

Effects of Silica Additive Concentration on Toner Adhesion, Cohesion, Transfer, and Image Quality

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This article discusses the effect of silica concentration on transfer of nominal 8.5 μm diameter surface-treated toners, with the silica concentration on the surface of the toner varying between 0 and 2% by weight of toner. In essence, it was found that, while transfer efficiency increased with increasing silica concentration, resolution decreased and dot structure after transfer was degraded. Toner adhesion measurements, performed using an ultracentrifuge, were found to correlate well with the transfer efficiency measurements. Analysis of the results suggests that the adhesion and cohesion of toner is dominated by van der Waals interactions. However, electrostatic forces associated with the charge on the toner become more significant with increasing silica concentration with the two types of interactions becoming comparable when the silica concentration reached 2%.

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Introduction

It is well established that the adhesional properties of toner particles affect transfer.^{1–3} Numerous methods have been employed to reduce toner-to-photoconductor adhesion in order to both improve transfer and facilitate cleaning. For example, surface treatments such as zinc stearate⁴ and Teflon have been demonstrated to significantly reduce toner adhesion.⁵ In two component developer systems, addition of third-component particulate addenda to the toners have shown marked effects on toner adhesion and improved the toner flow as well.^{6,7} Third-component addenda such as silica⁸ are a particularly efficient means to reduce toner adhesion both to itself and to photoconductors. Indeed, over the past few years, the use of particulate addenda has enabled the mean volume weighted average diameter of toner particles in commercially available electrophotography to decrease from about 12 μm to approximately 8.5 μm . Although the mechanism is not fully understood, it has been shown that particles having diameters in the range of tens of nanometers located on the surface of the toner particles affects the adhesive forces to non-toner surfaces and the cohesive forces between toner particles. The mechanism is presumably by the particulate addenda serving as asperities that reduce adhesion by roughening the surface, preventing intimate contact between the toner and the adherent surface or other toner particles.

The reduction of cohesion between toner particles can introduce new problems during transfer. As the images,

comprised of collections of charged toner particles, are transferred to the receiver, the repulsive electrostatic forces between toner particles can cause the images to fly apart. This effect is most severe in halftone dot images where the halftone dots literally can explode once they leave the stabilizing influence of the latent image charge pattern in the photoconductor. While dot explosions can occur in non-treated toner systems, Rimai and Sreekumar⁹ have observed that the use of submicrometer particulate addenda can aggravate the dot explosion problem, presumably by reducing the cohesion between toner particles and thereby accentuating the electrostatic repulsion between those particles. Alternatively, Tombs has proposed¹⁰ that when transfer is accomplished using an electrically biased transfer nip, dot explosion may be caused by transfer of some of the toner particles and halftone dots across the air gap in the prenip region due to high electrostatic fields. The surface forces must overwhelm the electrostatic repulsion between the like sign charged toner particles in order to keep the dots from exploding.

Turning now to the physics of adhesion, the adhesion of particles to a compliant substrate such as polyurethane is well described¹¹ by the JKR theory of adhesion.¹² According to that theory, the force F_S needed to remove a particle of radius R from a substrate is given by

$$F_S = -\frac{3}{2} w_A \pi R \quad (1)$$

where w_A is the thermodynamic work of adhesion and is related to the surface energies γ_p and γ_s of the particle and substrate, respectively, as well as their interfacial energy γ_{ps} by

$$w_A = \gamma_p + \gamma_s - \gamma_{ps} \quad (2)$$

It is apparent from Eq. 1 that the JKR theory predicts that the force needed to remove a particle from a sub-

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strate is independent of the Young's modulus of the substrate. Yet experimentally, the forces depend on the moduli of the substrate. The role of the elastic modulus in controlling particle adhesion can be understood by recognizing that particles are not perfect spheres as required by the JKR theory. Rather, they have asperities, and as shown by Fuller and Tabor,¹³ and more recently by Schaefer and coworkers,¹⁴ the engulfment of the asperities into the substrate governs the removal force. Soft photoconductors impede transfer by promoting particle engulfment, as discussed by Mastrangelo. This effectively serves to diminish the beneficial effect of the silica. Accordingly, the amount of silica, which effectively serves as asperities on the surface of a toner particle, should significantly affect the size of the removal force, especially for photoconductors that do not show substantial particle engulfment. In principle then, the addition of silica should facilitate transfer. However, as previously shown,⁹ the addition of submicrometer addenda can also enhance dot explosion. Indeed, dot explosion can occur whether due to the reduced adhesion permitting toner particles to transfer in the prenip region, or simply to a decrease in the interparticle cohesiveness.

The purpose of this study is to address several questions relevant to transfer. Among these questions are:

1. Is the use of particulate addenda really necessary?
2. How does the amount of the surface treatment affect transfer?
3. Does the amount of surface treatment affect resolution or dot integrity?
4. How large are the forces holding the toner particles to the photoconductor? Are these forces predominately due to van der Waals or electrostatic interactions?
5. Can a sufficiently large electrostatic field be exerted on toner particles and image structures, such as halftone dots, to allow them to jump across air gaps in the prenip region?

These questions were addressed in this study using image quality attributes as well as more fundamental measurements including transfer efficiency metrics and adhesion-force measurements.

Experiment

In this study, the transfer efficiency (percent of toner transferred divided by the amount of residual toner the photoconductor plus the amount of toner transferred), dot structure, and resolution of electrostatically transferred images were determined for a series of nominal 8.5 μm volume averaged diameter ground, cyan, toner particles. In addition, the force needed to remove the particles from a photoconductor was measured using a Beckman LM 70 ultracentrifuge.

Two series of toners were used in this study. The first consisted of a ground polyester with between 0% and 2% Aerosil R972 (produced by Degussa, Inc., <http://www.degussa.com>) silica particles, by weight, added to the surface of the toner particles. These particles have an average diameter, as reported by DeGussa, of approximately 16 nm although SEM micrographs show agglomerates in the range of 60 nm. The second series was quite similar except the toner particles also contained a silicone release agent. The volume-weighted average diameter of the toner, as determined using a Coulter Multisizer, was approximately 8.6 μm for the toner without the silicone additive and approximately 8.1 μm for the silicone-containing toner.

An electrophotographic developer was created by mixing the toner with a carrier comprising hard ferrite particles. The carrier particles had a volume-weighted diameter of approximately 30 μm . The initial toner concentration in the developer was approximately 6%. The toner charge was determined using an apparatus containing two planar electrodes spaced approximately 1 cm apart. Approximately 0.1 g of developer was deposited on one electrode, located above, but in close proximity to, a donut-shaped segmented series of magnets with alternating polarity. An electrometer was connected to the upper electrode. The electrodes were biased in such a manner as to attract the toner to the upper electrode as the magnets rotated, thereby simulating electrophotographic development. After all the toner was stripped from the developer, the charge on the upper electrode was determined and the mass of the toner giving rise to that charge was measured. This technique is more fully described elsewhere.¹⁵ The toner charge-to-mass ratio was found to be approximately $-37 \pm 3 \text{ mC/g}$ for each of the toners.

Twelve grams of developer were loaded into a sumpleless development station comprising a rotating core of alternating pole magnets and a concentric stainless steel shell. This type of station was chosen because it allowed small amounts of developer to be used, and avoided variations in the toner concentration and charge-to-mass ratio associated with larger, more conventional stations. Development was performed using the so-called "SPD" technique, as discussed by Miskinis.¹⁶ A commercially available organic photoconductor was initially charged to a predetermined negative potential using a grid-controlled DC corona charger and an electrostatic latent image formed by contact-exposing the photoconductor using a test target. Toner was deposited using discharged area development. The test target contained a series of continuous-tone neutral density steps, a 150-line rule 30% dot halftone pattern, and a resolution chart. The photoconductor was then passed over the development station where toner was deposited on the photoconductor in an image-wise fashion. In order to avoid complications associated with receiver variations, the toner was electrostatically transferred directly to a biased transfer roller having a resistivity of the order of $10^9 \Omega\cdot\text{cm}$. The speed of the photoconductor during the transfer process was approximately 2.5 cm/s. The width of the transfer nip formed between the transfer roller and the photoconductor was approximately 3 mm. Transfer voltages ranged between 500 and 2,500 V.

Transfer efficiency was measured using transmission densitometry for toned optical densities on the photoconductor between 0.1 and 1.0, using an X-Rite model 310 densitometer with Status A filters. The average transfer efficiency (determined by measuring the transmission density of the transferred image and dividing by the sum of the transmission densities of the transferred and residual densities) over the range of optical densities was determined as a function of voltage applied to the transfer roller. The conducting layer of the photoconductor was grounded and the maximum transfer voltage applied was 2500 V. The transfer efficiency increased with applied transfer voltage over the entire 0–2500 V range. The voltage, $V_{90\%}$, at which the average transfer efficiency exceeded 90% was then determined for each series of toners containing the various levels of silica mentioned above. In addition the average transfer efficiency over both the range of toned optical densities and the range of voltages between $V_{80\%}$ and 2500 V was also determined. This averaging proce-

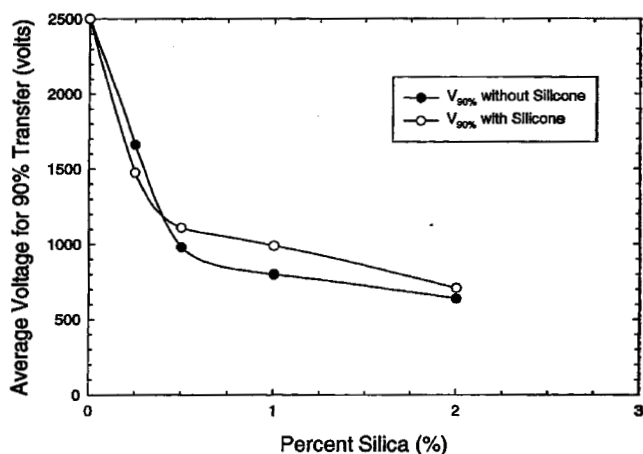


Figure 1. Average voltage for 90% transfer versus % silica addenda with (open symbols) and without (solid symbols) silicone adhesion additive.

ture was carried out using numerical integration of curves fit to the data over the aforementioned range. This method of averaging provides a measure of the “robustness” of the toner to transfer variations. Finally, the resolution and dot integrity were determined both before and after transfer at an applied transfer voltage of 1500 V. Each of these measurements was performed with and without the addition of a silicone release agent to the toner to promote release from the photoconductor.

The adhesion of the toner particles to the photoconductor was determined by developing low density patches and removing the toner in an ultracentrifuge capable of spinning at 70,000 rpm. The procedure is as follows. The initial number of particles on the photoconductor was established by counting, using suitable image analysis software. Next, the photoconductor was placed in the centrifuge and spun at the desired speed. The sample was then removed and the remaining particles counted. This process was repeated for a series of increasing speeds. Centrifugation was performed in a low vacuum of approximately 10^{-2} torr (roughing pump vacuum). The initial coverage was 0.5 density as measured in transmission corresponding to a 50–60% surface coverage by the particles.

Results

The applied voltage, $V_{90\%}$, where the transfer efficiency exceeds 90%, as a function of silica concentration, is shown in Fig. 1 for the toners with and without the silicone additive. As can be seen, the voltage necessary for 90% transfer drops rapidly with increasing silica concentration for both toners. However, the effect levels off for silica concentrations of more than 0.5% with the effect for 1% and 2% silica only incrementally larger than that at 0.5%. Moreover, it can be seen that the use of a silicone additive in conjunction with the silica not only does not result in a further reduction in the voltage needed for 90% transfer but actually reduced the effect of the silica treatment applied without the silicone additive. The silicone additive may be acting as a liquid bridge that actually reduces the efficiency of the silica in separating the toner from the surface. Further studies are needed to understand this issue in more detail.

Figure 2 shows the integrated averaged transfer efficiency above 80% for each of the two silica-treated toner series, normalized to the performance of the toner with-

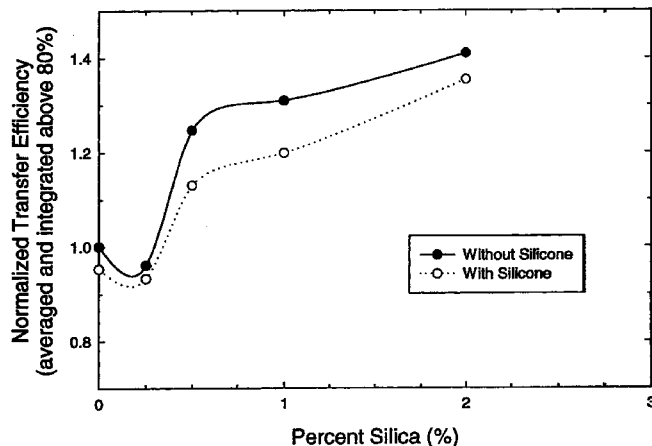
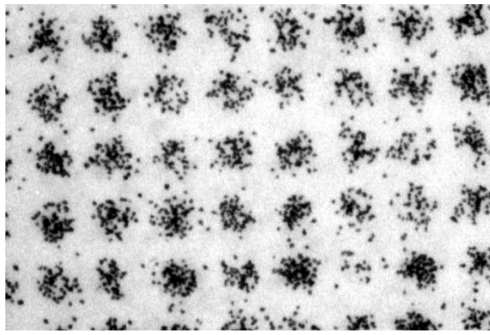


Figure 2. Normalized density averaged transfer efficiency integrated over voltage from the voltage needed for 80% transfer to the upper bound of 2500 V with (open symbols) and without (solid symbols) silicone adhesion additive as a function of silica content. Normalization is with respect to the integrated density averaged transfer efficiency for the toner without silica addenda and without silicone adhesion additive.

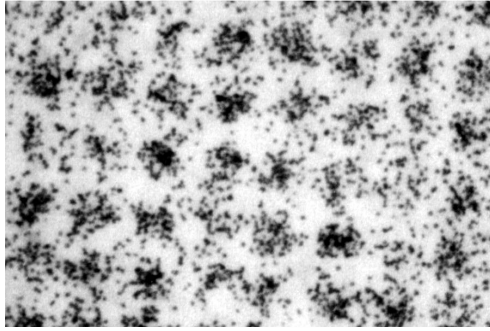
out silica or silicone additive. Solid symbols show the results without silicone additive while open symbols show the results when silicone additive is present. The integrated averaged transfer efficiency is determined by first averaging the measured transfer efficiency over a range of 10 density steps from 0.1 to 1.0 for each voltage from 0 to 2500 V in steps of about 200 V. A smooth curve is then fit to the average transfer efficiency as a function of voltage and this curve is integrated from the lowest voltage that produces an 80% average transfer efficiency to the maximum voltage examined, 2500 V. In this way, systems with sharply spiked average transfer efficiency versus applied transfer voltage will show a lower voltage integrated average and can be distinguished from more robust systems showing a broad maximum. It can be seen from these figures that the integrated average transfer efficiency, a measure of transfer robustness, despite an initial decrease, generally improves with increasing silica concentration, but at a decreasing rate once the silica concentration exceeds 0.5% by weight of toner. These results are consistent with the voltage results shown in Fig. 1. Also in agreement with Fig. 1, the data shows that the presence of the silicone additive reduced the integrated average transfer for all conditions.

From the data presented thus far, it may appear that the process of transferring toner can be made more robust, although perhaps reaching a point of diminishing returns, simply by increasing the concentration of silica on the toner particles. However, this is not quite correct. Transfer is not just the removal of toner from a photoconductor accompanied by a deposition of the toner on a receiver. Rather, it is that process with the additional constraint that image disruption must be minimized. Image disruption was characterized in this study by microscopically examining the halftone dot pattern and resolution chart before and after transfer.

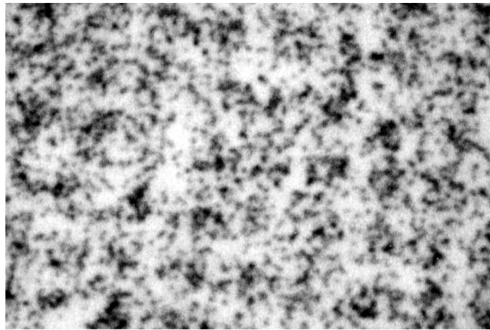
In this study the effect of the silica concentration on image disruption was determined by qualitatively examining the structure of the halftone dots and measuring the resolution in line pairs per millimeter before and after transferring the image using a 1500 V trans-



(A)



(B)



(C)

Figure 3. Halftone dot patterns after transfer for the silicone-containing toner with 0% 3(A), 0.5% 3(B), and 2.0% 3(C) silica.

fer bias. Before transfer, a resolution between 14 and 16 line pairs per millimeter was obtained. Moreover, the dots were well formed, exhibited minimal satellite formation, and, in general, appeared to reproduce the test target quite well. However, it was found that after transfer, the dots were disrupted, with the amount of disruption and the number of satellites increasing monotonically with increasing silica concentration. This effect is shown in Figs. 3A-3C for the silicone-containing toner with 0, 0.5, and 2.0% silica, respectively. As can be seen in Fig. 3(A), in the absence of silica, the halftone dots are still fairly well formed after transfer, although disruption and the presence of satellite toner particles are obvious. Increasing the amount of silica to 0.5% clearly resulted in significantly more dot disruption and satellite formation, as shown in Fig. 3(B). Upon further increasing the amount of silica to 2.0%, the dot structure has been nearly obliterated by disruption of the dots during transfer, as illustrated by Fig. 3(C). Resolution also tends to decrease with increasing silica concentration. This effect is shown in Fig. 4 for toners both without and with the silicone additive. The reduc-

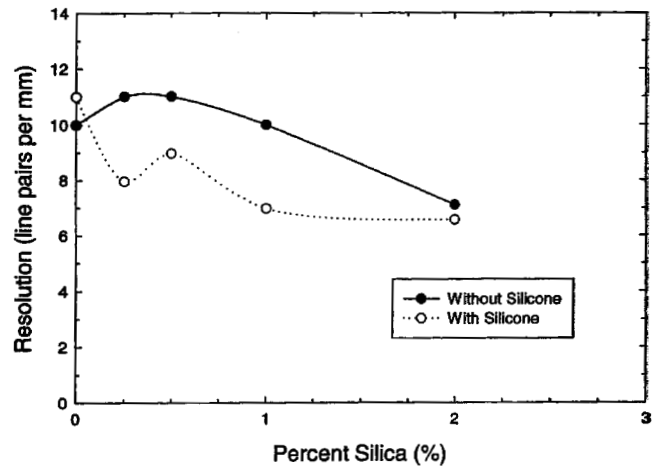


Figure 4. Resolution as a function of silica concentration for the toner with (open symbols) and without (solid symbols) silicone.

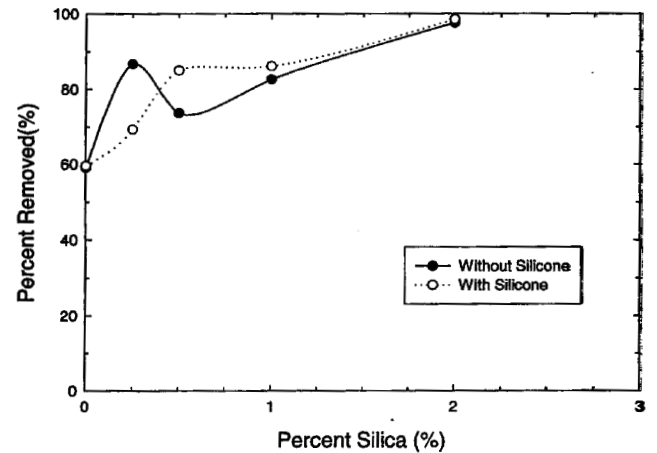


Figure 5. The percent of toner removed from the photoconductor at 70,000 rpm as a function of silica concentration, with (open symbols) and without (solid symbols) silicone.

tion in resolution is more severe for the toner system containing the silicone adhesion additive.

As indicated earlier, an ultracentrifuge was used to characterize the toner-to-photoconductor adhesion as a function of the weight percentage of silica. Figure 5 reports the percentages of toner with silicone (open circles) and without silicone (solid circles), that were removed from the photoconductor at 70,000 rpm for the five levels of silica examined. With the exception of an initial increase at 0.25% silica, the percent removed increases monotonically with increasing silica content, asymptotically approaching 100% removal at or around 2% silica by weight. The initial increase at 0.25% silica is viewed as an anomalous point that is correlated with the atypically smooth surface morphology of this particular toner mixture when examined by scanning electron microscopy (SEM). The presence of silicone in the toner mixtures showed no further reduction in the adhesion force, even in the absence of the silica. These results suggest that while the presence of silica significantly reduces the adhesional forces, the presence of silicone does not. The behavior of the toner-silica mixtures determined

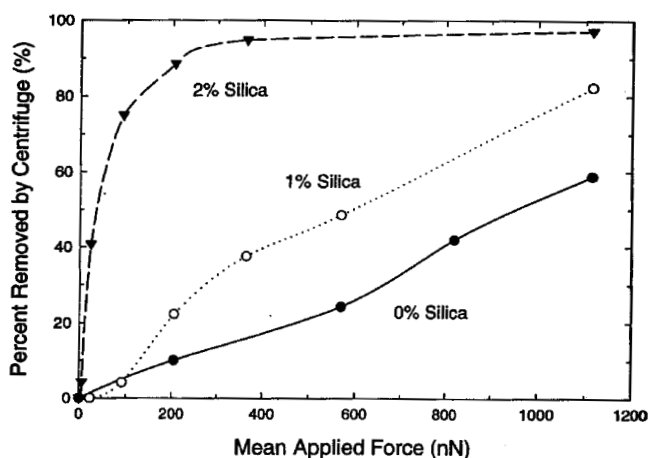


Figure 6. The percent removed by centrifuge as a function of removal force for three levels of silica: 0% (solid circles); 1% (open circles); and 2% (solid triangles); for toner without silicone adhesion additive.

by mechanical measurements in the ultracentrifuge are essentially unchanged by the presence of silicone in contrast with the systematic changes in the adhesional behaviors inferred from the transfer measurements mentioned earlier.

Figure 6 shows the percent of the toner (without silicone) removed from the photoconductor as a function of the mean applied force produced by different centrifuge speeds. Data for three silica concentrations of 0%, 1%, and 2% are shown. The highest force corresponds to 70,000 rpm so that the end points of the curves in Fig. 6 are the 1st, 3rd, and 5th data points from Fig. 5. As can be seen, the general shapes of the curves gradually change for increases in silica concentration. Without silica, the percent removed is nearly linear with the mean applied force over the range investigated. There is no tendency to reach an asymptote. With 2% silica, the curve rises steeply and then curves to asymptotically approach 100% particle removal as the mean applied force is increased. The result for 1% silica is intermediate following the 0% result initially and then rising as the centrifugation speed and hence mean force is increased. Because there is a distribution in toner sizes, the larger particles would be removed first. If 1% is insufficient to coat all the particles completely, this could be a rationalization of the behavior observed for 1% silica.

The mean applied forces reported above were calculated by assuming that the particles were spherical polyester toner with a radius of 4 μm and a mass density of 1.2 g/cm³. The removal force, P_s , estimated at the 50% removal point, was determined to be 970 nN, 580 nN, and 39 nN for the 0%, 1%, and 2% silica-coated toner particles, respectively.

Analysis

As shown in the previous section, transfer efficiency improves with increasing silica concentration while dot integrity and resolution are both degraded. Moreover, the force needed to detach the toner from the photoconductor also decreases with increasing silica concentration.

As is well known, there is much debate in the literature as to whether the force of adhesion of toner particles to a photoconductor arises from surface forces

such as those due to van der Waals interactions or electrostatic forces from a toner particle seeing its image charge. Although the resolution of that debate is well beyond the scope of this article, it is worthwhile to estimate to adhesional forces arising from both mechanisms.

Let us first assume that the uncoated toner particles are spheres with a radius of approximately 4 μm . The particle removal force, F_s , can be calculated from JKR theory using Eq. 1. Assuming a reasonable value of $w_A = 0.05 \text{ J/m}^2$, the particle removal force is estimated to be 943 nN. In light of the approximations made, this value is in reasonable agreement with the experimentally obtained value of 970 nN.

Estimates of the electrostatic contribution to particle adhesion are not as simple to make, owing to polarization and charge distribution effects. Although details of this problem are presented elsewhere,^{17,18} these issues will be examined briefly. Assuming that an irregularly shaped toner particle can be approximated as a dielectric sphere of radius R having a charge q uniformly distributed over its surface, the electrostatic image force of attraction, F_I , between that particle and a conducting substrate is given by

$$F_I = \alpha \frac{q^2}{4\pi\epsilon_0(2R)^2}. \quad (3)$$

When $\kappa = 4$, representing a value of the dielectric constant appropriate for toners, the value¹⁹ of α is 1.9. In the present situation, however, the toner is not adhered to a conductor. Rather, the photoconductor comprises an organic binder whose dielectric constant is similar to that of the toner. The problem of a charged dielectric particle adhering to a dielectric substrate has not been solved. Moreover, even for the case of a spherical particle in contact with a plane, there will be a finite contact area associated with deformations of the contacting materials due to adhesion-induced stresses. For polymeric materials, such deformations can be quite large, with the contact radius being of the order of 10% of the particle radius.²⁰ For irregularly shaped toner particles, independent sets of measurements by Eklund and co-workers²¹ and by Bowen and co-workers²² both report contact areas being of the order of 10% of the projected cross-sectional area of the toner particles. In the case where the dielectric constants of the two contacting materials are equal and there are no air gaps, $\alpha = 1.0$. Presumably, the present case would lie between these extremes. Using the values of charge to mass reported earlier, ($37 \pm 3 \mu\text{C/g}$, $\rho = 1.2 \text{ g/cm}^3$), it is then calculated that F_I would be in the range of 20 to 40 nN for the present toner particles. This value is far less than the measured force needed for detachment shown in Fig. 6.

However, as is discussed by Hays, the charge on a toner particle may not be uniformly distributed over its surface. In that instance, the electrostatic contribution to the force of adhesion, F_E , is related to a surface charge density, σ , and the actual area of contact between the particle and substrate, and A_C , by

$$F_E = \frac{\sigma^2 A_C}{2\epsilon_0}. \quad (4)$$

Using Eq. 4 and assuming that the contact area is approximately 10% of the cross-sectional area, one could simply solve for the charge density needed to give the measured removal force. Upon substitution, one finds that $\sigma = 1.85 \times 10^{-3} \text{ coul/m}^2$. Using a parallel plate capacitor

approximation, one finds that this charge density would result in an electric field of approximately 2.1×10^8 V/m. This would clearly exceed the Paschen limit in air and would result in dielectric breakdown as the toner particle approached the photoconductor during development.^{23,24}

Alternatively, it is worthwhile to estimate F_E within the confines of the Paschen limit. Again, this is not simple to do, as the Paschen limit decreases with increasing air gap. Assuming that the particle can get to within 10 μm of the photoconductor without discharging, the supportable field would be approximately 3.5×10^7 V/m. The attainable surface charge density would then be of the order of 3×10^{-4} coul/m² and F_E would be of the order of 30 nN, which is consistent with estimates of F_I . Therefore, the force of adhesion due to the presence of localized charged patches is much smaller than those contributions attributed to van der Waals interactions.

The electric field needed to detach the particle from the photoconductor can also be estimated. As discussed by Hays, the force needed to detach a particle from a substrate F_D is given by

$$F_D = \beta q E_D - \gamma (2R)^2 E_D^2 \quad (5)$$

where E_D is the electric field needed to detach the particle and β and γ are the polarization correction factors with values approximately 1.6 and 0.063 for a dielectric constant of $\kappa = 4$. Following Hays,¹⁸ it is assumed that detachment occurs when the electrostatic detachment force equals or exceeds the forces driving attachment,

$$F_D - F_A \geq 0 \quad (6)$$

where F_A represents the total force adhering the toner to the photoconductor. It should be noted that Hays' assumption that $F_A = F_I$ or $F_A = F_E$ is not strictly correct due to the compliance of the contacting materials. To correctly solve the problem, one needs to include the effects of mechanical deformations of the particle and substrate, along with the forces that arise from works of adhesion, as discussed by Johnson and co-workers.¹² Naturally, these deformations will impact the solutions to the image charge and removal force calculations due to the substantial changes in geometry that can be caused by surface forces. However, the present approximation is frequently used in the literature and should suffice for the present calculations.

As before, the contributions due to polarization are difficult to precisely determine because the dielectric constant of the particle and substrate, which are in intimate contact, are essentially the same. However, estimates can still be made. Following Hays, it was assumed that the second term on the right-hand side of Eq. 5 is small and can be neglected. If polarization effects are then ignored ($\alpha = \beta = 1$), using the experimental removal force of 970 nN suggests that E_D takes on a value in the neighborhood of 8×10^7 V/m, which is too large a field to sustain in air. The detachment field would be even larger if polarization were significant. Accordingly, it should not be possible to electrostatically detach this toner from the photoconductor without balancing surface forces, as discussed in Ref. However, the ability of toner particles to jump air gaps is generally required, as discussed earlier, in order to achieve good transfer due to tent poling effects such as those arising from receiver roughness, toner stack height variations, toner particle-size polydispersity, etc. Therefore, the transfer efficiency of such a toner that cannot traverse an air gap is generally relatively poor, which was indeed, observed in earlier studies.³

Evaluating the detailed physics of the toner-to-photoconductor interaction requires some clarifying assumptions. First, assume that the toner is held to the photoconductor principally by relatively short-range van der Waals forces and that the role of the silica is to physically separate the toner from the photoconductor. A precise determination of the effect of the silica on the toner detachment forces will require a detailed knowledge of how the toner-to-photoconductor contact deforms under the influence of the surface forces. This depends on a number of factors such as the size and distribution of the silica, the shape of the toner, the range of the interactions, and the compliance of the materials. However, one may still make some order of magnitude estimates of the detachment forces of the silica-treated toner particles.

The percent of the surface coverage of the toner by the silica can be estimated by assuming both the toner and silica are spherical. For the purpose of this calculation, assume the weight fraction of the silica is 1%. The primary particle size of the silica is 16 nm diameter but it is clustered into particles of 60 nm average diameter, also assumed to be spherical. Using $\rho = 1.75$ g/cm³ as the mass density of the silica and $\rho = 1.2$ g/cm³ as the mass density of the toner, and knowing that the toner has a mean diameter of 8 μm , the fraction of the surface area of the toner covered by silica clusters is 25%. For 2% silica by weight, the area coverage calculated is 50%. These estimates are consistent with SEM micrographs of the toner.

Again, assuming a spherical toner particle, the contact radius a_{JKR} , estimated using JKR theory, is given by

$$a_{JKR} = \left(\frac{6\pi w_A R^2}{E} \right)^{1/3} \quad (7)$$

where E is the Young's modulus of polyester,²⁵ approximately 3 GPa. In the absence of silica, $a_{JKR} = 196$ nm. Assuming a similar contact region exists when silica is present, it is then estimated that approximately 10 silica particles would be in contact with the photoconductor when the silica concentration is 2%. The separation force F_S' is then given by

$$F_S' = n \frac{3}{2} w_A \pi r \quad (8)$$

where $n = 10$ is the number of contacts and $r = 30$ nm is the radius of the silica particle clusters. Assuming that the work of adhesion for silica to photoconductor remains at $w_A = 0.05$ J/m², upon substitution it is found that $F_S' \approx 70$ nN. The experimentally obtained value of F_S' was approximately 39 nN. In view of the approximations made, the experimentally obtained value is in reasonable agreement with the estimated value. It is interesting to note that these values are also close to the estimated contributions of the electrostatic image charges to the total force of adhesion, suggesting that, at this level of silica treatment, both van der Waals and electrostatic interactions are significant factors in determining the total force holding the toner to the photoconductor. The applied electrostatic field needed to effect separation of the toner from the photoconductor was estimated, using Eq. 5, to be in the range of 3 to 6×10^6 V/m, which is readily obtainable. Accordingly, transfer efficiency should be quite good in the presence of the silica particles in agreement with the experimental observations.

The detachment force for the toner particles containing 1% silica was determined by the centrifuge experiments to be approximately 580 nN, or about an order of magnitude larger than the estimated image charge contributions. In this case, the detachment field was calculated to be approximately 4.9×10^7 V/m, ignoring polarization effects. This result suggests that transfer of the toner across an air gap would not be feasible even with this level of silica present. Rather, it is necessary for the receiver to contact the toner, thereby supplementing the electrostatic transfer forces with surface forces.

The observed losses in dot integrity and resolution can also be explained in terms of decreasing adhesion. As discussed previously, the highly charged toner particles would tend to repel one another rather than exist as a coherent mass, as in a dot or alpha-numeric character. However, at short ranges,²⁶ i.e., less than 30 nm, the attractive van der Waals forces dominate over the Coulombic repulsion stabilizing the images during transfer. While offering beneficial effects for transfer by reducing the toner-to-photoconductor adhesion, the presence of the nanometer-size silica particles reduces the interparticle cohesion as well, thereby increasing the propensity for clusters of toner particles comprising the images to fly apart during transfer. Indeed, increases in toner cohesion with aging, attributed to the silica being engulfed by the toner particles and thereby losing their spacer effect, was reported by Ott.⁸

Conclusions

It was found that the transfer efficiency of an electrophotographic toner increases with an increasing concentration of nanometer-size silica particles on the surface of the toner. However, accompanying the improved transfer efficiency is a loss of resolution and a decrease in dot integrity. These results track with a decrease in the adhesion of the toner to the photoconductor, as measured with an ultracentrifuge. The size of the removal forces measured appear consistent with estimates that assume van der Waals interactions, but, in general, appear too large to be attributed to electrostatic interactions alone. As the concentration of silica approaches 2%, the contributions

of the van der Waals and the electrostatic forces become comparable in magnitude. Δ

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