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THE ADHESION OF SPHERICAL PARTICLES: CONTRIBUTIONS OF VAN DER WAALS AND ELECTROSTATIC INTERACTIONS

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*The forces needed to detach monodisperse spherical polystyrene particles having radii between approximately 1 μm and 6 μm from a polyester substrate were determined using electrostatic detachment. It was found that the removal force varied linearly with particle radius, as predicted by the JKR theory (K. L. Johnson, K. Kendall, and A. D. Roberts, Proc. R. Soc. London, Ser. A **324**, 301 (1971)). In addition, the work of adhesion, estimated from JKR theory, was found to be approximately 0.01 J/m². This is a reasonable value for a system such as this. These results are, however, inconsistent with the predictions of models that assume that particle adhesion is dominated by electrostatic forces due to either a uniform charge distribution over the surface of the particle or localized charged patches.*

INTRODUCTION

The need to understand the type of interactions giving rise to the adhesion of particles in the micrometer-size range to various substrates is important both technologically and scientifically. As such, it has been the subject of much investigation for more than two decades. Unfortunately, despite the many excellent studies, the controversy continues to this day. In order to understand the nature of the controversy and the significance of the present contribution, it is first necessary to review the literature critically.

Two types of interactions give rise to particle adhesion: electrostatic forces arising from an electric charge on a particle polarizing

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a neighboring substrate and electrodynamic forces such as those arising from dispersion or van der Waals-type interactions. The underlying mechanisms giving rise to these two distinct types of interactions can be simply described. The first arises from a particle becoming charged through interactions with its surrounding. Tribocharging is perhaps the best known way that a particle develops such as charge. However, other effects, such as fractoemissions [1, 2], can result in an electrical charge being left behind on particles as a result of their generation. The second relates to forces between electrically neutral atoms and is a direct result of the time-varying charge distributions within the atoms as the electrons orbit the nucleus.

Understanding the nature of the particle adhesion interactions is important for technological reasons as well as scientific ones. Consider, for example, the problem of removing particulate contaminants from semiconducting wafers during the device fabrication process. If the particles were attached to the wafer by electrostatic forces, it would be relatively easy to improve cleaning by installing an AC corona charger to discharge the particles, thereby facilitating removal. However, corona and plasma treatments of surfaces are known methods of increasing surface energies and, thereby, enhancing adhesion. Accordingly, if van der Waals forces determine the adhesion of the contaminant particles to the wafer, the use of an AC charger would be one of the worst things that could be done.

Perhaps nowhere has the nature of the forces controlling particle adhesion been the subject of more research than in electrophotography. In the formation of an electrophotographic image, an electrostatic latent image on a photoconductor is developed into a visible image using toner particles. These particles, which are typically about 10 μm in diameter, are comprised of pigmented polymers and are deliberately charged. After deposition on the photoconductor, they are transferred to paper, typically upon application of an electrostatic field. The paper is then passed through a fuser, where the toner is melted, thereby permanently fixing the image. Any untransferred toner must be removed from the photoconductor by cleaning. In this technology there are a number of areas where the nature of toner adhesion is important. For example, prior to fusing, toner particles are positioned in tightly packed groups, corresponding, for example, to the letters being printed by a laser printer. Why do they not simply fly apart due to Coulombic repulsion? It is clear that some sort of attractive force, sufficient to overcome the Coulombic repulsion, must be acting between the particles.

The relative strengths of the attractive and repulsive forces are dependent on the shapes of the particles. For example, as argued by

Hays and Wayman [3, 4], the bulk of a particle's charge tends to lie on the asperities of the irregularly-shaped particles. As a result of this concentration of charge, the electrostatic attraction should be greater than would be the case for a uniformly-charged particle. However, as discussed by Fuller and Tabor [5] and by Schaefer et al. [6], the presence of asperities should reduce adhesion forces arising from van der Waals interactions. Accordingly, if one wished to facilitate toner transfer and cleaning, and if toner adhesion was dominated by electrostatic forces, one should make toner particles more spherical. Conversely, if the adhesion forces were due to electrodynamic interactions and one wished to facilitate transfer and cleaning, one should make the toner particles more irregular.

As illustrated by the previous examples, the ability to control a technological process depends strongly on understanding the nature of the forces controlling particle adhesion. Accordingly, there has been much effort aimed at understanding these interactions, especially in the area of electrophotography, where the presence of both types of interactions has long been recognized [7, 8].

Despite all the interest in understanding the mechanisms giving rise to particle adhesion, the experimental results appear to be somewhat contradictory. For example, Goel and Spencer [7] measured the forces needed to detach several types of Xerox[®] toners, with diameters between approximately 3 and 50 μm , from selenium photoconductors using electrostatic and centrifugal detachment techniques. Based on their results, they concluded that both electrostatic and electrodynamic interactions were important in toner adhesion. They also reported that adhesion increased over time.

Hays [8] studied the detachment of spherical 13 μm -diameter toner particles from carrier and concluded that, assuming that the charge was uniformly distributed over the toner particle, electrostatic forces could account for only about 1/4 of the total detachment force. He also discussed the possibility that nonuniformly charged patches might increase the electrostatic contribution to the total adhesion force.

Subsequently, Hays and Wayman [3] measured the adhesion forces of 12 μm spherical toner particles by bouncing the particles between a pair of electrodes. They concluded that surface and electrostatic forces contribute roughly equally to the total adhesion force. In a later experiment, Hays and Wayman [4] used similar techniques to study the adhesion of irregularly-shaped, 99 μm diameter dielectric particles and concluded that nonuniform charge distributions were the dominant contributor. Eklund et al. [9] also concluded that nonuniformly charged patches dominate adhesion for irregularly shaped, poly-disperse toners with a mean diameter of 20 μm .

Mastrangelo [10] used ultracentrifugation to determine the force needed to detach toner particles with diameters between approximately $6.5\ \mu\text{m}$ and $20\ \mu\text{m}$ from various photoconductors. He concluded that van der Waals interactions dominate over electrostatic contributions to toner adhesion. Moreover, he found that irregularly-shaped toner was less adhesive than spherical toner. Finally, he reported that increasing the toner charge from 1 to $40\ \text{esu}/\text{cm}^2$ resulted in only a modest increase in the detachment force from 400 to 650 nN on an IBM toner. Similarly, Nebenzahl et al. [11] reported only a weak dependence of cleaning efficiency on toner charge for similar toners. These results would seem to suggest that electrodynamic, rather than electrostatic, forces dominate the adhesion of particles, even allowing for nonuniform charge distributions, as such nonuniform charge distributions should be more pronounced for irregularly shaped particles than for spherical ones [12].

Both electrostatic and electrodynamic interactions are long range in the sense that they occur even when the particle and substrate are distinctly separate. In a recent study, Gady et al. [13] were able to distinguish the roles of these attractive forces by attaching spherical polystyrene particles between approximately $6\ \mu\text{m}$ and $12\ \mu\text{m}$ in diameter to an atomic force microscope (AFM) cantilever and measuring both the attractive force and force gradient as a function of separation distance. They reported that the van der Waals forces become increasingly dominant at separation distances less than approximately 10 nm. However, they also reported an increase in both the attractive and separation forces with the number of times the particle was allowed to contact a triboelectrically dissimilar substrate. Moreover, washing the particle with methanol decreased these forces. These results suggest that localized charged patches also play a role in determining the separation forces.

In contrast to the results obtained in the aforementioned studies, Donald [14] determined that electrostatic forces dominate the adhesion of a variety of much larger beads (approximately $\frac{1}{2}\ \text{mm}$ in diameter).

Lee and Jaffe [15] also measured the force needed to detach $20\ \mu\text{m}$ diameter toner particles from a photoconductor by centrifugation. They found that the measured force agreed with the value predicted assuming the dominance of van der Waals interactions. They argued, however, that such a model could not possibly be correct because the presence of asperities on the particles would both reduce the contribution of van der Waals forces and serve as sites for electrostatically charged patches that would increase the electrostatic contribution of the attractive force. It should be noted, however, that scanning

electron micrographs of the actual particles in contact with the photoconductor reveal relatively smooth particles with irregular shapes that seem to be resting on flat surfaces rather than sharp points. As discussed by Bowling [16] in the same reference, such a contact may actually increase the effect of van der Waals forces.

Finally, Gady et al. [17] recently reported measurements of the force needed to detach 8 μm toner particles from an organic photoconductor as a function of concentration of submicrometer-size silica particulates on the surface of the toner, which act as asperities on the surfaces of the toner particles and reduce the detachment force. They concluded that, for silica concentrations less than 2% by weight of toner, the separation force was dominated by van der Waals interactions. They also concluded that only when the silica concentration reached about 2% were the effects of van der Waals and electrostatic forces comparable. Moreover, they also calculated that for the electrostatic charge patch model to explain successfully the measured separation force the fields generated by the localized charges would be so high as to result in air breakdown, often referred to as Paschen discharge.

Although the examples given might appear to be relevant only to toner adhesion, in fact they were chosen simply because the electro-photographic literature is rich with that discourse. In fact, the same issues would be of significance elsewhere.

There are several plausible explanations for the discrepancy in the proposed particle adhesion mechanisms. Certainly, the variations in particle size—from about 3 μm to 99 μm —can contribute to apparently contradictory results. Indeed, there is ample reason to assume that the dominant interactions controlling adhesion for particles on the micrometer-size scale will be different for particles having diameters of the order of 100 μm . In addition, there appears to be a theme in the literature that leans to an either-or scenario, i.e., the interactions are either electrostatic or van der Waals. Indeed, many authors have argued that since they have observed a charge dependence to the applied forces needed to effect separation, adhesion must be dominated by electrostatic forces. In fact, both electrostatic and electrodynamic interactions are present and contribute to both the attractive and detachment forces.

However, a large part of the discrepancy may be due to the particles chosen by previous researchers, which tend to cause experimental difficulties. Specifically, polydispersity in toner size and shape complicate attempts to analyze data. For example, an investigator may choose to look at nominal 20 μm -diameter particles. These particles are often irregular. Even the more spherically symmetric particles tend to be far from truly spherical, with bumps and other irregularities

on their surfaces, giving rise to large variations in the radius of curvature at interaction sites. The nominal diameter of the particles is obtained first by averaging over a variety of pseudo-radii or by assuming sphericity, and then averaging over variations in particle size within a sample. Indeed, the nominal 20 μm particles alluded to in this example will also contain a number of 10 and 30 μm particles, as well as many other size particles. These dispersities give rise to a broad range of detachment forces and complicate any sort of analysis.

Moreover, there is a tendency for researchers to measure the detachment force of one nominal-size particle. However, the mechanisms giving rise to particle adhesion tend to have different power-law dependencies [13]. Accordingly, it would be more valuable to determine the dependence of the detachment force on particle diameter than to simply determine the detachment force for one nominal-size particle in order to understand the respective roles of electrostatic and electrodynamic interactions. Finally, as is often reported in the literature, there is often a temporal dependence to particle adhesion, with particles generally becoming more tightly bound to the substrate over time [18]. While several mechanisms could give rise to such an effect, and a discussion of that topic is beyond the scope of this paper, it can play a role in understanding particle adhesion. Specifically, commonly used detachment-force measuring techniques, including centrifugation and electrostatic detachment, often take several hours, with the actual amount of time needed varying from sample to sample. Such lengthy times and time variations obviously confound the resulting measurements with noise.

In this paper we report short-time detachment force measurements of a series of monodisperse spherical polystyrene particles, having diameters between 2 μm and 12 μm , from a polyester substrate.

EXPERIMENT

The force needed to detach monodisperse, spherical, polystyrene particles from a polyester substrate was determined electrostatically. The particles used had diameters between approximately 2 μm and 12 μm and were made using the method of Ugelstad [19] as modified by Hoskyns [20]. A scanning electron microscope (SEM) micrograph of typical sampling of these particles is shown in Figure 1. As can be seen, these particles are highly spherical and show little size differences from each other. In addition, in order to examine the role of materials on adhesion, spherical polyester particles were also produced. These were made by dissolving the polyester in dichloromethane and forming the particles by spray drying. The particles were

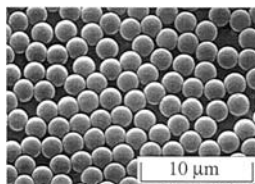


FIGURE 1 Scanning electron micrographs of a typical sample of particles used in this study.

then classified to give a narrow size distribution. Although the polyester particles were neither as uniform in size nor quite as spherical as the polystyrene, they were still of adequate quality to allow accurate, quantitative measurements to be obtained.

The particles were deposited onto a polyester substrate using electrostatic deposition, in a manner analogous to a copier or laser printer. The substrate consisted of a commercially available organic photoconductor, which, for all practical purposes, consisted of a photoconductor-doped polyester binder coated onto a nickelized Estar[®] (polyethylene terephthalate) support. The particles were charged by mixing them with larger magnetic particles, similar to the carrier particles used in an electrophotographic process. The charge of the particles deposited on the substrate was measured with a Faraday cage. The receiving electrode consisted of a 4 mil (0.1 mm) thick Estar support over which was evaporated a coating of clear, electrically conducting material referred to as “chrome cermet” (chromium silicate).

Figure 2 shows a schematic of the experimental setup. The particles were deposited on the polyester photoconductor by grounding the conducting layer and initially charging the photoconductor positively, and then optically discharging it to ensure that the photoconductor was initially uncharged. This process was followed to produce a well-defined initial (zero) voltage independent of the initial charge on the photoconductor. The photoconductor was then brought into proximity with a magnetic brush development station [21], similar to one used in a laser printer, that was biased in such a manner that a uniform, submonolayer layer of particles was deposited. The substrate was then positioned in the “transfer station” where an electromagnetic field could be applied to urge the particles towards the receiver.

The photoconducting substrate was then illuminated to ensure that it was in its “conducting” mode. The receiver was gently pressed against the photoconductor during the transfer process using a roller.

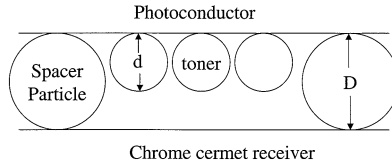


FIGURE 2 Schematic illustration of the experimental apparatus. Larger particles control the dimensions of the air gap between the substrate and the receiver.

A DC electrical bias was directly applied to the chrome cermet layer to urge the toner to transfer. This bias was increased and the fraction of smaller toner that traversed the air gap was determined by statistically counting toner particles in representative areas of both the receiver and the photoconductor after transfer. In order to establish a known, finite gap between the photoconducting and receiving substrates, a small percentage of larger particles were mixed in with the smaller ones. For example, when it was desired to measure the detachment force of the $2\ \mu\text{m}$ particles, a small number of $5\ \mu\text{m}$ particles was added prior to the deposition process. The resulting small and well-controlled air gap between electrodes allowed relatively high fields to be applied without the occurrence of Paschen discharge as the two electrodes would be gently pressed together. The force needed to detach the particles was determined by increasing the applied voltage until half the particles transferred to the receiving electrode. Because of the tight particle-size distribution and the spherical nature of the particles, the transition between no particles and all particles transferring was less than 25 V out of approximately 350 V applied.

By simulating the electrophotographic process, the time between particle deposition and detachment could be kept fairly short. In this particular study, this time was kept to less than 1 minute. However, longer or shorter times could be accommodated, if desired, by either introducing appropriate time delays between deposition and detachment or by speeding up the process.

In order to distinguish further between the electrostatic and electrodynamic contributions to particle adhesion, it is worthwhile to lower the surface energy of the substrate by using various release agents, such as Teflon[®] zinc stearate, and DC 200[®] silicone oil. In essence, if the particles were held to the substrate due to van der Waals interactions, a corresponding decrease in the detachment force should be observed. Conversely, if the adhesion force were dominated by longer-range electrostatic contributions, the presence of these

release agents should not affect the size of the force needed to effect separation. The release agent was generally rubbed onto the photoconductor with a cloth pad and as much as possible removed. This generally left about a monolayer-thick coating, as determined using ESCA.

RESULTS

Table 1 lists the toner diameters and ratios of charge-to-mass. The charge per particle was calculated using a mass density of 1.0 g/cm^3 for polystyrene and 1.2 g/cm^3 for polyester.

The applied field was calculated by assuming that the electrode configuration could be approximated as a parallel plate capacitor, with the spacing determined by the diameter of the larger particles. As the photoconductor was both illuminated and in the presence of a substantial field, it could be treated as a conductor. In addition, the applied pressure was the minimum required to bring the receiver into contact with the photoconductor so as to minimize any distortions.

As previously discussed, when the adhesion of particles to surfaces is measured, there is a large distribution about the mean force needed to effect detachment. This is due to the variations in particle shape and size, differing particle-to-substrate contacts, and variations in the particle charge and charge distribution. In this study, however, the use of monodisperse spherical toner particles narrowed the voltage window between transfer efficiencies of less than 10% to transfer efficiencies of more than 90% to ± 10 –15 volts. The force needed to separate the particles from the substrate was taken as that whereby half the smaller toner particles were electrostatically detached from the photoconductor.

TABLE 1 Particle Diameter, Charge-to-Mass Ratio, and Average Individual Particle Charge

Particle material	Particle diameter (μm)	q/m ($\mu\text{Coul/g}$)	Charge per particle (Coul)
Polystyrene	2	100	4.0×10^{-16}
Polystyrene	5	110.7	7.25×10^{-15}
Polystyrene	8	33.1	8.85×10^{-15}
Polystyrene	12.5	23.1	2.36×10^{-14}
Polyester	8.6	43.5	1.66×10^{-14}
Polyester	9.3	23.9	1.15×10^{-14}
Polyester	13.5	29.7	4.38×10^{-14}

The force, F_E , exerted on a particle with charge, q , dielectric constant, ϵ_P , and radius, R , in contact with a substrate of dielectric constant, ϵ_S , by an applied electric field, E , acting through a medium of dielectric constant, ϵ_M , can be calculated from electrostatics. Accordingly, this force is given by [22]

$$F_E = -\beta qE, \quad (1)$$

where

$$\beta \approx 1 + \frac{1}{2} \left(\frac{\epsilon_S - \epsilon_M}{\epsilon_S + \epsilon_M} \right) \left(\frac{\epsilon_P - \epsilon_M}{\epsilon_P + 2\epsilon_M} \right). \quad (2)$$

For typical polymeric particles and substrates ($\epsilon_S \approx \epsilon_P \approx 3$) in air ($\epsilon_m \approx 1$), β is approximately unity. Therefore, the electrostatic detachment force applied to the smaller toner particles is simply

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

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

The applied electrostatic force, F_E^S , needed to separate a particle from the substrate is shown in Figure 3 as a function of the particle diameter. This force, by definition, must equal the total force, F_{Total} , that one needs to be apply to the particle in order to effect separation

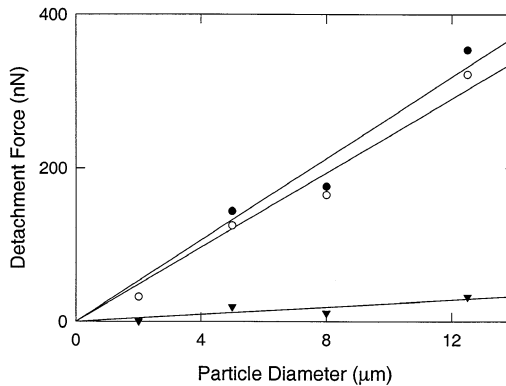


FIGURE 3 The detachment force as a function of particle diameter, the total detachment force (solid circles) well as the electrostatic (solid triangles) and van der Waals (open circles) contributions. For the 2 μm particle, the electrostatic contribution was sufficiently small so that the measured force and the net van der Waals force are both shown as the single open circle.

from the substrate. It should be noted that in the area of electro-photography, where the detachment of charged particles from a substrate is most frequently discussed, it is generally assumed that this force is comprised of two terms and is given by [12]

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

where E_S is the applied electric field needed to effect separation, d is the toner diameter, ϵ_0 is the permittivity of free space, and α and γ are constants. The values of α and γ are equal to 1.9 and 0.063, respectively, for a particle with a relative dielectric constant of 4 in proximity to, but not contacting, a conducting substrate [12]. The terms on the right hand side of Equation (4) are due to the polarization of the particle by the applied field and the image charge arising from the charge on the particle. In addition, the first term on the right hand side of Equation (4) is often assumed to be negligible [12].

Unfortunately, the analysis leading to Equation (4), although commonly used, is incorrect for several reasons. First, typical detachment fields are of the order of 10^7 V/m. These are not small and, accordingly, the first term on the right hand side of Equation (4) should not be neglected. In addition, constants α , β , and γ each depend on the differences between the dielectric constants of the particle and those of the substrate and/or surrounding medium. However, as is well known, the stresses associated with the forces of adhesion cause particles and/or substrates to deform, resulting in finite contact regions that effectively exclude any intervening medium in the regions of intimate contact where polarization effects should be most significant. In the limit of large contacts, when the dielectric constants are equal (as would be the case for many common materials), $\gamma = 0$ and $\alpha = 1$.

Another problem with the assumptions leading to Equation (4) is that electrodynamic forces are neglected. However, these forces can be considerable [17] and must be included in the analysis.

Finally, the assumption that detachment results from the simple balancing of attractive and applied forces is fundamentally incorrect. Rather, in order to determine the force needed to detach a particle from a substrate, one must approach the problem from the perspective of the work needed to separate the materials. This is the approach taken by Johnson et al. in their classic paper on adhesion, generally referred to as the JKR theory [23].

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

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

Here, K is related to the Young's moduli and Poisson's ratios of the contacting materials. It should be noted that the solutions to Equation (5) must be real, i.e., Equation (5) predicts a real contact radius as a function of particle diameter and applied force. As this theory is derived from contact mechanics considerations, it is implicitly assumed that all interactions occur solely within the actual zone of contact. An applied force leading to separation is equivalent to a negative load. The requirement that the solutions to Equation (5) be real leads directly to the JKR criterion that detachment occurs when

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

The use of JKR analysis is not quite legitimate when dealing with the adhesion of charged particles. Electrostatic forces are long range, and therefore the interactions extend far beyond the contact region. In addition, the field generated by the charged particle changes as a result of the adhesion-induced deformations. As a result, an actual determination of the detachment force would be difficult to calculate and is beyond the scope of this paper. However, if one assumes that the perturbation of the field due to the deformations is small and that the effects of the long range electrostatic interactions on the JKR predictions are small, then

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

If one further assumes that the deformations are sufficiently large so as to exclude any intervening media (e.g., air or vacuum) and that the dielectric constants of the particle and substrate are comparable, as would be the present case, implying that $\alpha = \beta = 1$, $\gamma = 0$, then the applied electrostatic detachment force, F_E^S , is simply

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

and the corresponding separation field, E_S , is given by

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

It is apparent from Equation (8) that the force needed to separate a particle from a conducting substrate increases rapidly with particle charge. This can readily explain the commonly observed effect that the detachment force increases with charge. However, it is also apparent from Equation (8) that such an observation does not rule out the contribution of electrodynamic forces, including those arising from van der Waals interactions. It is also seen from Equation (9) that there must be a range of charges for which electrostatic detachment of particles from conducting substrates can be effected. For example, as the particle charge decreases, the first term on the right hand side of Equation (9) increases, whereas the second vanishes. In this limit, surface forces dominate over electrostatics and one cannot exert a sufficient field to detach particles. Alternatively, as q increases, the effect of the image force increases, whereas the contribution from surface forces becomes negligible. Realizing that one can only increase the applied field to the Paschen limit, corresponding to about 3.5×10^7 V/m for a $10 \mu\text{m}$ size air gap, one can also see that high values of particle charge can impede electrostatic detachment.

It is also worthwhile to consider the effects of the diameter of the particle on the relative contributions of surface and electrostatic forces to particle adhesion. If one assumes that the charge on the particle, which generally arises from triboelectric interactions, is proportional to the surface area of the particle, then one can define a surface charge density, σ . If one further assumes that the surface charge density, σ , is approximately constant, then

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

Equation (8) can then be rewritten as

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

The present analysis can be extended to include localized charged patches. This would be done by defining σ as a function of position on the surface of the particle. The electrostatic component to the attractive force could then be calculated using potential theory. Such calculations, however, are beyond the scope of this paper.

It is seen from Equation (11) that, whereas both the surface and electrostatic forces decrease with decreasing particle diameter, the electrostatic forces decrease at a faster rate. Accordingly, for small particles the surface forces tend to dominate over the electrostatic forces. Conversely, for larger particles electrostatic forces would dominate. The diameter at which electrostatic forces dominate over

surface forces clearly depends on a number of properties, including the surface charge density and work of adhesion. However, assuming that $w_A = 0.01 \text{ J/m}^2$ and $\sigma = 9.2 \text{ Coul/m}^2$ (corresponding to the $5 \text{ }\mu\text{m}$ diameter particles used in this study), the cross-over diameter is estimated to be about $98 \text{ }\mu\text{m}$. The effects of particle size become even more complex when they are confounded by shape, contact, and charge distributions. Considering the range of particle sizes, charges, etc., discussed in the literature and summarized earlier in this paper, it should not be surprising that the results appear inconsistent.

According to Equation (11), one should be able to differentiate between the effects of surface and electrostatic forces on particle adhesion by determining the power-law dependence of the detachment force on the particle diameter. In particular, if particle adhesion is dominated by surface forces, the removal force should vary linearly with the diameter of the particles. Conversely, if electrostatic forces dominate adhesion, the separation force should vary as the particle diameter squared for ideal particles such as those approximated in this study. As is readily apparent from Figure 3, the total detachment force was found to vary linearly with particle diameter, suggesting that surface forces dominate over electrostatics. Similar results were reported by Gady et al. [13].

The contributions of the surface and electrostatic forces can be deconvoluted using Equation (8). This is done by subtracting the contribution to the particle charge, listed in Table 1, from both sides of Equation (8). This would then equate the JKR detachment force with the total applied electrostatic force minus the image charge contribution to the attractive force. It is recognized that this approximation is not strictly correct, due to interactions between the surface forces and other applied loads. However, a rigorously correct treatment of this problem would require a generalization of the JKR theory to allow for long-range interactions. This is beyond the scope of this paper. The total detachment force, as well as the van der Waals and electrostatic contributions to that force, are shown in Figure 3. As is readily apparent from this figure, the estimated contributions to the total force of adhesion arising from electrostatic contributions are small compared with those due to the surface forces. However, the fraction of the total force due to the electrostatic contributions increases with increasing particle diameter, ranging from less than 1% for the $2 \text{ }\mu\text{m}$ toner to about 10% for the $12 \text{ }\mu\text{m}$ toner. The work of adhesion, calculated using Equation (6) and the slope of F_{Surface} from Figure 3, is approximately 0.01 J/m^2 . This is a reasonable value for the present combination of polystyrene particles and a polyester substrate.

Further information about the nature of the interactions governing particle adhesion can be obtained by coating the surface of the substrate with various release agents such as various silicones, Teflon, and zinc stearate. Specifically, if the adhesion of the particles is dominated by its charge, the use of thin layers of release agents should not affect the detachment force. However, the converse effect would be expected if adhesion were dominated by van der Waals interactions. The effect of these materials on the detachment force is shown in Figure 4 as a function of particle diameter. As is apparent, each material decreases the force needed to detach the particle from the substrate, with silicone showing the least benefit and zinc stearate having the greatest effect. Moreover, the observed detachment forces continue to be linear with particle diameter, also suggesting the dominance of van der Waals, rather than electrostatic, interactions.

The type of material of which the particle is composed would also affect its adhesion if the adhesion is dominated by van der Waals interactions. Conversely, if adhesion is dominated by the charge on the particle, materials considerations should be minor. Thus, determining the effect of particle materials on adhesion can also be used to further the understanding of the nature of the interactions. The measured detachment forces, as a function of particle diameter, are shown in Figure 5, for both polystyrene and polyester particles on the same polyester substrate. As is readily apparent, the force needed to detach

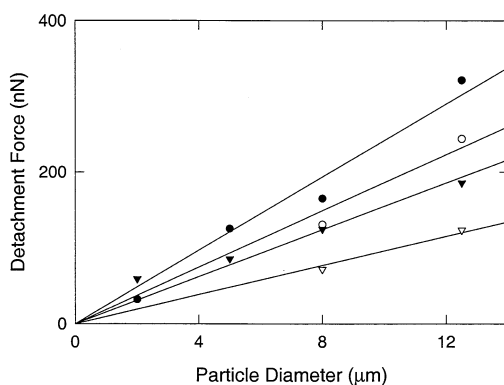


FIGURE 4 The effect of release agents on the force needed to remove particles from surfaces, as a function of particle size. The solid circles represent the van der Waals force in the absence of any release agent. The open circles, solid triangles, and open triangles represent the van der Waals component when the substrate was coated with silicone, Teflon[®], and zinc stearate, respectively.

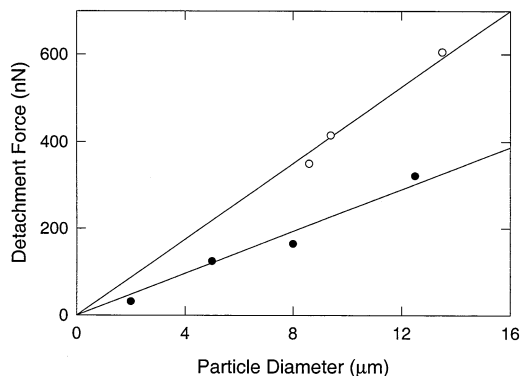


FIGURE 5 A comparison of the detachment forces for polyester (open circles) and polystyrene (solid circles) particles as a function of particle diameter.

a polyester particle is significantly greater than that needed to detach the same size polystyrene particle. For both materials, however, the detachment force varies linearly with the particle diameter. This linearity, together with the observed dependence on the particle materials, suggest that the adhesion is dominated by van der Waals interactions rather than by electrostatic forces.

The work of adhesion calculated for the polyester particles using Equation (6) is 0.019 J/m^2 , or almost twice that of the polystyrene particles. It should also be noted that the charge on the $12.5 \mu\text{m}$ polystyrene particles is higher than that on either the 8.6 or $9.3 \mu\text{m}$ polyester beads. However, the force needed to detach either of the polyester particles from the substrate was greater than that needed to remove the polystyrene particles. Again, this argues that van der Waals forces, rather than electrostatic interactions, dominate particle adhesion for these cases.

CONCLUSIONS

The force needed to detach spherical particles having diameters between approximately 2 and $13 \mu\text{m}$ from an organic substrate was measured using electrostatic detachment and found to vary linearly with diameter of the particle. Moreover, it was also found that various release agents such as silicone oil, Teflon, and zinc stearate also reduced the force needed to detach the particles from the substrate. Finally, a larger applied detachment force was required to remove polyester particles from the substrate than was necessary to remove polystyrene spheres. The electrostatic contribution to the total

adhesion force was found to be small compared with the surface forces. However, this contribution was found to increase with increasing particle diameter. The cross-over diameter, where electrostatic forces would become the dominant mechanism of particle adhesion, was estimated to be about 100 μm for spherical, electrically insulating particles. However, as the calculations depend on the specific charge distribution and size of the van der Waals forces, the cross-over point for highly irregular, electrically conducting particles may be lower.

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