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Comparison of Toner Adhesion Theories

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Abstract. *Recent measurements of toner adhesion have been reported [Dejesus et al., J. Imag. Sci. Technol.* **52***, 010503 (2008)] in which the ground plane was separated from the charged toner particles by a thin dielectric coating of varying thickness (0.8, 4.5, 9, and 22 μm thick), which is less than and approximately equal to the diameter of the toner particles used in the experiment, 7.1 μm. It is claimed that such data can be understood only in terms of an adhesion theory based on van der Waals adhesion. It is demonstrated in this article that the data are, in fact, consistent with the Proximity Theory of toner adhesion, which is an electrostatic theory of toner adhesion that assumes that there is electrostatic adhesion at every contact point due to the discreteness of charge. Combining this result with a comparison of theories of toner adhesion with data showing the effects on toner adhesion of changing the toner charge-to-mass ratio and the extraparticulate concentration leads to the conclusion that the Proximity Force dominates toner adhesion.*
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INTRODUCTION

Toner adhesion is of enormous practical importance in electrophotography. Overcoming toner adhesion is crucial for the development, transfer, and cleaning subsystems.[1] In fact, it has recently been argued that a key aspect of the invention of new electrophotographic development systems has been the identification of means of overcoming toner adhesion.[2] For example,

(1) the invention of the magnetic brush development system led to solid area and high speed development. Adhesion is overcome by using three-body contact events which cancel the adhesion of the toner to the carrier particles by an approximately equal adhesion of the toner to the photoreceptor.[1]
(2) The invention of Canon's magnetic monocomponent development system led to small, low cost copiers and printers and the cartridge concept. Adhesion was overcome by lowering the toner's charge-to-mass ratio and using ac electric fields in the development zone.[1]
(3) The invention of Xerox's iGen3 technology led to single transfer, high speed, offset quality printing. Toner adhesion was reduced by applying ac voltages to thin wires adjacent to the monocomponent roller surface.[3]
(4) The invention of Aetas' dc-jump nonmagnetic, monocomponent development system has led to the design of a desk-top, small size, low cost color electrophotographic printer.[4]

Toner adhesion was overcome by reducing it by a factor of 10 compared to other commercially available toners by adjusting the concentration of extraparticulates to minimize contact points. Further reductions in toner adhesion may make viable direct marking technologies which offer the possibilities of even less expensive and smaller printers.[2]

Attempts to identify the dominant force of toner adhesion have been the subject of many papers, including this one. Three theories have been suggested. Rimai and co-workers have argued that van der Waals forces dominate toner adhesion. Hays and co-workers along with Lee have argued that toner adhesion is based on electrostatic forces associated with nonuniform charge "patches" on the toner. Schein and co-workers suggested the Proximity Theory of toner adhesion which takes into account, for the first time, the discrete nature of charge. There almost certainly are contributions from the mechanisms posited by all three theories to the actual toner adhesion. As Dejesus et al.[5] have recently emphasized, the issue is, which one dominates, because the control and reduction of adhesion has significant practical importance.

It is commonly agreed that the simple model of toner adhesion force F, based on the assumption that an irregularly shaped toner particle can be approximated as a dielectric sphere with the charge uniformly distributed over the surface,

$$F=\alpha\frac{1}{4\pi\varepsilon_0}\frac{Q^2}{4r^2} \tag{1}$$

is not correct because all measurements indicate that the values calculated from this equation are too small by large factors, between 7–47 among many published papers, according to Hays.[6] In Eq. (1), Q is the total charge, r is the toner radius, α is a correction factor that takes into account the dielectric constant K of the particle ($\alpha=1.9$ and 1.53 for $K=4$ and 3, respectively, as given in Ref. 7), and ε_0 is the permittivity of free space.

Recent measurements of toner adhesion have been reported by Dejesus et al.[5] in which toner particles were de-

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veloped onto a polycarbonate dielectric surface whose thickness was varied (0.8, 4.5, 9, and 22 μm) over a nickel ground plane. These thicknesses are less than or comparable to the diameter of the toner particles used, 7.1 μm. It is claimed that such data can only be understood in terms of an adhesion theory based on van der Waals adhesion. It is argued in Ref. 5 that any electrostatic adhesion theory fails because the adhesion is observed to be independent of the dielectric coating's thickness, which is associated with a change of the image charge position and therefore the electrostatic image force.

It is the purpose of this article to review the experimental results reported in Ref. 5 and to compare them with the three theories of toner adhesion, the van der Waals, charge patch, and Proximity Force theory. Combining this result with a comparison of the three theories of toner adhesion with data showing the effects on toner adhesion of changing the toner charge-to-mass ratio and the extraparticulate concentration leads to the conclusion that the Proximity Force dominates toner adhesion.

Excellent reviews of toner adhesion papers are available and the topic will be only briefly reviewed below. For a good historical discussion of adhesion models suggested prior to the introduction of the Proximity Theory, see Lee[8] or Feng and Hays.[9] For an in-depth discussion on the van der Waals theory of adhesion, see the book *Fundamentals of Particle Adhesion* by Rimai and Quesnel.[10] Discussions of the Proximity Theory are referenced below. In this article we focus on the technical issues raised by Dejesus et al.[5] Aspects of the Proximity Theory relevant to the Dejesus et al. paper are reviewed so that the reader can understand why it is suggested that Proximity Theory is consistent with the data given in Ref. 5; aspects of the Dejesus et al. experiment are also reviewed. A comparison of the adhesion theories and all relevant experiments are then summarized and our conclusions are drawn.

TONER ADHESION THEORIES

Charge Patch Theory

It has been known since the first measurements by Goel and Spencer[11] that the simple model of electrostatic toner adhesion, which assumes that a toner can be approximated by the charge being uniformly distributed around a spherical dielectric particle, Eq. (1) fails. The measured adhesion is at least one order of magnitude higher than this model predicts, as reviewed by Hays.[6]

In order to address this discrepancy, Lee[8] and Hays[6,9] suggested that the charge distribution on the toner particle is not uniform. Lee based his ideas on direct observations of the movement of toner particles. Hays quantified the nonuniformity using many different types of nonuniformities.[9] Perhaps best known is Hays' charge patch model,[6] which makes the assumption that the charges on the toner particle are on its high points. This was modeled by assuming the charges on the high points of the toner are on planes with an area much less than the actual area of the toner particle. The adhesion F_E was then calculated to be

$$F_E = \frac{Qf\sigma}{2\varepsilon_0}, \tag{2}$$

where Q is the total charge on the toner particle, f is the fractional area in contact with the substrate divided by the charged area on the toner, and σ is the total charge on the toner divided by the charged areas. By fitting the observed adhesion data to the theory, and assuming $f=0.2$, it was found that σ was in range of 0.5 to 5 mC/m^2.

This theory, based on nonuniformities of the charge distribution on the surface of a toner particle, is compelling and reasonable. By looking at a scanning electron microscopic picture of toner particle, e.g., Fig. 2.9 in Ref. 1, the high points are easily identified. Lee's direct observations[8] are convincing. But the issue is whether such nonuniformities are the source of the *dominant* force of toner adhesion. Based on Hays' quantitative estimates some problems have been identified. It was pointed out by Gady et al.[12] that such high values of surface charge density exceeds Paschen breakdown in air, i.e., such high charge densities will not be stable in normal air environment, but will be discharged as the toner approaches the photoreceptor. The electric field in air is $\sigma/2\varepsilon_0$. This equals 56 V/μm for 1 mC/m^2; it is 289 V/μm for $\sigma=5$ mC/m^2 which is needed to fit some of the data. It is known that air breaks down (Paschen breakdown) at electric fields of 3 V/μm for large gaps. At micron size air gaps this value can be considerably higher, 70 V/um,[13,14] but that is still smaller than the electric fields needed to fit the data with this model. Furthermore, in the author's opinion, the value of f (the ratio of the contact area to the charged area) that is assumed, 0.2, appears to be higher than reasonable. For example, a physical picture of $f=0.2$ is that there are five equal-area high points that are charged on a toner particle and only one makes contact with the ground plane. It is difficult to see how there are only five high points on a toner particle. But if a lower value of f is assumed, then the σ-value needed to fit the data with the charge patch theory will need to be even higher.

Furthermore, it was pointed out by Schein,[15] that such high values of surface charge density would also predict that the charge-to-mass (Q/M) ratio would not depend on toner concentration (the ratio of the mass of toner to the mass of the carrier beads), inconsistent with the universality observed behavior of toner-carrier mixtures. This prediction is a consequence of the experimental demonstration that the low density theory of toner charging (which assumes surface states on the toner and carrier exchange charge to equalize a surface Fermi level) is invalid, which was shown in a series of papers.[15–19] Only the high density theory, sometimes called the electric field of toner charging, is consistent with all of the available data. In this theory, toner particles charge until a material-dependent electric field, called the effective electric field, is reached at the interface of a toner and carrier particle.

By using the electric field theory of toner charging, it is shown in Ref. 15 that the charge patch theory predicts that the charge-to-mass (Q/M) ratio is independent of the toner concentration. This argument is quantified in Ref. 15. A qualitative description of the argument can be made in three sentences: (1) The contributions to the electric field at the contact point of a toner and carrier particle come from both the toner's charge and the carrier's charge. (2) The toner's Q/M dependence on toner concentration reflects the fact that as the number of toner particles increase on a carrier surface, the electric field due to the carrier particle increases (due to charge neutrality) so the electric field due to the toner particles (and consequently the toner charge) must decrease. (3) However, if the electric field due to toner is highly enhanced by the hypothesis of a charge patch, the electric field due to the toner overwhelms the electric field due to the carrier at their contact point and the normal Q/M dependence on toner concentration is no longer predicted, inconsistent with data.[15]

To the author's knowledge there is no discussion in the literature of the effect of extraparticulates on the charge patch theory. In the opinion of the author, the high points of the toner particles, which are assumed to be charged in the charge patch theory, will still be charged if extraparticulates are present. Therefore the charge patch theory predicts no dependence of toner adhesion on the surface concentration of extraparticulate, inconsistent with data (see below).

The charges in the charge patch theory reside on the top points of the toner particles, closest to the plane to which the toner adheres. In the opinion of the author the charges are therefore either in intimate contact with the plane or are spaced at most nm away if the charges are separated from the plane by the extraparticulates or toner surface roughness.

Van der Waals Forces

In a book and many papers (see Refs. 10, 12, and 20 among others) including the present one under discussion,[5] Rimai and co-workers have suggested that toner adhesion is dominated by van der Waals adhesion. The concept is that molecules in close contact across an interface interact by dipole–dipole interactions. These interactions can in principle deform a material around a point of contact. Assuming that a deformation occurs (quantified in the so-called JKR theory), the force of adhesion can be estimated[12] to be

$$F_{vdw} = 1.5\omega_A \pi R, \tag{3}$$

where ω_A is the thermodynamic work of adhesion (which does not vary by more than a factor of 4 among materials and is chosen in Ref. 12 to be $0.05\ \mathrm{J/m^2}$) and R is the effective radius of the asperities of the particle in contact with the plane. If silica particles are present on the toner then R is the effective radius of the asperities of the silica particles.

In many fields, van der Waals forces clearly dominate adhesion and "are frequently assumed to be the dominant mechanism by which particles adhere to subtracts" (p. 18 in Ref. 10). Almost surely, the adhesion of a bare toner particle is dominated by van der Waals adhesion. Especially interesting are published photomicrographs by Rimai's group[21–23] which show toner, without silica, deformed on the surface of a substrate after sitting for 7–10 days on the substrate.

Toner particles in electrophotography, however, are special: they are charged and are coated with extraparticulates such as silica nanoparticles with diameters of about 10 nm. The charge introduces electrostatic forces. The presence of silica changes the area of contact.

The effect of silica on a model of adhesion based on van der Waals forces does not appear to be understood. In an attempt to take into account the presence of the silica nanoparticles, an estimate was made[12] of the contact radius of a particular toner without silica (196 nm) using JKR theory and then it was assumed a similar contact region exists when silica is present (and R is assumed to be the radius of the silica particles). Such a procedure predicts that the adhesion should increase as the silica concentration increases (because the number of silica per unit area increases), inconsistent with the data in the original paper in which this was suggested[12] and other papers in the literature.[24,25]

Furthermore, it seems to the present author that this procedure overestimates the contact area when silica is present because the establishment of the contact area requires actual contact according to JKR theory, which does not occur when silica is present. In Ref. 20 the data clearly show again that more silica leads to lower adhesion. In Ref. 20 it is stated "Although the decrease in detachment force with increased silica concentration has been well established, the reason for this effect is not presently well understood." In Ref. 5 it is estimated that the van der Waals force for the particle under study is 1300 nN without silica and "while a detailed explanation of the effect of the…silica concentration on adhesion is beyond the scope of this article…it suffices to say that the detachment forces…are typically several hundred nanonewtons" which is taken from data, not theory, in Ref. 26. In this reference, the authors are puzzled and challenged by the effect of silica on adhesion. In the Introduction they say, "The adhesion of nonideal (i.e., not spherical) particles is far more complicated…confounding the role of the heights and numbers of asperities with the curvature of the particle has proved to be a daunting task. Moreover, specific sizes and concentrations of (silica) are often affixed to the surface of the particles to control adhesion and flow." (Parentheses added by present author.) They use an estimate of the contact area without silica present to estimate the number silica contact points (p. 734 in Ref. 26) in their main attempt to understand data which, as pointed out above, is inconsistent with the observation that increased silica leads to decreased adhesion. As pointed by the authors of Ref. 26 and Lee,[8] using spherical toner particles (i.e., toner particles with roughness less than the diameter of the silica) might be helpful in sorting out the effect of silica on van der Waals adhesion.

Proximity Force

In the late 1990s, Aetas Corporation[4] set for itself the goal of building the smallest, lowest cost, color, electrophotographic printer. It was clear from the onset that this required accu-

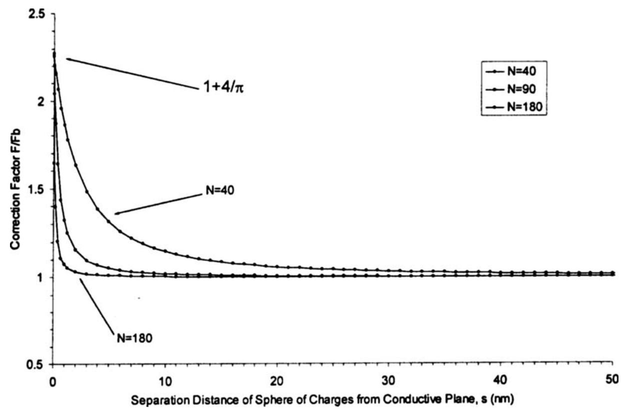

Figure 1. Correction factor[27] to the electrostatic force, normalized to the usual image force [Eq. (1) with $\alpha=1$] vs separation distance s between the sphere and the conductive plane, and N, the number of annuli. The three curves are for $N=40$, 90, and 180. The proximity force is the force in excess of the Eq. (1), which is $4/\pi$ at zero separation. Note all of the curves, independent of the assumed value of N extrapolate to this value, consistent with analytical results. (Reprinted from the Journal of Electrostatics, Vol. 61, with permission from Elsevier Ltd., copyright 2004.)

mulation of toner on the photoreceptor (see Ref. 4 for a detailed explanation) which could only be achieved if the electric fields of the latent image could overcome toner adhesion. To accomplish this it can be shown that toner adhesion would have to be reduced by at least a factor of 10 compared to published adhesion measurements.[6] In order to better understand the charge patch theory, Czarnecki and Schein undertook a theoretical calculation of the electrostatic forces between a sphere with a uniform but *discrete* distribution of charges on the surface and a ground plane. Out of these calculations, the proximity force unexpectedly emerged.[27,28]

The Proximity Force is due the discreteness of charge, which is the way nature gives us charge: one electron has 1.6×10^{-19} coulombs of charge. The magnitude of the proximity force can be calculated approximately: assume one electron is spaced 1 Å from the surface of ground plane. This force, as realized by many, and published by Schmidlin,[29] is on the order of the observed toner adhesion force. But one quickly realizes that such a model is extremely sensitive to the assumed distance between the charge and the ground plane, and it did not lead to a theory of toner adhesion. (Also, as pointed out in Ref. 5, if there is no change in dielectric, no image charges or adhesion force are predicted.) What was done in the Proximity Theory[27,28] was to place the discrete charges uniformly around a sphere in uniformly distributed annuli and to calculate the total force by adding all of the forces between every charge and every image charge. It became clear, both analytically and by computer calculation, that the total force obtained was independent of almost all assumptions about the charge distribution and was different and larger than Eq. (1) by a factor of $(1+4/\pi)$ (see Figure 1). The total adhesion force was found to be equal to two terms: (1) the usual electrostatic force (as though all the charge was placed in the center of the sphere), i.e, Eq. (1) with $\alpha=1$ plus (2) an additional force, the $4/\pi$ term, that was due to the charges in closest proximity to the point of contact. The latter force was named the Proximity Force. This theory was subsequently verified by Okada et al.[30]

It was then realized that the Proximity Force should be operative at every contact point and the number of contact points could be controlled with extraparticulates. Normal toner is soft and under the pressure of a development system can have many contact points with a plane or photoreceptor. It was suggested that the addition of a monolayer of extraparticulates has created a particle with uniform, small protrusions around the surface which, when contacted to a plane, only makes contact at a minimum number of protrusions.[4]

Experiments were done and published[31,32] that showed that at about a monolayer of extraparticulate coverage the Proximity Force was determined by a distribution of between 1 and 3 contact points. It was argued that values below 3 contact points were due to some toner particles being balanced against other toner particles. No data were obtained with lower adhesion. The values of 1–3 contacts were obtained by using Monte Carlo simulations to take into account the size and charge distributions.

It was also observed that the van der Waals force observed in Ref. 32 was 1.4 nN (using the last term in Eq. 4 of Ref. 32 and $n=0.4$ from the fit), compared to 14.2 nN for the electrostatic adhesion force at the 50% point (page 420 of Ref. 32). This 1.4 nN force is the van der Waals force which is smaller than observed in Refs. 24 and 25 (about 25−45 nN, depending on conditions). This could be regarded as further proof that the number of contacts has been reduced to a minimum by using a monolayer of extraparticulate coverage: the van der Waals force should be proportional to the total contact area of the silica which is proportional to the number of contact points. In Ref. 32 it is claimed that this number is 1–3; in Refs. 24 and 25 in which a monolayer of extraparticulates was not used, the number of contact points should be much higher. Further ideas of the effects of extraparticulates on the position of the charges on toner particles are discussed in Ref. 30.

The Proximity Force should be observed in a force microscopy experiment in which the distance between a ground plane and a toner particle is varied.[33] Physically this occurs because the Proximity Force has a finite range as shown in Fig. 1. In published force microscopy data of Gady, Rimai, and co-workers[34,35] an adhesion force was detected that has a longer range than van der Waals force, but a shorter range than long-range image forces associated with the charge in the center of the particle. Such data were fit with an ad hoc charge patch that was not independently verified and, as pointed out by the authors,[34,35] exceeds the electric field that air can support at large air gaps by a very large factor, 170! These data were successfully fit to the Proximity Theory: taking into account the discrete nature of charge naturally predicted the existence of forces above a toner particle on the distance scales observed in the force microscopy experiments.[33] These measurements[34,35] can be

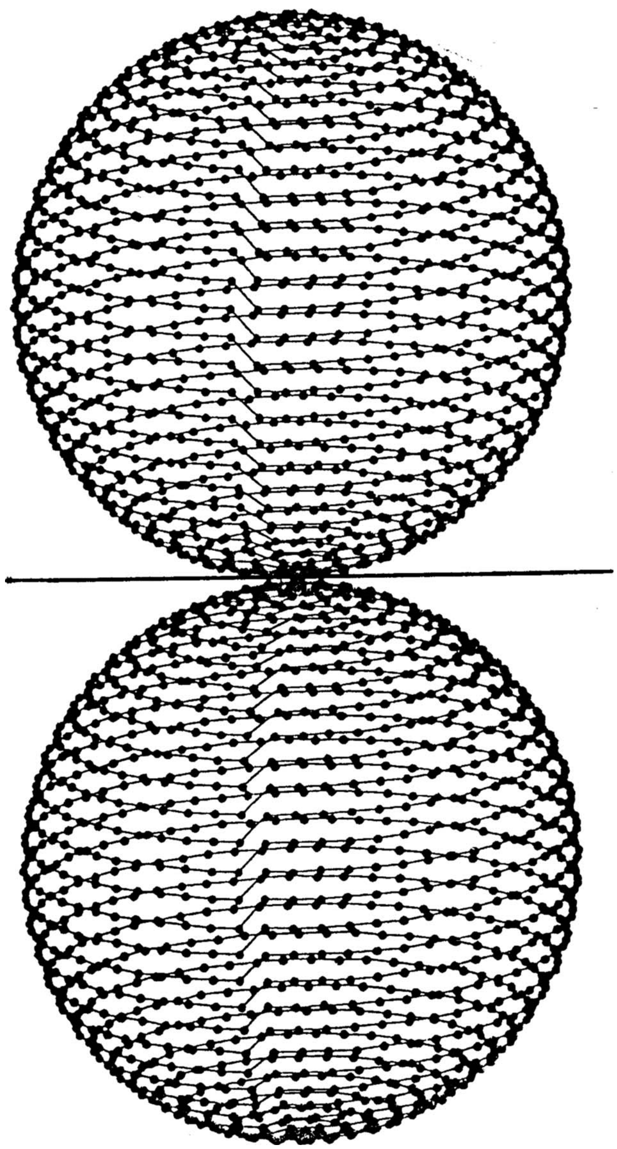

Figure 2. Shows sphere and ground plane and the image charges from which the proximity force has been calculated.

regarded as a direct observation of the proximity force—no other reasonable physical explanation for the published observations exists, to the author's knowledge.

SOME ASPECTS OF THE PROXIMITY THEORY OF TONER ADHESION RELATED TO REF. 5

The theory and experimental verification of the Proximity Force are already published[27,28,31,32] and discussed above. We focus our attention in this section on the aspects of the Proximity Theory that are needed to understand the data published by Dejesus et al.[5]

In Figure 2 is reproduced the sphere with the discrete charge points that were used for the calculation of the Proximity Force.[27,28] The charges are located in K charge points uniformly distributed around the surface in N annuli parallel to the plane. The charge q in each charge point is the total charge on the sphere Q divided by the number of charge points K which are related to N by

$$q = \frac{Q}{K} = \frac{Q\pi}{4N^2}. \tag{4}$$

In Refs. 27 and 28 it is shown that the Proximity Force is due to the charges in closest proximity to the contact point (this is the origin of the name of the force). In the geometry shown in Fig. 2, the charges in closest proximity are the ones on the first annulus, which are positioned at a distance of z_0 from the ground plane where

$$z_o = \frac{R}{2}\left(\frac{\pi}{2N}\right)^2. \tag{5}$$

In the example given in the original paper, $z_0 = 2.3$ Å for $R = 6$ um and $N = 180$ planes (which puts about two electrons in each charge point for $Q/M = 12$ μC/g for a 12 micron diameter toner particle). The critical point to note here is that there is an air gap between the charge points on the sphere and the ground plane. Whenever there is an air gap, there are boundary conditions which must be met by the electric fields. This is the source of image charges. And this is the source of the electrostatic force on the charged particles. The distance from the charge point to the plane is just z_0; for a metal plane the image charge is located z_0 below the ground plane. For a dielectric plane of dielectric constant K_p, the image charge is located a distance of approximately z_0 $(K_p - 1)/(K_p + 1)$ below the ground plane. This distance is on the order of angstroms, which is much smaller than the thinnest dielectric used in the experiment under discussion,[5] 0.8 μm.

The assumed position of the charges on annuli is not a critical aspect of the theory. In fact it is probably that the precise number, $4/\pi$, depends on the annular geometry. What is critical is the realization that each contact point has an electrostatic attraction which arises because of the discrete nature of charge.

SUMMARY OF EXPERIMENT PUBLISHED IN REF. 5

In Ref. 5 toner adhesion measurements were made on a polycarbonate dielectric of varying thickness coated onto an Ni ground plane. The concept of the experiment was the following: if the distance to the ground plane (the thickness of the dielectric) was varied and was on the order of the toner diameter, then any electrostatic adhesion image force should depend on, while van der Waals forces should be independent of, the dielectric thickness. The thicknesses were chosen to be 0.8, 4.5, 9, and 22 μm, which were smaller than and on the order of the toner diameter, 7.1 μm.

There are three aspects of this experiment which bear directly on the conclusions in this paper, the toner Q/M, the silica coverage, and, of course, the position of the image charges.

The toner charge-to-mass ratio is given as -24.3 μC/g. This is the average Q/M of the toner in the developer (the toner in the toner-carrier mixture). The Q/M of the toner that is developed is not reported. In the experiments with the magnetic brush development system the development voltage was only 10 V, chosen to be much less than normal (about 400 V) to ensure that toner development was low so that no toner-toner adhesion interactions were possible. In addition the speed ratio (developer velocity to photoreceptor velocity) was set to unity for the same reason. But these two conditions are well known to select special toner, not the average toner: the low development voltage selects only low adhesion toner; the speed ratio of one is known to be at a minimum for development, unlike all other speed ratios.[36] Using these two conditions it is likely that the toner developed is not the average toner particle, i.e., the Q/M developed is not equal to the Q/M in the developer. Q/M of the developed toner can be obtained using a standard vacuum pencil.[1] The difference between these two values does not affect the conclusions in the published paper[5] but will be important in future experimental tests in which the quantitative results are important.

The second aspect of the experiment that is important for adhesion theories is the surface coverage of the extraparticulates. The authors used 1.2% Degussa Aerosil R 972, which has a diameter of 12 nm. The Proximity Theory of toner adhesion has identified the importance of extraparticulate surface coverage, as discussed above. And it is well known from the literature that exparticulates can have a strong effect on toner adhesion.[12,24,25] Surface coverage S_c of silica is related to fractional weight of silica on a toner c_m by[37]

$$S_c = 0.6 c_m \frac{\rho_T}{\rho_{\mathrm{Si}}} \frac{D_T}{D_{\mathrm{Si}}}, \tag{6}$$

where ρ and D are the density (1.1, 2.2, respectively) and diameter of the toner (T) or the silica (SiO_2) particles. The factor of 0.6 is needed to empirically take into account the size distribution and the nonspherical nature of the particles (verified with scanning electron microscopy). Using Eq. (6), the surface coverage of the silica used in Ref. 5 is 0.66, below a monolayer. The Proximity Theory suggests that below a monolayer of coverage there are many contact points between the toner and the substrate; at a monolayer of silica coverage the number of contact points approaches a minimum of three.

The result of the experiment reported in Fig. 1 of Ref. 5 is that the adhesion is independent of the thickness of the dielectric layer from 0.8 to 22 μm. It is argued by these authors that no electrostatic force can account for the data because the image charge in the metal substrate is changed as the dielectric thickness of the coating is changed. The image force F_{A} is assumed to be of the form [their Eq. (4)]

$$F_A = \frac{1}{4\pi\varepsilon_0}\left(\frac{Q}{2(R+d)}\right)^2, \tag{7}$$

where d is the thickness of the dielectric coating, R is the radius of the toner, Q is the charge on the toner, and ε_0 is the permittivity of free space. This obviously assumes a uniformly charged sphere [Eq. (1)] and ignores the effect of the dielectric constants of the toner and dielectric coating. The point made by Eq. (7) is qualitatively correct: if the ground plane is moved further away then the force should change for the force modeled in Eq. (1). However, as noted in the discussion above of Eq. (1), it is accepted that Eq. (1) does not describe the force of adhesion of a toner particle.

The same argument is made to demonstrate that the charge patch and the proximity force theories are not consistent with the data. It is recognized that a dielectric can polarize and affect electric fields and therefore affect forces, but it is stated "for a particle in intimate contact (i.e., there is no intervening dielectric medium), the polarization force depends on the difference between the dielectric constants. In this study both the polycarbonate substrate and the polyester particles have a dielectric constant of approximately 3, so the polarization force should vanish." This argument ignores the air gap that exists between the discrete charges on the toner particle and the ground plane that is at the heart of the Proximity Theory (and would probably exist between the charges on a charge patch and a ground plane since charge patches are not perfectly flat, in the opinion of the author). This is the key assumption in the analysis which does not take into account the physical basis of the Proximity Theory: The Proximity Theory of toner adhesion identifies discrete charges near the point of contact as the dominate determinant of the adhesion force; these charges have image charges located at a distance of Ångstroms below the surface of the dielectric. Therefore the Proximity Theory of toner adhesion is consistent with the data.

There is a second experimental measurement reported in Ref. 5 in which the dielectric layer is corona charged. As argued in Ref. 8, this is expected to give the same experimental results, independent of any specific toner adhesion model, because the size of toner is much larger than any nonuniformities associated with the corona charge.

COMPARISON OF THEORIES AND EXPERIMENTS

Consider first the experiment described in Ref. 5 in which the thickness of the dielectric coating over a ground plane is changed from 0.8 to 22 μm. Toner adhesion is observed to remain constant. The author agrees that this experiment implies that Eq. (1) is not a valid description of toner adhesion, which assumes that an irregularly shaped toner particle can be approximated as a dielectric sphere with the charge uniformly distributed over the surface.

The van der Waals theory of toner adhesion may be consistent with the experiment described in Ref. 5, since van der Waals forces are based on short-range interactions between electron clouds on the toner and the dielectric surface. As shown above, the Proximity Theory of toner adhesion is also consistent with the experiment described in Ref. 5 because the image charges of the charges in closest proximity to the dielectric surface are only angstroms from the surface. And, in the opinion of the author, the charge patch theory is also consistent with the experiments described in Ref. 5 because the charges on the high points of the toner are not in perfectly flat planes and may be separated from the dielectric by the size of the extraparticulates.

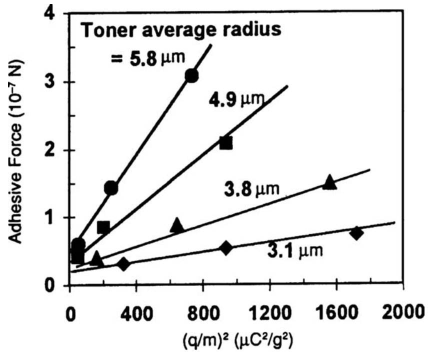

Figure 3. Adhesive force (in 10^{-7}) N averaged over toner samples with an average radius *r* vs square of average charge-to-mass ratio $(Q/M)^2$ (data from Ref. 24).

The key test of whether van der Waals or electrostatic forces dominates toner adhesion is well known. All electrostatic theories (including the charge patch and the Proximity Force theories) predict that the adhesion depends on Q^2, where Q is the charge on the particle. Such experiments have been carried out. For a history of these experiments, see Ref. 8. We quote two: In Ref. 24 (see Figure 3) are shown the measured adhesion forces for variable toner diameter with a surface coverage of about 35% of a hydrophobic silica as a function of the charge-to-mass ratio squared, $(Q/M)^2$. The curves are linear, as expected for an electrostatic model of toner adhesion with a y-axis intercept which is due to van der Waals forces. The values of the der Waals force are 25–45 nN, which is small compared to the electrostatic force of adhesion (250 nN at 22 μC/g for 5.8 μ toner). The van der Waals force is very close to the values obtained in Ref. 25 in which both uncharged and charged toner were studied. With even 5% surface coverage in Ref. 25, the adhesion due to van der Waals forces is below 50 nN and decreases for both uncharged and charged toner as the surface coverage increases. There are only two papers in the literature,[20,38] to the author's knowledge, in which it appeared that there is no relationship between adhesion force and Q^2. The problems in Ref. 38 were discussed by Lee.[8] In Ref. 20 two variables, charge and extraparticulate concentration, were varied at the same time convoluting the effects on adhesion of the change of extraparticulate concentration and charge, as pointed out by the authors themselves: "the effects of toner charge on toner adhesion are confounded, in this instance, by the varying concentrations of silica,…"

Any valid theory of toner adhesion must be able to account for the dramatic change in adhesion with extraparticulate concentration. As discussed above, the effect of silica extraparticulate concentration on a model of adhesion based on van der Waals forces does not appear to be understood; also, as discussed above, in the opinion of the author, the high points of the toner particles, which are assumed to be charged in the charge patch theory, will still be charged if extraparticulates are present. Therefore the charge patch theory predicts no dependence of toner adhesion on the surface concentration of extraparticulate. The Proximity Theory predicts that as the surface concentration of extraparticulates increases, the number of contact points decrease and the adhesion should decrease until it is minimized at approximately one monolayer of extraparticulates. As we have pointed out, this experiment has been reported several times[12,24,25] where it has been observed that adhesion decreases as the extraparticulate concentration increases. In the experiments done in which a monolayer of silica coverage is used, the contact points were minimized to three.[32]

CONCLUSIONS

A comparison of the three forces of toner adhesion proposed in the literature with experimental data suggests that all three forces are active. Van der Waals adhesion has been directly measured by measuring the toner adhesion force versus Q^2 and extrapolating to $Q=0$; it is found in Refs. 19, 20, and 32, to be small compared to electrostatic forces. Nonuniformities in the surface charge distribution probably exist—it is a reasonable hypothesis, looking at the morphology of toner particles and reading Lee's report on his experiments.[8] But if charge patch nonuniformities dominate toner adhesion, Hays' quantitative model leads to unphysical consequences, including electric fields at the surface of toner particles in excess of what air can sustain, and the prediction that Q/M is independent of toner concentration in toner-carrier mixtures, inconsistent with known data. It appears that the dominant force of toner adhesion is therefore the Proximity Force. This model can account for all known data. Furthermore the theory has now been independently verified by Okada et al.,[30] and Gady, et al.[34,35] may have directly observed the Proximity Force in their force microscopy experiments.

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