force needed to effect separation, one must approach the problem from the perspective of the work needed to separate the materials rather than simply balancing the applied force with the attractive forces. In effect, this was the approach taken by Johnson and co-workers in their classic paper on adhesion (generally referred to as the JKR theory).²⁰

According to the JKR theory, the adhesion induced contact radius a is related to the particle diameter d , the work of adhesion between the particle and substrate w_A , and any external load P by

$$a^3 = \frac{d}{2K} \left\{ P + \frac{3}{2} w_A \pi d + \left[3 w_A \pi d P + \left(\frac{3}{2} w_A \pi d \right)^2 \right]^{1/2} \right\}. \quad (5)$$

Here, K is related to the Young's moduli and Poisson's ratios of the contacting materials. It should be noted that the solutions to Eq. 5 must be real, i.e., Eq. 5 predicts a real contact radius as a function of toner diam-

eter and applied force. A force tending to remove the toner from the photoconductor is equivalent to a negative load. However, the term within the square root brackets cannot be less than zero and still have a real contact radius. Accordingly, the toner must separate from the photoconductor when there is a critical electrostatic force P_S applied to the toner such that

$$P_S = \frac{3}{4} w_A \pi d. \quad (6)$$

Because the field generated by the charged toner particle changes as a result of the deformations resulting from the electrostatic and surface force interactions between the toner particle and substrate when the two are in contact, the actual determination of the separation field is difficult to calculate and is beyond the scope of this article. However, if one assumes that the perturbation of the field due to the deformations is small, then

$$P_S = -\beta q E_S + \frac{\alpha q^2}{4 \pi \epsilon_0 d^2} + \gamma \pi \epsilon_0 d^2 E_S^2 = \frac{3}{4} w_A \pi d. \quad (7)$$

If one further assumes that there is intimate contact between the toner and photoconductor with a sufficiently large contact area, so as to exclude any intervening medium, and that the dielectric constants of the toner and photoconductor are similar (implying that $\alpha = \beta = 1$, $\gamma = 0$), then the applied electrostatic separation force F_E^S is simply

$$F_E^S = \frac{3}{4} \pi w_A d + \frac{q^2}{4 \pi \epsilon_0 d^2} \quad (8)$$

and the corresponding separation field E_S is given by

$$E_S = \frac{3}{4} w_A \pi \frac{d}{q} + \frac{q}{4 \pi \epsilon_0 d^2}. \quad (9)$$

It is apparent from Eq. 8 that the force needed to remove a toner particle from a photoconductor increases rapidly with toner charge. This can readily explain the commonly observed effect that the removal force increases with charge. However, it is also apparent from Eq. 8 that such an observation does not rule out the effect of surface forces in determining the adhesion of the toner to the photoconductor.

It is also seen from Eq. 9 that there must be a range of charges where toner can be electrostatically detached from a photoconductor. As the toner charge decreases, the first term on the right hand side of Eq. 9 increases, whereas the second vanishes. At this limit the surface forces dominate and one cannot exert a sufficient field to remove the toner. Alternatively, as q increases, the effect of the image force increases, whereas the contribution from surface forces becomes negligible. Realizing that one can only increase the applied field to the Paschen limit (corresponding to about 3.5×10^7 V/m for a $10 \mu\text{m}$ size air gap), one can also see that too high a toner charge can impede electrostatic detachment.

It is also worthwhile to consider the effects of toner diameter on the relative contributions of surface and electrostatic forces to the adhesion of the toner to the

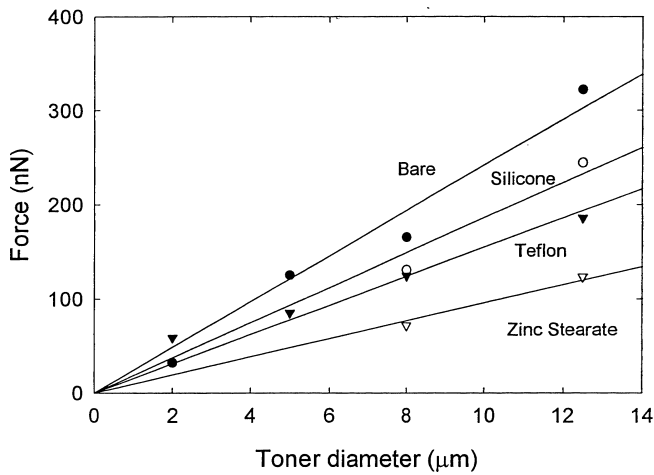


Figure 4. Surface force as a function of toner diameter for organic photoconductors overcoated with a silicone, Teflon and zinc stearate as well as the bare photoconductor.

photoconductor. This can be done by considering Eq. 8. However, it must first be realized that the toner charge is not independent of the toner diameter. Rather, as is well known, the toner charge-to-mass ratio increases with decreasing toner diameter. This presumably is due to the fact that most toner acquires its charge through triboelectrification and, thus, depends on surface area. Accordingly, if it is assumed that the surface charge density σ is approximately constant, then

$$q = \sigma \pi d^2. \quad (10)$$

Eq. 8 can then be rewritten as

$$F_E^S = \frac{3}{4} \pi w_A d + \frac{\sigma^2 \pi d^2}{4 \epsilon}. \quad (11)$$

It is seen from Eq. 11 that, whereas both the surface and electrostatic forces both decrease with decreasing toner diameter, the electrostatic forces decrease at a faster rate. Accordingly, for small toners, the surface forces tend to dominate over the electrostatic forces. Conversely, for larger toners, the forces associated with the toner being attracted to its image charge are dominant. The diameter at which electrostatic forces dominate over surface forces clearly depends on a number of properties including the surface charge density and work of adhesion. However, assuming that $w_A = 0.01 \text{ J/m}^2$ and $\sigma = 9.2 \text{ Coul/m}^2$ (corresponding to the $5 \text{ } \mu\text{m}$ diameter toner used in this study), the cross-over diameter is estimated to be about 98 microns. Indeed, it is readily apparent from Eq. 11 that, in trying to determine whether surface or electrostatic forces dominate toner-to-photoconductor adhesion, one must consider the toner size. This becomes even more complex when size effects are confounded by shape, contact, and charge distribution effects, as would be the case for irregularly shaped ground toner. Considering the range of toner sizes, charges, etc. discussed in the literature (as summarized earlier in this article), it should not be surprising that the results appear inconsistent.

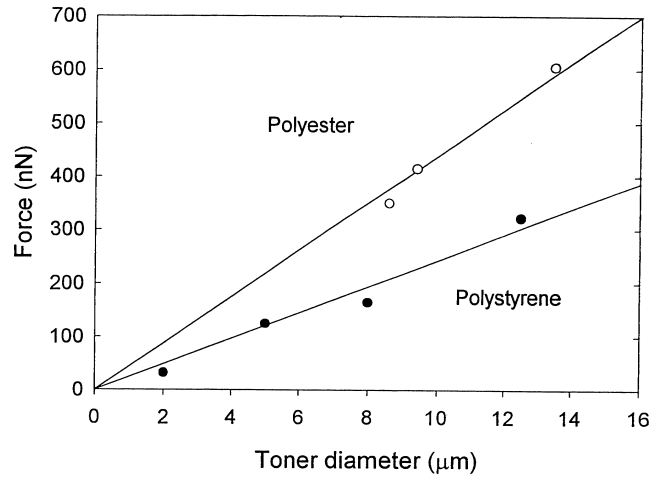


Figure 5. Surface force vs. toner diameter for spherical polyester and polystyrene toners.

By using Eq. 11, one should be able to differentiate between surface and electrostatic force dominated toner adhesion through the power law dependence of the detachment force on the toner diameter. In particular, if the toner-to-photoconductor adhesion is dominated by surface forces, the removal force should vary with the diameter of the toner particles. Alternatively, if electrostatic forces dominate the toner adhesion to the photoconductor, ideally the separation force should vary as the toner diameter squared. As is readily apparent from Fig. 3, the total separation force was found to vary linearly with toner diameter, suggesting that surface forces dominate over electrostatics. Similar results were reported by Gady and co-workers.¹⁰

A more thorough analysis of these results requires separating the contributions of the surface from those of the electrostatic forces. This is readily accomplished using Eq. 8, and the results have been shown in Fig. 3. As is readily apparent from this figure, the estimated contributions to the total force of adhesion arising from electrostatic contributions are small compared to those due to the surface forces. However, the fraction of the total force due to the electrostatic contributions increases with increasing toner diameter, going from less than 1% for the $2 \text{ } \mu\text{m}$ toner to about 10% for the $12 \text{ } \mu\text{m}$ toner. The work of adhesion, calculated using Eq. 6 and the slope of F_{Surface} from Fig. 3, is approximately 0.01 J/m^2 . As the work of adhesion is simply the sum of the surface energies of the two contacting materials minus the interfacial energy, this is a reasonable value for this combination of polystyrene toner and a polyester photoconductor.

Release agents such as various silicones, Teflon, and zinc stearate have often been coated onto photoconductors to improve transfer and facilitate cleaning. The effect of these materials on toner adhesion to the photoconductor is shown in Fig. 4. As is apparent, each material decreases the force needed to separate the toner from the photoconductor, with silicone showing the least benefit and zinc stearate having the greatest effect, reducing the toner to photoconductor adhesion by almost a factor of 3. It should be noted that these measurements were made using the same developers. Had the

toner adhesion been dominated by the electrostatically induced image forces, these release agents should have had minimal effect on the separation forces.

Toner materials can also affect adhesion. This is shown in Fig. 5, where the adhesion of the polyester and polystyrene toners to the same photoconductor are compared. As is readily apparent, the polyester toner is significantly more adhesive than is the polystyrene. The work of adhesion calculated for the polyester toner is 0.019 J/m^2 , or almost twice that of the polystyrene toner. It should also be noted that the charge on the $12.5 \mu\text{m}$ polystyrene is higher than that on either the 8.6 or $9.3 \mu\text{m}$ polyester toner. However, the force needed to separate either of the polyester toners from the photoconductor was greater than that needed to remove the polystyrene particles. Again, this argues that some material property other than its charge contributes significantly to the detachment force.

Conclusions

The force needed to remove spherical toner particles having diameters between approximately 2 and $13 \mu\text{m}$ from an organic photoconductor, was measured using electrostatic detachment, and found to vary linearly with toner diameter. Moreover, it was also found that various release agents such as silicone oil, Teflon, and zinc stearate, also reduced the force needed to separate the toner from the photoconductor. Finally, it was necessary to apply a stronger force to remove polyester toner particles from the photoconductor than it was to remove polystyrene toner. The electrostatic contribution to the total adhesion force was found to be small compared to the surface forces. However, this contribution was found to increase with increasing toner diameter, suggesting that the adhesion of very large toner particles (i.e., those with diameters greater than about $50 \mu\text{m}$) may be dominated by electrostatic forces. The results of this study suggest that, in order to understand the nature of the interaction between toner particles and the photoconductor, one must pay particular attention to factors such as toner charge and toner particle size.

Appendix: Detailed Description of the Toner

Styrene monomer was distilled from sodium methoxide²⁰ and stored in a freezer. Benzoyl peroxide was also stored in a freezer and used as received from Aldrich Chemical Company.

The 2 (Methylamino)ethanol, chlorododecane, potassium persulfate, sodium chloride, potassium dichromate and adipic acid were each used as received. Ludox TM was used as it came from DuPont Inc. Deionized, distilled water was used throughout. The Vinol 523 was used as it came from Airco Chemical Company.

The adduct of adipic acid and 2-(methylamino)ethanol (meaadipate) was made by heating a 1:1 mole mixture of the above at 150°C until 15 ml of water was collected. The product was diluted to 10% w/w, with water and stored in a refrigerator.

The 5%, w/w, Vinol 523 solution was prepared by sifting the solid into stirring water, at room temperature. The water was then heated to 90°C and stirring continued overnight. The product was diluted with water to 5%, filtered and stored in a refrigerator.

A. Monodisperse, 1 Micron Seed Latex

1. Procedure 1: (X253-55). To a $12,000 \text{ ml}$, 3-neck, round-bottom flask containing a paddle stirrer, con-

denser, and N_2 inlet tube, was added 6400 milliliters of water and 5.12 g NaCl . The flask was put into a 70°C , constant temperature bath and evacuated (aspirator) from the top of the condenser (being certain not to remove water), four times to the incipience of boiling, and venting each time with N_2 .

Next, 768 g of distilled styrene was added and the system evacuated, as before. Then 256 g of a solution containing 3.75 g of $\text{K}_2\text{S}_2\text{O}_8$ per liter of water, was added and the mixture stirred 60 minutes at 100 rpm at the liquid:liquid interface (bleeding N_2 slowly into the flask) and a sample taken. Using a parastaltic pump, 1920 milliliters of a solution containing 2560 milliliters of water and 41 g of $\text{K}_2\text{S}_2\text{O}_8$ was pumped into the flask below the surface of the liquid in an 8 h time period, at 70°C , while stirring at 80 rpm at the liquid:liquid interface (N_2 bleed). The flask contents was then stirred for an additional 12 h at 70°C and then heated 16 h at 75°C product dispersion. 7.34 w/w \% solids.

The resultant latex was filtered on Reeve-Angel 230 paper, using vacuum, and dialyzed overnight in a 10K cellulose acetate bag against distilled water at room temperature; 6.51 w/w\% solids, 0.404μ mean radius, N_{AV} radius 0.404μ , W_{AV} radius 0.408μ , $\sigma = 0.0281$,

$W_{\text{AV}} \text{ radius}/N_{\text{AV}} = 1.01$, $n = 1000$. (These values were determined in the Polymer Physical Chemistry Laboratory of the Chemistry Division by electron microscopy).

2. Procedure 2: (X253-175-1). To a 500 ml , 3-neck, round-bottom flask was added 250 milliliters of water and 10 milliliters of a solution containing 0.0625 g of NaCl per 100 milliliters of water. The flask was evacuated in the same manner as above, and 4.0 g of distilled styrene was added. The flask was evacuated again and 1.25 g of the catalyst solution mentioned in procedure 1 was added and the mixture stirred overnight at 70°C , at 100 rpm at the liquid surface (N_2 bleed) and then a sample was taken.

Next 26 g of undistilled styrene was added and the flask evacuated as before. 75 milliliters of a solution containing 100 milliliters of water, 0.80 g of $\text{K}_2\text{S}_2\text{O}_8$ and 0.62 g of sodium lauryl sulfate was pumped below the surface of the liquid in 8 hours using a syringe pump. The flask was stirred at 100 rpm at the liquid:liquid interface at 70°C (N_2 bleed) and stirring was continued 12 h after pumping was finished. 7.08 w/w\% solids, 0.872μ mean diameter, N_{AV} diameter 0.872μ , W_{AV} Diameter 0.873μ , $\sigma = 0.0159$, $W_{\text{AV}}/N_{\text{AV}}$ diameter = 1.002 , $n = 90$ (by electron microscopy).

B. The Swelling of a Monodisperse, 1 Micron Seed Latex with Chlorododecane: (X253-81).

To a Manton-Gaulin, Model 15, submicron disperser was added 6825 milliliters of water, 2.46 g of sodium lauryl sulfate and 171 milliliters of chlorododecane (CDD). This mixture was milled for 10 min at 4000 PSI with brisk stirring in the hopper.

To a 3000 milliliter, 3-neck flask containing a paddle stirrer, condenser and stopper was added 800 g of the above CDD emulsion, 1259 g the seed latex from procedure 1 and 225 milliliters of acetone. This mixture was placed in a 35°C bath for 16 hours without agitation.

This dispersion was next concentrated by distillation in a rotary evaporator at 60°C from 2210 g down to 395 g and then diluted, with water, to 2000 g . The dispersion was then filtered through number 230 Reeve-Angel filter paper using aspirator vacuum. A final filtration, using a thin pad of super-cel filter aid on the same paper was applied. 3.21 w/w\% solids, 1.647μ mean diam-

eter, N_{AV} diameter 1.647 μ , W_{AV} diameter 1.653 μ , 0.0499; W_{AV}/N_{AV} diameter = 1.004, $n = 514$ (by light microscopy).

C. The Formation of a Monodisperse, 5 Micron Seed Dispersion: (X253-144).

To a 2000 milliliter, 3-neck, round-bottom flask containing a paddle stirrer, condenser, and N_2 inlet tube was added 560 milliliters of water, 240 g of 5% Vinol 523, 1.52 g of sodium lauryl sulfate, 48 milliliters of 2.5 w/w% solution of $K_2Cr_2O_7$ in water, 90.4 g of CDD swollen latex (section B above), and a solution of 216 g of undistilled styrene and 10.8 g of benzoyl peroxide.

This mixture was stirred at 250 rpm for 3 h at 30°C. The constant temperature bath was then raised to 60°C and the flask evacuated as before. The charge was then stirred overnight at 60°C at 100 rpm at the liquid:liquid interface (with N_2 bleed). 19.24 w/w% solids, 4.27 μ mean diameter, N_{AV} diameter 4.27 μ , W_{AV} diameter 4.39 μ , $\sigma = 0.385$, W_{AV}/N_{AV} diameter = 1.027, $n = 364$ (by light microscopy). For an accurate solids determination by baking in a 105°C oven, addition of 0.1 g hydroquinone per 2 g sample was necessary.

D. The Swelling of Monodisperse, 5 Micron Seed Particles with Chlorododecane: (X253-149).


Into a Manton-Gaulin disperser was added 100 milliliters of water, 0.36 g of sodium lauryl sulfate and 25 milliliters of chlorododecane (CDD) and the contents were milled 5 min at 4000 PSI.

The 5 micron seed particles (208 g) (section C above) were washed with water three times, centrifuging the particles and using ultrasonics to redisperse them. Each time the washed particles were diluted with water back to 208 g.

To 208 g of the washed 5 micron particles (which appeared to be slightly flocculated) was added 1.61 g of sodium lauryl sulfate and the mixture was sonified for 3 min at 70 watts, using a Branson Model 200 sonifier with a 1/2 inch horn. This redispersed dispersion was combined with 97.6 g of the above made CDD emulsion, 600 milliliters of water, and 95 milliliters of acetone and stirred at 50 rpm at the flask bottom overnight at 35°C.

The dispersion was then distilled in a rotary evaporator from 971 g to 87.2 g and rediluted with water to 400 g. 3.53 w/w% solids, 5.02 μ mean diameter, N_{AV} diameter 5.02 μ , W_{AV} diameter 5.09 μ , $\sigma = 0.437$, W_{AV}/N_{AV} diameter = 1.014, $n = 531$ (by light microscopy).

E. The Formation of Monodisperse 10 Micron Particles From Chlorododecane Swollen, 5 Micron Seed Particles: (X253-169).

A mixture of 150 milliliters of water, 100 g of 5% Vinol 523, 66.5 g of CDD swollen 5 Micron particles (section D above), 25 milliliters of filtered Ludox TM, 10 g of MAE-Adipate and 26.25 milliliters of 2.5 w/w% $K_2Cr_2O_7$ was adjusted to pH 4, using 1 normal hydrochloric acid. To this was added, 80 g of undistilled styrene and 4.0 g of benzoyl peroxide (peroxide totally dissolved). The total charge was placed in the flask and stirred at 30°C for 3 h at 250 rpm. The bath temperature was then raised to 60°C and the flask evacuated as before. The contents were stirred overnight, at 60°C, at 100 rpm, at the liquid:liquid interface (N_2 bleed). 23.37 w/w% solids, 9.91 μ mean diameter, N_{AV} diameter 9.91 μ , W_{AV} diameter 10.1 μ , $s = 0.958$, W_{AV}/N_{AV} diameter = 1.016, $n = 733$ (by light microscopy). 

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