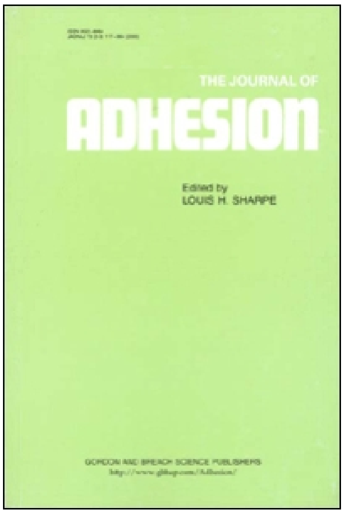

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Effects of Electrostatic and van der Waals Interactions on the Adhesion of Spherical 7 μm Particles

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Effects of Electrostatic and van der Waals Interactions on the Adhesion of Spherical 7 μm Particles

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The force needed to detach spherical particles having a number average diameter of 7.1 μm from a polymeric, photoconducting substrate was determined by ultracentrifugation. In the absence of any release agents applied to the substrate, it was found that only a small fraction of the particles could be removed from the substrate even at the highest centripetal accelerations (354,000 g). However, when the substrate was coated with a thin layer of a release aid (zinc stearate), the force needed to separate the particles from the substrate was greatly reduced, thereby allowing the detachment force to be determined. Under these conditions, it was found that the release force varied with the square of the particle charge-to-mass ratio. Moreover, it was also found by extrapolation that the detachment force at zero charge, corresponding to the residual van der Waals interactions, was finite. These results suggest that both van der Waals and electrostatic interactions affect the adhesion of particles and, for micrometer-sized particles, electrostatic forces can become dominant under some circumstances. Conversely, the large increase in the adhesion of the particles to the substrate, in the absence of a good release agent, suggests that van der Waals forces would often dominate adhesive interactions of particles in this size range.

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INTRODUCTION

Particles generally have an electric charge and, as a consequence, the adhesion of electrically charged particles to various substrates has been a topic of interest for many years. This is clearly manifest in a variety of technological applications ranging from electrostatic air filters to electrostatic deposition of toner and dry paint particles to controlling the charge on dust in silos. In the area of electrophotography, this interest has intensified as the demand for improved image quality has pushed the diameter of toner particles down from approximately 20 μm two decades ago to about 8 μm today together with the fact that the smaller toner particles are both more difficult to transfer from the photoconductor to a receiver and the untransferred residual is more difficult to remove from the photoconductor during subsequent cleaning operations [1].

Two distinct mechanisms, one based on electrostatic interactions and the other based on electrodynamic interactions such as those giving rise to van der Waals forces, have been proposed in order to explain the adhesion of particles to a various substrates. In reality, both types of interactions contribute to the attractive forces that give rise to the adhesion of particles, as discussed by Gady et al. [2]. The proper questions to ask are: (1) what are the relative magnitudes of these forces and (2) under what circumstances does one type of interaction dominate over the other.

In recent years, there has been a plethora of papers reporting experimentally measured detachment forces of particles from surfaces, principally in the area of electrophotography. However, the interpretation of the results from these experiments has been contradictory. For example, Goel and Spencer [3] measured the detachment forces required to separate Xerox E and K toners, having diameters between approximately 3 and 50 μm, from selenium photoconductors and concluded that both electrostatic and surface forces played significant roles in toner adhesion. They also noted an increase in the adhesion with time of the particles to the selenium, suggestive of plastic flow arising from the adhesion-induced stresses, as proposed by Krupp [4] and advanced by Maugis and Pollock [5] and by Rimai et al. [6, 7].

In another paper related to electrophotography, Hays [8] reported the measured force needed to remove spherical 13 μm-diameter toner particles from magnetic carrier particles. That paper concluded that electrostatic forces could account for only about 1/4 of the total force of adhesion if it were assumed that the charge were uniformly distributed over the surface of the particles. However, he also proposed that the surface charge density might not be constant, resulting in "charged patches." The presence of such charged patches could increase the electrostatic contribution to the total adhesion force.

In yet another paper related to electrophotography, Hays and Wayman [9] reported the results of a novel experimental study. In that study, the adhesion forces of 12 μm spherical toner particles were probed using a technique in which the particles were "bounced" between a pair of electrodes. They concluded that van der Waals and electrostatic forces contributed approximately equally to the total adhesion force. In a later date, however, Hays and Wayman [10] used a similar experimental technique with 99 μm diameter dielectric particles and concluded that nonuniform charge distributions were the dominant contributor to toner adhesion. It should be noted, of course, that the size of the particles could be a significant factor in determining whether electrostatic or van der Waals interactions dominate the adhesion of a certain group of particles. In yet another study, Eklund et al. [11] also concluded that charged patches enhance the electrostatic contribution to adhesion and dominate adhesion of 20 μm diameter toners.

Mastrangelo [12] directly measured the detachment force of IBM toner particles having diameters between approximately 6.5 μm and 20 μm from hard and soft photoconductors using ultracentrifugation. He concluded that van der Waals interactions dominated over electrostatic contributions to the adhesion of these toner particles. Moreover, he found that the detachment force of irregularly shaped particles was less than that for spherical. Finally, he reported that increasing the particle charge from 1–40 esu/cm^2 only increased the detachment force from 400–650 nN. In yet another study, Nebenzahl et al. [13] reported only a weak dependence of cleaning efficiency on particle charge. These results would seem to argue against the electrostatic charged patch model [14].

Donald [15] also studied the types of interactions giving rise to particle adhesion and determined that electrostatic forces dominate the adhesion of a variety of beads approximately 1/2 mm in diameter. Donald and Watson [16] used an ultracentrifuge to detach toner from magnetic carrier particles commonly used in electrophotographic engines. They then measured the charge on the detached toner as a function of centrifuge speed and concluded that toner to carrier adhesion was dominated by electrostatic forces.

Lee and Jaffe [17] used toner particles with a 20 μm diameter to study toner to photoconductor and toner to carrier adhesion. The former was measured 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 then argued that, although the measured detachment forces seemed to agree with what would be predicted if adhesion were dominated by van der Waals interactions, such interactions could not possibly be correct for two reasons. Lee and Jaffe first argue that the van der Waals force model overestimates the force of attraction because the irregular shape of toner gives rise to the asperities that reduce the magnitude of van der Waals interactions. Second, they assumed that the particle would not be uniformly charged and that the corresponding electrostatically charged patches would cause the electrostatic forces to be substantially larger than would be the case if the charge distribution were uniform. It should be noted that this same article shows scanning electron micrographs of toner particles in contact with the photoconductor. These particles appear to be relatively smooth although irregular in shape, appearing like small lumps of coal, and seem to be resting on the flat faces of the particles. As discussed by Bowling [18] in the same reference, such a contact would actually increase the effect of van der Waals forces. Finally, it should also be noted that, to date, no one has measured the charge density on particles in this size range.

In other studies, Rimai et al. [19, 20] used electrostatic detachment to determine the force needed to separate monodisperse spherical particles from a polymeric substrate. Using particles with diameters between 2 and 12 μm, they reported that the van der Waals interactions appear to be much greater than the electrostatic contributions to adhesion.

As should be apparent by the examples cited thus far, most of these paticle-substrate interaction studies have focused on measuring the detachment force. The authors then inferred the nature of the interaction from the size of that force. This approach, however, is fraught with difficulties because the detachment force depends not only on the nature of the potential, but also on interactions that occur between the particle and substrate that arise from the mechanical and geometric properties of the materials. These difficulties were overcome by Gady et al. [21] who took a novel approach to distinguish between the van der Waals and electrostatic contributions to particle adhesion. Instead of measuring the force needed to separate a particle from a substrate, they measured the attractive force and the attractive force gradient as a function of particle-to-substrate separation. This was accomplished by attaching spherical polystyrene particles between approximately 6 μm and 12 μm to an atomic force microscope (AFM) cantilever. Then, by comparing the power-law dependence of the force and force gradient with the theoretical dependences, they concluded 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 detachment forces with the number of times the particle was allowed to contact a triboelectrically dissimilar substrate. This was attributed to an exchange of charge between the contacting materials. They also observed that washing the particle with methanol after repeated contacting decreased both the attractive and detachment forces. They attributed these variations to varying the charge in the contact area, suggesting that localized charged patches play a role in determining the separation forces.

Understanding the roles of the electrostatic and van der Waals forces to particle adhesion has become more important in recent years, especially in the area of electrophotography. While a detailed discussion of the issues causing this is discussed elsewhere [22], there are three underlying reasons for this. The first reason is that the toner particles used in electrophotography have monotonically decreased in size over the past three decades, going from approximately 20 μm in diameter 30 years ago to 8 μm today. Second, as the particle size is changed, the charge-to-mass ratio, and thus the charge per particle, also changes. This, together with the fact that the contributions to adhesion from electrostatic and van der Waals forces scale differently with particle size implies that the respective roles of the two interactions can change with particle size. Third, particle adhesion is complicated by the role played by the asperities. This is especially true in the area of electrophotography, where the surface of virtually all modern toner particles are coated with silica clusters or similar particulate addenda, each cluster having a diameter of approximately 50 nm.

The presence of the silica particles complicates the analysis of the experimental results for both the charged patch and van der Waals interaction models. In the case of charged patch interactions, the silica does create particles that are reminiscent of microscopic medieval maces, with the silica serving as the points on the mace. In this context, the silica can prevent the bulk of the particle's surface from contacting other materials, thereby localizing any tribocharging to the asperities, as proposed by Hays [23]. On the other hand, the asperities would also serve to decrease van der Waals interactions due to the facts that surface forces are short range and not all the asperity contacts need to be severed at one time [24].

Experimental results and analysis have been presented arguing for both electrostatic and van der Waals interactions. For example, in a recent study Iimura et al. [25] ascribed a measured decrease in the adhesion of toner particles to a photoconductor with increasing silica concentration to the charged patch model. Iimura argued that the increase in the number of silica particles caused a decrease in the charge density on each charged patch, thereby decreasing the detachment force. They did not discuss, in their model, the effects of multiple charged patches, nor did they take into account the long-range nature of electrostatic forces.

In contrast to Iimura, Gady et al. [26] studied the effects of silica concentration on particle adhesion and cohesion, transfer, using ground particles having a diameter of approximately 8.6 μm. They concluded that van der Waals interactions dominated the adhesion forces for silica concentrations less than about 2% by weight. When the silica concentration reached 2%, the van der Waals and electrostatic forces were comparable. They also argued that dielectric strength of air would limit the size of any electrostatic force obtained for either a uniformly charged particle or one with localized charged patches to the range of 20–40 nN, and that the presence of charged patches would not significantly increase the magnitude of the attractive force, again due to the limitations imposed by the field that air can support.

There are a number of reasons for the apparent discrepancies in the findings of so many researchers. First, of course, is the issue of the particle size. A detailed discussion of this topic is beyond the scope of this paper and has been presented elsewhere [27]. Qualitatively, the effect of particle size on the detachment force can be understood by considering the dependence of van der Waals and electrostatic interactions on the particle radius. For a van der Waals bonded particle, the detachment force will vary linearly with the radius. On the other hand, since the charge on the particle is a result of triboelectrification, it is more likely to vary as the square of the radius. Although this approximation may be overly simplistic, it has been shown experimentally to be reasonable for spherical particles [19, 20]. Since, according to Coulombs law, the force of attraction varies as the square of the charge and inversely as the square of the separation distance, the attractive force, calculated using the method of images, would then be found to vary as approximately the square of the particle radius. As shown elsewhere [19, 20], the JKR prediction of the detachment force F_{detach} could then be generalized as

$$F_{detach} = -\frac{3}{2}\pi w_A\, R - \frac{\sigma^2 \pi R^2}{\varepsilon_0}. \tag{1}$$

where w_A, σ, and R represent the work of adhesion, the surface charge density, and the particle radius, and ε_0 is the permittivity of free space.

It should be noted that, in deriving equation (1), the electrostatic attractive force was simply treated as part of the externally applied load in the JKR detachment force equation. This is not quite correct.

As is well known, the JKR theory is based strictly on contact mechanics and does not allow for any long-range interactions. Obviously, electrostatic forces are long range. The correct way to treat electrostatic forces (and, for that matter, the Lennard-Jones potential commonly used to derive van der Waals interactions) would be to recalculate the work by bringing the particle in from infinity to in contact with the surface. This calculation, although worthwhile, is beyond the scope of this paper. As will be shown in this paper, equation (1) appears to approximate the detachment force data reasonably well.

One reason for the apparent discrepancy in deciding what type of interaction is dominant is due to the range in the size of the particles studied. As the power law dependences of van der Waals and electrostatic interactions on the radius of the particle are different, it is unrealistic to expect toner particles having diameters between 50 and 100 μm to have the same dominant forces as those having diameters that are smaller than 10 μm. More specifically, van der Waals interactions increase with particle radius at a slower rate than do electrostatic interactions. Conversely, while both types of interactions vanish at zero particle radius, van der Waals interactions decrease more slowly. Thus, it would be expected that, for sufficiently small spherical particles, van der Waals interactions would be the dominant interaction, whereas for larger particles, electrostatic interactions should dominate. For intermediate-sized particles, the contributions from both types of inactions can be comparable.

The problem of determining the dominant force is further complicated because many substrates of interest are fairly complex and are often ill defined. For example, in the area of electrophotography, toner adhesion to the photoconductor is often studied, as should be apparent from the preceding discussion. However, present day photoconductors often consist of multiple layers of organic materials. The photoconductor may also comprise a release agent such as zinc stearate, Teflon, various silicones, and soon. Such layers would affect the level of van der Waals interactions. Even in the absence of deliberately applied release agents, there might still be residual contaminants of the manufacturing process, such as coating surfactants, that, although quite transient in nature and usually wear off within a few hundred prints, can be present on tested photoconductors and which serve as release agents.

In addition to effects associated with particle size and ill-defined surfaces, the shape of a particle can also affect adhesion. Specifically, most particles are highly irregular in shape. Such particles present a spectrum of local radii of curvature at the points where they interact with surfaces and, thus, should exhibit a range of apparent behaviors even for a fixed mechanism. The shape effects makes analysis of experimental results more difficult and can also confound both the van der Waals interactions and the distribution of charge on the surface of the particle.

Finally, one must be concerned with the ways that particle-particle interactions can affect the interactions that give rise to particle adhesion. Consider, for example the effect of the induced image charge of neighboring charged particles on the detachment force of a test particle. This effect is often neglected. This may be appropriate if the particles are far apart, but would be inappropriate when the particles are close together, as would occur in the case of a heavy lay down. As discussed by Goel and Spencer [3], charged particles can see the induced image charge associated with the presence of neighboring particles. In the case of a hexagonally close-packed monolayer, the effect of the additional image charges would be to increase the electrostatic component by a factor of 6.95.

In order to more fully understand the relative roles of the toner charge and van der Waals interactions, this paper reports measurements of the forces needed to detach spherical particles from polymeric substrate as a function of particle charge. In a separate paper [28] this study is expanded to include irregularly shaped particles and particles in which asperities are added by coating the surface with nanometer-size silica particles.

EXPERIMENT

The force needed to detach spherical polyester particles, having a number-averaged diameter of 7.1 μm, from an organic substrate was measured using ultracentrifugation.

The particles were made from a commercially available polyester binder having a mass density of $1.2\,\mathrm{g/cm^3}$, using the limited coalescence process [29]. These particles have a narrow size distribution, with 84% of the particles having a radius no greater than 1.1 times the mean radius and less than 16% having a radius of less 0.91 of the mean radius. In addition, these particles are relativelyspherical. The mean number-averaged particle radius was determined using a Coulter Multisizer (Fullerton, CA). Figure 1 shows a photomicrograph of the particles.

The substrate consisted of a commercially available organic photoreceptor. In essence, this comprised a nickelized polyester terephthalate (PET) support that had been overcoated with a polyester binder containing photoconducting pigments and charge transport agents.

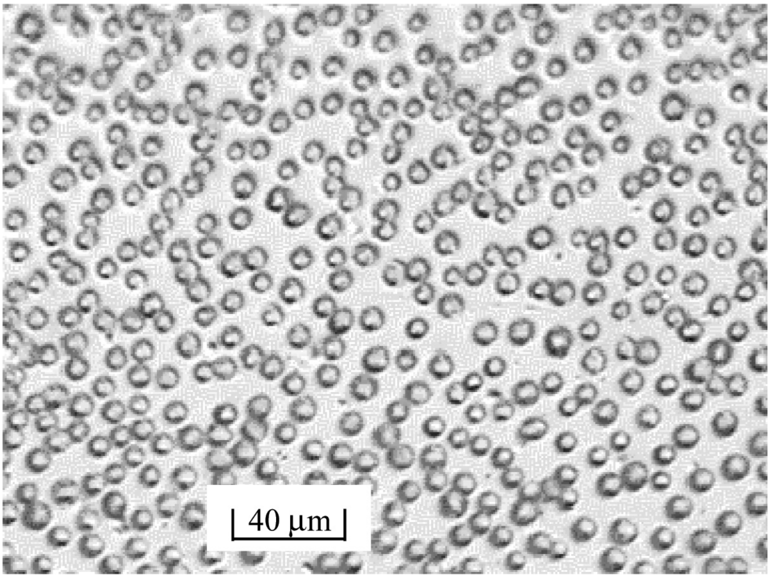


FIGURE 1 A photomicrograph of the toner deposited on the photoconductor.

This choice of material allowed the substrate to be treated as a grounded, conducting plane while simulating, in an ideal manner, the commercially important problem of toner adhesion to an imaging member.

The particles were electrically charged and deposited onto the substrate in a manner similar to that used to develop an electrostatic latent image into a visible image in an electrophotographic engine. The particles were charged by mixing 0.6 g of the particles with 11.4 g of larger particles comprising a ferrite core, a polymer coating, and an electronegative charging agent in a small vial and agitating the contents of the vial using a paint shaker. The charge-to-mass ratio of the particles was determined using the method of Maher [30] as discussed by Gady et al. [26]. The contents were then dumped onto a stainless steel shell that was coaxial with a cylindrical array of rotating magnets. An electrical bias of a few volts (typically in the range of 10–50 V, depending on q/m) was applied to the shell and the magnetic core spun, until a random deposition of toner covering between 30 and 40% of the substrate was obtained. In addition to transporting the particles to the substrate, the magnetic core also attracted the ferrite core particles, thereby preventing them from depositing onto the substrate. A more detailed description of the particle deposition apparatus is given by Miskinis [31]. The substrate was grounded and allowed to pass over the shell of the deposition apparatus at a speed of 5 cm/s, with a shell-to-substrate spacing of 500 μm.

Initially, the particles deposited onto a substrate that had not been coated with any release agents. However, it was found that only a small percentage of the particles could be removed from the substrate, even for the lowest charged particles (−18.3 μC/g) and the highest centripetal accelerations (3.47×10^6 m/s^2). Since the fraction of the particles removed, under such circumstances, represents the statistical outliers and the percent removed is a highly nonlinear function of the centripetal acceleration, it would be incorrect to draw any conclusions about the detachment force from such data. As an important goal of this study was to determine the effects of the particle charge on the detachment force, it was first necessary to significantly decrease the van der Waals forces so that the particles could be removed. This was accomplished by first coating the substrate with a monolayer of zinc stearate by sprinkling the zinc stearate powder, which is known to greatly diminish the adhesion of particles to various substrates [19, 32–34], onto the substrate and wiping it with a cotton Webril pad until as much as possible was removed. ESCA has shown that such this process leaves a uniform coating of zinc stearate approximately 4 nm thick on the substrate.

The removal force of the particles from the substrate was determined using a Beckman (Fullerton, CA, USA) L8-70M ultracentrifuge, which is capable of achieving speeds of 70,000 rpm. The samples were placed in a rotor with a radius of 6.45 cm. The number of particles on five representative regions of each sample of the substrate was determined both initially and after spinning at a chosen speed under a microscope, using Image-Pro particle counting software. In order to minimize effects associated with increases in adhesion measured with time, as previously reported in the literature [13, 35] all samples were run in the centrifuge on the same day that the toner was deposited on the photoconductor. In addition data points at different speeds were determined by two methods. The first method consisted of generating the general curve of the percent detached as a function of the centrifuge speed by simply increasing the speed to which a given sample was subjected. Next, additional data points were obtained by running the centrifuge at different speeds selected randomly. In effect, each curve shown represents the data obtained in two independent sets of measurements and each data point represents the average of 5 particle counts on the sample after centrifugation divided by the average of five data points taken on that same sample immediately prior to centrifugation. The data obtained from these two methods were found to be indistinguishable and are presented in the figure contained herein. The force needed to detach the toner particles from the photoconductor was considered to be the centrifugal force applied when 50% of the toner separated from the substrate.

The detachment force was taken to be the applied force wherein half of the particles were removed from the substrate. This value represents the mean detachment force and, as other values such as the point where 90% or 20% or some other arbitrary value are occasionally seen in the literature, this is not correct as those values represent the statistical outliers. As the curve of the percent removed as a function of the applied force is highly nonlinear, it is also not possible to extrapolate to the 50% removal point.

It is also recognized that restricting the present analysis to the 50% removal point is utilizing only a small subset of the data available in the present study, or, for that matter, in any similar study. However, to be able to take advantage of the additional data available would require that one be able to quantify a number of factors that affect particle adhesion. These include particle size and shape variations, as well as variations in the charge per particle and the charge density on each particle. In addition, the proximity of a nonlocalized charge to the substrate would also affect the adhesion of a given particle to the substrate. While some of this data, such as the size distribution of the particles remaining on the substrate can be gleaned with some effort, knowledge of the other factors such as the per particle charge and charge distribution cannot be determined at the present time. Accordingly, the results reported in this paper are restricted to the average values of the detachment forces.

RESULTS

The detachment force F_{detach} exerted on a particle is related to the mass m of the particle, the angular frequency ω, and the radius R of the rotor by

$$F_{detach} = m\omega^2 R. \tag{2}$$

Because the particles were both approximately monodisperse and spherical, the mass of each particle was readily estimated to be 2.34×10^{-10} g. For particles with this mass, the maximum detachment force that can be exerted with this centrifuge is approximately 811 nN.

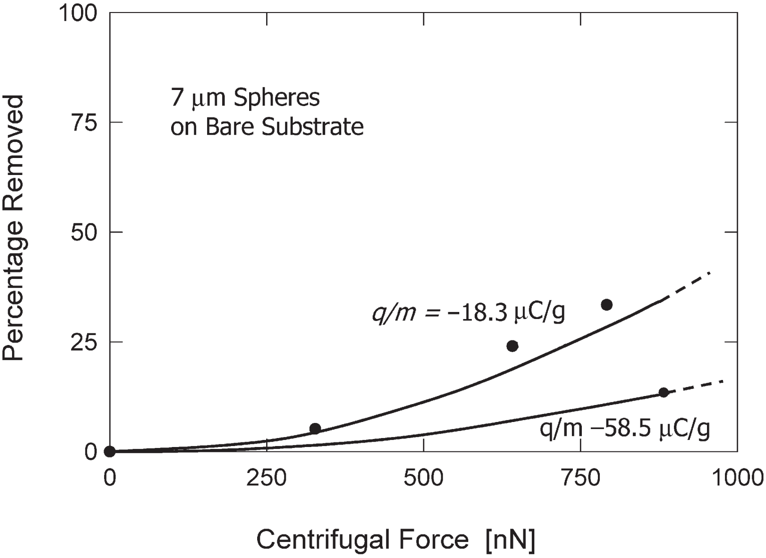


FIGURE 2 The percent of toner removed from a bare (no zinc stearate) photoconductor as a function of the applied detachment force for q/m = 18.3 (2a) and 58.5 (2b) μC/g.

Figure 2 shows the percentage of the particles removed from the substrate as a function of the applied force for charge-to-mass ratios of 18.3 and 58.5 μC/g. It should be noted that these data were obtained from a "bare" substrate, i.e., one that had not been coated with zinc stearate.

As can be seen, the centrifuge was unable to exert sufficient force to remove more than a small fraction of the particles from the substrate even at maximum speed. Since substantially less than 50% of the particles were removed for even these lowest values of the charge-to-mass ratio, it was not possible to determine the detachment forces as a function of charge-to-mass from the bare substrate. However, there does appear to be a decrease in the fraction of particles removed from the substrate with increasing q/m ratio. This is not surprising, as, even if van der Waals forces are dominant in determining toner adhesion, electrostatic forces should also contribute to the total force of adhesion.

The inability to determine the force of adhesion between the particles and substrate is, perhaps, not surprising if one simply estimates the necessary force using JKR theory [36], as discussed elsewhere [26, 19]. According to that theory and ignoring, for the time being, electrostatic contributions to the attractive force, the detachment force is given by

$$F_{detach} = -\frac{3}{2}\pi w_A \, R \tag{3}$$

where w_A is the work of adhesion, which, in turn, is related to the surface energies of the toner and photoconductor γ_T and γ_{Ph} and their interfacial energy $\gamma_{T\text{-}P}$ by

$$w_A = \gamma_T + \gamma_{Ph} - \gamma_{T-P.} \tag{4}$$

It was not possible to measure the surface energy of the particles directly. However, the surface energies of the substrate and of the materials from which the particles were made were found to be between 0.040 and 0.045 J/m^2, as determined from measuring the contact angles of planar sheets of those materials, that were made by depositing an fusing the particles on a smooth substrate, with distilled water and diiodomethane. If one then allows a small but finite value for the interfacial energy, one can estimate that the work of adhesion is approximately 0.070 J/m^2. Accordingly, the detachment force should be approximately 1100–1200 nN. This, of course, neglects contributions to the attractive forces due to the presence of any electrostatic charges, which should further increase the detachment force. These results and estimates are in reasonable agreement with experimentally determined 1100 nN detachment forces for 8.6 μm ground toner without silica, reported by Gady et al. [26].

To experimentally determine the contribution of the electrostatic forces to the adhesion of charged particles, it is first necessary to determine the total force needed to remove those particles from the substrate as a function of the particle charge-to-mass ratio. Then, by extrapolating the detachment force as a function of particle charge to the case where $q/m = 0$, one can determine both the van der Waals and electrostatic contributions to the adhesion of the particles. This, unfortunately, could not be done using the bare substrate with this size particle due to the small fraction of the particles that could be removed. Another approach towards determining the relative contributions of van der Waals and electrostatic interactions to the adhesion of charged particles must be taken.

Assuming that van der Waals interactions contribute significantly to the adhesion of charged particles in this size range, it should be possible to reduce the detachment force by coating the substrate with a known release aids such as zinc stearate or Teflon. Conversely, if the application of such a release agent does not significantly reduce the detachment force, it would be likely that the dominant adhesive interaction is electrostatic in nature. Assuming that the release agent does not affect particle charge, the electrostatic contribution to adhesion should be the same whether or not the substrate is overcoated with a release agent. It should be noted that, were the particle charge significantly altered by the presence of the zinc stearate coating, the manner that the particles were deposited onto the substrate in this experiment would result in a significantly different particle density on the substrate at a given development station potential. This was not observed in this study.

For this experiment, zinc stearate was chosen as the release agent because it has previously been found to show the greatest reduction in particle adhesion [19]. The mechanism by which zinc stearate reduces particle adhesion is not presently known and it is beyond the scope of this paper to speculate on this topic. However, it does not seem that such a mechanism can be due predominantly to variations in the electrostatic interactions. The number of particles deposited on the substrate at a given deposition station bias did not vary significantly, arguing that the charge on the particles did not change. The increased separation distance between the electrically conducting substrate only increased by about 4 nm upon application of the zinc stearate. This is insignificant. Moreover, the medium around the particle would still be air and it would still be possible to draw a Gaussian surface around the particle, so calculating the electrostatic force of attraction using a spherical Gaussian surface and the method of images, as discussed forthwith, should still be valid. The thinness of the zinc stearate coating would also seem to preclude the occurrence of any significant dielectric shielding of the conducting substrate. Finally, as discussed in the introduction, there have been studies that have quantified the relative magnitudes of van der Waals and electrostatic attractive interactions [21] in the absence of zinc stearate. Those studies have shown that the electrostatic interactions are relatively small, compared to van der Waals forces for this size particles at distances less than a few nanometers. To attribute the present role of the zinc stearate to reducing the electrostatic interactions via dielectric screening would be inconsistent with those results. Figure 3 shows examples of the effect of the zinc stearate on particle adhesion for particles with a charge-to-mass ratio of $-18.3\,\mu C/g$. Although the thickness of this layer was not determined in the present instance, previous ESCA studies suggest the thickness of the zinc stearate coating is approximately 4 nm, when similar means of deposition were employed. It should be noted that, in previous studies [19] zinc stearate was found to significantly reduce the adhesion of positively charged particles to similar substrates. In this case, the particles were negatively charged, arguing

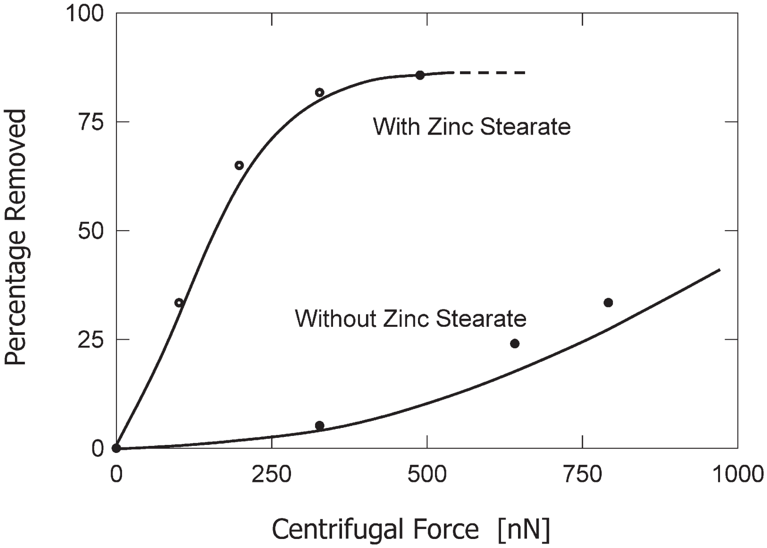


FIGURE 3 Comparison of the percent removed as a function of the applied force with and without zinc stearate on the photoconductor.

that the role of the zinc stearate is effective in reducing van der Waals interactions, rather than altering the magnitude of the particle charge. Moreover, from the measured potentials on both the untreated and zinc stearate coated photoconductors after development and the initial particle counts on the photoconductor prior to centrifugation, it would appear that, in this instance, the presence of zinc stearate did not appreciably alter the particle charge, as might be expected if there were significant triboelectric interactions. A direct comparison of q/m, as measured by capturing the particles in a Faraday cage, in the presence and absence of zinc stearate coated would, of course be desirable. Unfortunately, the adhesion of the particles from the uncoated substrate was too great to allow such a measurement. Figures 4a through 4f show the percentage of the particles removed at different centrifugal forces for particles with q/m ratios of -18.3, -34.8, -41.1, -44.7, -62.1, and $-75.6\,\mu C/g$, respectively. For comparative purposes, the highly charged toner particles of this approximate size used in electrophotographic engines have charge-to-mass ratios whose magnitudes are approximately $35\,\mu C/g$. As can be seen from these figures, there are relatively sharp transitions from conditions where few particles are removed to ones where most of the particles are removed. It should be stressed that, with the present experimental

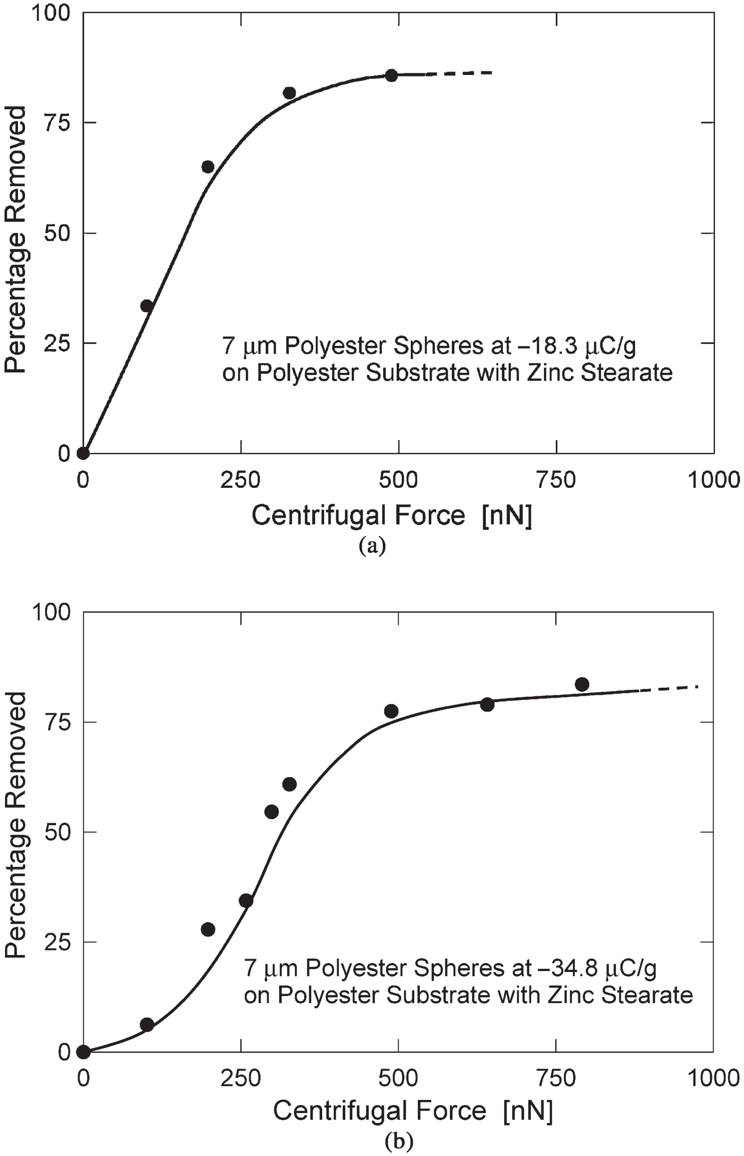
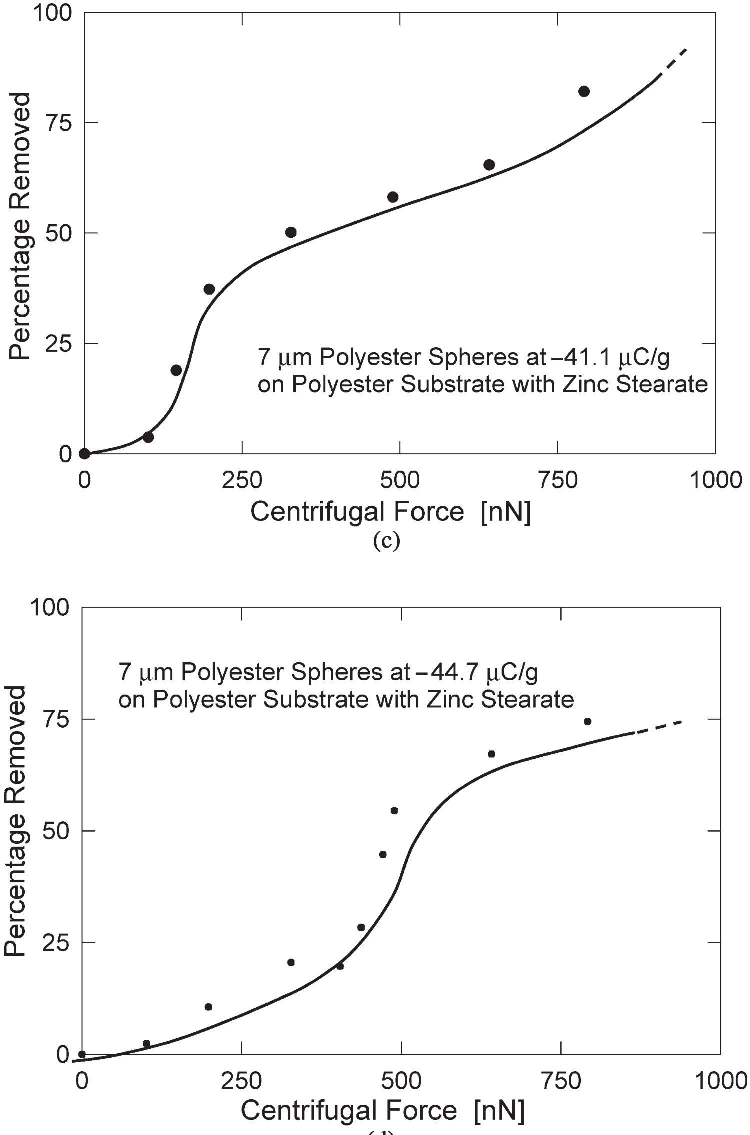


FIGURE 4 The percent of toner with charges of −18.3 (4a), −34.8 (4b), −41.1 (4c), −44.7 (4d), −62.1 (4e), and −75.6 (4f) μC/g removed from zinc stearate overcoated photoconductor as a function of the applied centrifugal force.

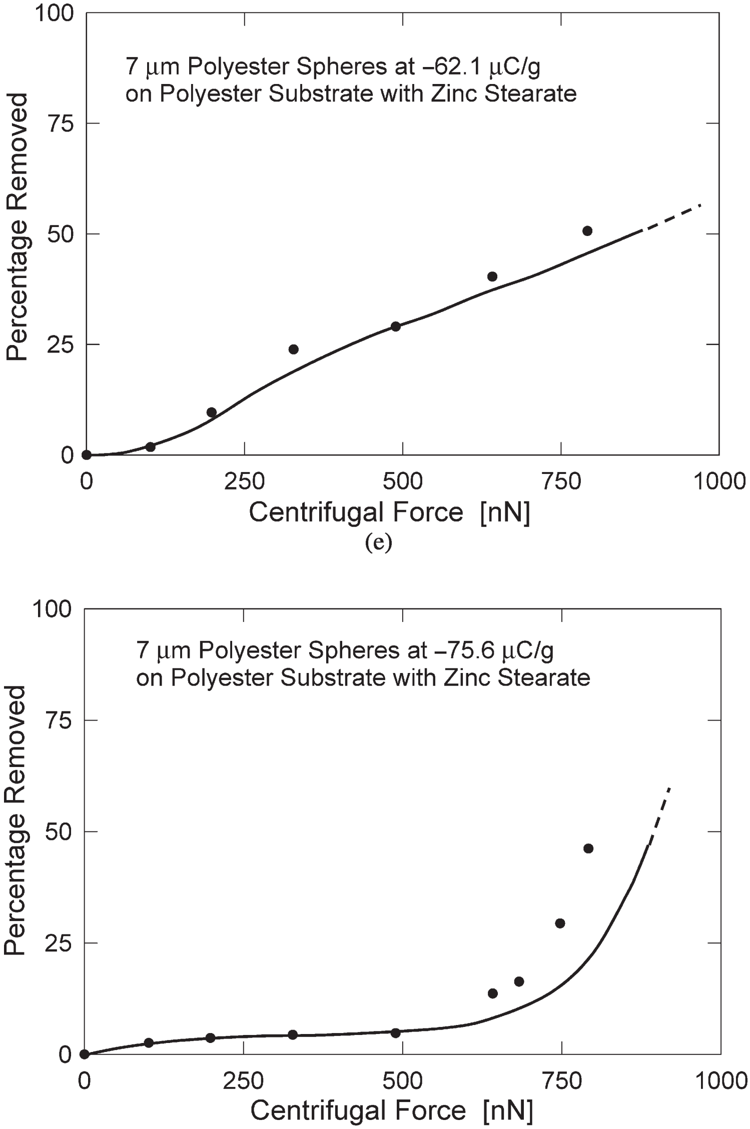


(c)

(d)

FIGURE 4 Continued.

conditions, this degree of detachment could only be achieved by first decreasing the van der Waals contributions to the particle adhesion. It should be further noted that the force needed to detach the particles



(e)

(f)

FIGURE 4 Continued.

from the substrate appears to increase monotonically with increasing q/m.

That the force needed to separate micrometer-sized particles from various substrates such as electrophotographic photoreceptors increases with particle charge has been clearly established in both this paper and aforementioned references. The two questions that need to be addressed are (1) what are the relative contributions to particle adhesion from van der Waals and electrostatic interactions and (2) can the electrostatic contribution to particle adhesion be accounted for assuming a relatively uniform charge distribution or does one have to include enhancements to the electrostatic attraction arising from a nonuniform charge distribution such as the charged patches proposed by Hays [14]. Let us consider the second question first.

As is well known, a uniformly charged spherical particle will induce in a neighboring grounded conducting substrate image charge. This results in a net force of attraction F_I between the particle and substrate given by

$$F_I = \frac{1}{4\pi\varepsilon_0}\frac{q^2}{(2R)^2} \tag{5}$$

where q is the charge on the particle and ε_0 is the permittivity of free space. As discussed by Hays [14], equation (5) can be generalized to include polarizable materials by multiplying the right hand by some constant α. However, when the dielectric constants of the contacting materials are equal, as would be the present case, $\alpha = 1$.

Alternatively, as proposed by Hays [10, 14] the electrostatic charge can be localized to certain areas, rather than uniformly distributed over the surface of the particles. These localized areas of concentrated charge are often referred to as charged patches. According to this model, the charge of the toner is related to the total area of the toner A_t by

$$q = \sigma A \tag{6}$$

where the surface charge density σ is a function of position on the surface of the particle. Hays then assumed that the extent of the charged area of the particle $A_c$in contact with the substrate is large compared to the separation distance between them, the electrostatic attractive force F_E can be calculated assuming a parallel plate capacitor approximation. In this case,

$$F_E = \frac{\sigma^2 A_C}{2\varepsilon_0}. \tag{7}$$

If the charge density were constant, then F_E would simply vary as the square of the particle charge. It should be noted, however, that the assumption giving rise to equations 6 and 7 are generally not consistent with the more fundamental assumptions of the charged patch model. Rather, σ would be a function of position on the particle surface and q

would not simply be proportional to the surface area of the particle. Rather, the total charge would be given by

$$q = \oiint \sigma(r, \theta, \varphi) dA(r, \theta, \varphi), \tag{8}$$

which, in most cases, would not simply reduce to equation (6). Similarly, equation (7) is derived from the parallel plate capacitor approximation and also assumes a constant charge density. Moreover, equation (7) also assumes that the contribution to the attractive force by any charge located outside the contact region is negligible. However, within the approximations commonly used in the charged patch model, one would expect the attractive force to also vary as the square of the particle charge.

Fowlkes and Robinson [37] proposed a different mechanism whereby electrostatic interactions polarize neighboring materials, thereby causing attractive forces between those materials. According to the Fowlkes-Robinson model, an electrically charged dielectric particle in contact with a conducting substrate would induce an electrostatic image charge. The image charge would then induce a dipole in the particle. The dipole, in turn, would induce a charge distribution in the substrate corresponding to a quadrupole. The quadrupole would induce an octopole in the particle. This process would go on *ad infinitum*, thereby generating an infinite series. As each term in the series adds to the attractive force, the series would converge slowly. Because of the presence of the higher order terms, the attractive force would not be expected to vary simply as the square of the particle charge according to the Fowlkes-Robinson model.

Figure 5 shows a plot of the force needed to detach half the particles from the zinc stearate coated substrate as a function of the charge-to-mass ratio of the particles. (The reader should note that q/m, rather than simply q, was plotted because q/m was the actual measured quantity. The charge per particle can be calculated simply by multiplying q/m by the particle mass $m = 2.34 \times 10^{-10}$ g). The detachment force appears to vary linearly with $(q/m)^2$, as can be seen from Figure 5. This is consistent with the predictions of both uniformly charged and the charged patch models. However, this result does not appear to be consistent with the assumption that multipole moments contribute significantly to the attractive forces. It should be noted that increased contact areas caused by the combination of the electrostatic and van der Waals forces should not result in an increase in the detachment force as long as the resulting deformations of the contacting materials are elastic [36].

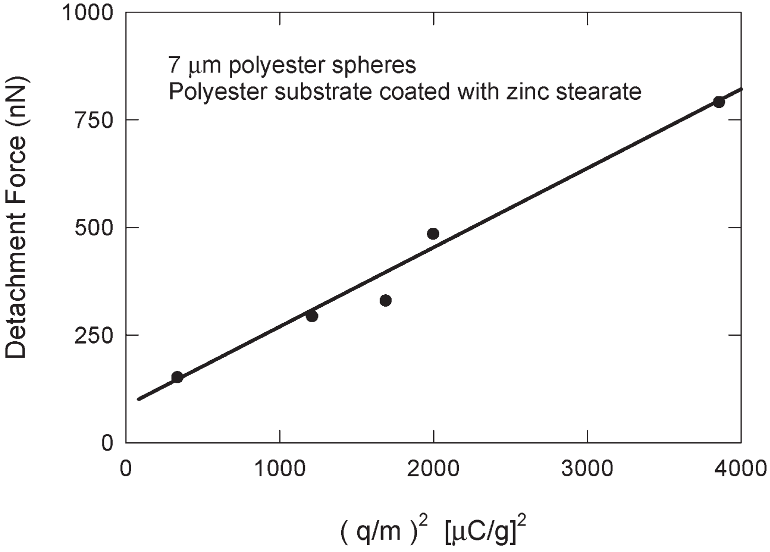


FIGURE 5 The applied force needed to detach 50% of the toner from zinc stearate coated photoconductors as a function of $(q/m)^2$.

That the predictions of the multipole model are not consistent with the experimental results should not, perhaps, be surprising. The multipoles (aside from the monopole moment, which is simply the charge) all depend on the differences between the dielectric constants of the contacting materials. When the particle is in contact with the substrate, there is no intervening medium such as air. In that case the multipoles would depend on the difference between the dielectric constants of the two materials, which, in this instance, is approximately zero. Beyond the contact radius, the multipole contributions to the attractive force decrease very rapidly with increasing separation distance. This results in only small contributions to the attractive forces from the multipole moments. Therefore, it would appear that there are no significant contributions to the attractive forces that originate from multipoles in the present particle-substrate system.

Let us now quantify the effects of the electrostatic and van der Waals forces on the adhesion of the particles. This is accomplished by first factoring out the van der Waals interactions by extrapolating the detachment force versus charge curve in Figure 5 to the value $q/m = 0$. Upon doing so it is found that there is a residual force of approximately 100 nN. This is an order of magnitude smaller than is the adhesion force observed for the case in which the particles are in contact with the substrate that had not been coated with zinc stearate. This result suggests that, in the absence of the zinc stearate, the adhesion of spherical, 7 μm diameter polyester particles to a polyester substrate is dominated by van der Waals interactions, but that the van der Waals interactions can be significantly reduced upon proper surface treatment.

The electrostatic contribution to the attractive force for a uniformly charged isolated sphere can be calculated using equation (5). For example, consider the case where $q/m = -18.3\,\mu\text{C/g}$. The measured detachment was found to be approximately 180 nN. The calculated electrostatic contribution to the attractive force is approximately 40 nN. Adding this value to the van der Waals force gives a total force of adhesion of 140 nN.

Calculating the electrostatic interaction by assuming an isolated charged particle in contact with the substrate may underestimate this contribution to the force of adhesion [13]. Let us consider, for example, the random deposition of particles giving rise to a particle density comparable to that observed in Figure 1. As previously discussed, the random deposition of charged particles results in the particles lining up in close proximity and forming "pearl chains." Each particle creates its own image charge, which interacts with every other charged particle in the system. Remembering that the electrostatic attraction falls off with the square of the separation distance, it is easy to show that contributions from particles beyond the nearest neighbor rapidly become insignificant. If one vectorally adds to the attraction from the primary image charge, the attraction due to the image charge of the two nearest neighbors, it is found that the total electrostatic attractive force is twice that experienced by an isolated particle. In this case the electrostatic attraction would then be 80 nN, rather than 40, for a total attractive force of 180 nN. This is in good agreement with the measured detachment force. For a more typical case, where the charge is approximately twice that of the example just cited, the total electrostatic attraction, including the effect of the two nearest neighbors, would be four times as large as the cited example, or 160 nN. The total attractive force would be approximately 260 nN. The force needed to detach particles with this charge from the zinc stearate coated substrate was experimentally determined to be approximately 270 nN. Similar agreement is found with other values of q/m.

At this point let us examine the effect of q/m on the adhesion of the particles to the substrates that had not been coated with zinc stearate. Assuming that the presence of zinc stearate affects neither the particle charge nor charge distribution, both of which are discussed earlier in this paper, and further assuming that the electrostatic and van der

Waals forces are additive within the context of the JKR theory, one can estimate the total force of adhesion for particles such as the ones used in this study to substrates that had not been coated with zinc stearate. Accordingly, from Figure 5 for $q/m = -58.5\,\mu C/g$, the total force of adhesion would be approximately 700 nN per particle. Subtracting approximately 100 nN attributed to nonelectrostatic interactions for the zinc stearate coated substrate gives a contribution to the force of adhesion of approximately 600 nN. The total force of adhesion of this particle from the uncoated substrate can be approximated by the sum of the electrostatic and nonelectrostatic contributions, whereby the nonelectrostatic contribution to the adhesion force is calculated from JKR theory, for a total of 1700–1800 nN. Similarly, if $q/m = 18.3\,\mu C/g$, the force of adhesion from the zinc stearate coated substrate is approximately 340 nN. Again, subtracting approximately 100 nN would give an increment to the total adhesion force of approximately 240 nN. This then gives a total estimated force of adhesion for the particles on the uncoated substrate of approximately 1340 nN and 1440 nN. Thus, even in instances where the particle adhesion is dominated by van der Waals interactions, there can still be an observable contribution to the total force of adhesion due to electrostatic effects.

It is recognized that the analysis presented in this paper does not preclude the occurrence of charged patches or their contributions to adhesion. However, these results do show that electrostatic contributions to adhesion can be treated more simply, without invoking a more complicated and unproven model. Indeed, more research is necessary to characterize the actual occurrence of charged patches and map out the surface charge densities. In addition, the present results highlight the need to clearly specify the nature of the surfaces when trying to characterize the type of interactions that dominate particle adhesion.

CONCLUSIONS

The contributions of electrostatic and van der Waals interactions between electrically charged, spherical polyester particles having a mean diameter of approximately 7.1 μm from a substrate similar to an organic electrophotographic photoreceptor were determined using ultracentrifugation. In the absence of any release agents that reduce van der Waals interactions, the force of adhesion was found to exceed 800 nN. Using JKR theory, the detachment force was estimated to be approximately 1100 nN. In contrast, upon the application of a thin layer of zinc stearate onto the substrate, the van der Waals forces were reduced to approximately 100 nN. The detachment force was then found to vary as the square of the particle charge. The calculated value due to electrostatic forces, however, is estimated to double if one includes the image charges associated with two adjacent particles found in the pearl-chain–like structures of the randomly deposited charged particles. These results argue that, unless van der Waals interactions are significantly reduced through the use of release agents such as zinc stearate, such interactions appear to be more significant than electrostatic forces in the adhesion of these particles. However, by using suitable release agents, the van der Waals forces can be reduced to the point where they account for less than half of the adhesion of the particles, depending on the charge of the particles.

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