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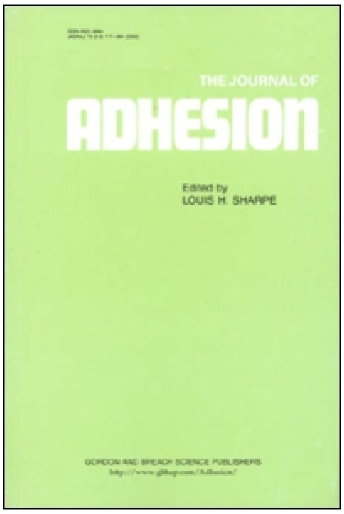

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Effects of submicrometer particulate silica addenda on the adhesion of micrometer-size particles to a polyester-composite substrate

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EFFECTS OF SUBMICROMETER PARTICULATE SILICA ADDENDA ON THE ADHESION OF MICROMETER-SIZE PARTICLES TO A POLYESTER-COMPOSITE SUBSTRATE

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The force needed to detach five sets of different size particles, having number-averaged diameters between 3.6 and 8.5 μm, from a composite substrate was measured using an ultracentrifuge. In addition to size variations, the asperity concentration for each size particle was adjusted by varying the silica concentration, adjusted so that the surface area concentration at each level was kept constant for the five sizes of particles. Due to the changing silica concentration and particle size, the charge per particle also varied. It was found that the detachment force appeared to be virtually independent of charge, with any correlation actually appearing slightly negative, if anything. However, the detachment force increased monotonically with increasing particle diameter and decreased monotonically with increasing silica concentration. Moreover, upon normalizing the detachment force to the particle diameter and the silica concentration to the surface area concentration of silica, it was found that the detachment force clustered into groups in which the force needed to separate the particle from the substrate depended only on the silica concentration. These results suggest that van der Waals interaction, rather than electrostatic forces, are the dominant mechanism controlling toner adhesion in this instance.

Keywords: Particle; Silica; Asperities; Toner; Adhesion; Charge; van der Waals

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INTRODUCTION

The nature of the underlying interaction giving rise to the adhesion of particles to various substrates has long been of interest [1–19]. Specifically, particles are generally electrically charged. This charge is fundamental to the operation of various pieces of equipment such as electrostatic dust filters and electrophotographic engines. In addition, particles can also interact with substrates *via* electrodynamic interactions such as those giving rise to van der Waals forces. Indeed, both types of forces are present and their relative importance varies with a number of parameters including particle size and shape, materials properties, particle charge, and the distribution of the charge on the surface of the particles. The absence of a clear understanding of the relative roles of electrostatic and van der Waals interactions has been a major impediment in understanding particle adhesion.

A further complication in understanding the physics of adhesion of particles is that most of the analysis has been restricted to spherical particles. Although such particles may exist in the real world, most particles are irregular. Furthermore, even those that are generally classified as spherical are more often spheroidal. Even the most spherical of the particles have surfaces that would not be classified as atomically smooth. Indeed, the very nature of atomic bonding would result in virtually any particle being, at best, a polyhedron if examined at the atomic level.

That being said, most real particles are formed as the result of a fracturing process. Often, the particles are coated with other particles to reduce adhesion and enhance flow. This is especially true in electrophotography, where micrometer-size toner particles are commonly coated with nanometer-size silica particles. Such particles are commonly referred to as "surface-treated toners." As a result of the importance of surface-treated toners, there have been numerous scientific investigations in recent years aimed at understanding the role of such treatment on properties such as toner-to-photoconductor adhesion, toner flow, and image quality. The last property is a direct result because toner particles, being similarly charged, would tend to repel one another. Only by balancing the electrostatic repulsion with some form of cohesive force, such as one arising from van der Waals interactions, can halftone dots and alphanumeric characters be formed.

As previously mentioned, the commercial interest in surface-treated toners has spurred much research in recent years. Ott and Silence [20] determined, using an AFM, the effect of relative humidity on the

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adhesion of toners that had been coated with hydrophobic and hydrophilic silica. Although they did not disclose the size of the toner particles used, they did find that the detachment force was in the range of a few hundred nanonewtons and depended on both contact time and relative humidity (RH). Iimura *et al.* [17] measured the detachment force of nominal 8 μm diameter toner with and without silica. They reported a detachment force of about 70 nN for uncharged toner without silica. Moreover, the detachment force decreased with increasing silica concentration. Iimura *et al.* proposed that the decrease in the detachment force was due to localized charged patches becoming more diffuse, thereby decreasing the charge at each site, with increasing silica concentration. Gady *et al.* [18] studied the effects of silica concentration on toner adhesion, cohesion, transfer, and image quality. They found that increasing silica concentration reduced toner adhesion and cohesion, improved transfer efficiency, but resulted in a decrease in the integrity of halftone dots. In another study, Rushing *et al.* [21] found that the number of "satellite" toner particles, that is, those toner particles that surround the dots but are not integral to those dots, observed in an electrostatically transferred image increased directly with silica concentration and inversely with the toner-to-photoconductor detachment force.

As previously stated, both electrostatic and van der Waals forces contribute to the adhesion of electrically charged particles. Moreover, the relative magnitudes of the two types of forces depend on a variety of factors. In a recent study, Rimai *et al.* [22] recently reported, for example, that the detachment force of spherical particles varied as the square of the particle charge. Moreover, the magnitude of the electrostatic force was found to range between about 100 for the low charged particles to about 700 nN for those with the highest charge used in that study. The contribution to the adhesive force arising from van der Waals forces was reported to be approximately 100 nN. However, these measurements could only be made after the substrate used in that study was coated with zinc stearate to reduce the van der Waals forces from an estimated 1100 nN prior to the deposition of the particles. In a different study, Rimai *et al.* [19] found that the detachment force for a series of monodisperse spherical particles varied linearly with the radii of the particles. This result is consistent with adhesion theories that assume van der Waals interactions.

As discussed in the references cited herein and summarized elsewhere [22], there is evidence and arguments supporting both van der Waals and electrostatic interactions as the underlying force behind particle adhesion. This question has been difficult to resolve even for monodisperse spherical particles. However, most "real" particles are far from spherical. Rather, they are highly irregular. Indeed, many have their irregularity augmented by deliberately adding asperities in the form of addenda particles such as the silica particles that are appended to the surface of toner particles. Such addenda can also occur naturally, if inadvertently.

Determining the relative contributions of van der Waals and electrostatic forces is sufficiently complicated for monodisperse spherical particles. This problem becomes much more difficult if the particles are highly irregular and polydisperse. Add to that the additional complications introduced when particulate addenda are involved and one has a rather complicated problem with which to contend. However, this is the world of real particles and such an understanding is important. To distinguish between the effects of van der Waals and electrostatic interactions in such a case requires that the detachment forces be determined as a function of multiple parameters in a self-consistent experiment, rather than by simply varying a single parameter such as particle charge, size, or concentration of addenda. In this study, the dependence of the detachment force on particle size, concentration of silica addenda, and particle charge has been determined.

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EXPERIMENT

The force needed to detach five different sets of polyester particles, having number-average diameters between 3.6 μm and 8.5 μm, with each set having four levels of silica, from a polymeric substrate was determined using an ultracentrifuge. The silica concentrations were adjusted for each set of particles so as to maintain four constant surface area coverages by the silica. The charge-to-mass ratio q/m varied with both particle size and silica concentration. This allowed the determination of the effects of toner charge, toner diameter, and silica concentration on the detachment force.

The particles were comprised of a commercially available polyester binder (Kao-C) (mass density $\rho = 1.2$ g/cm^3) and were produced by a compounding and grinding process. The final particle sizes and size distributions were set by classification. The volume and number-average radii of the particles were determined using a Coulter Multisizer (Beckman, Fullerton, CA, USA). The particles were then blended with appropriate amounts of RY200 silica, produced by Degussa (Watertown, MA, USA). According to the manufacturer's specifications, the fundamental particle diameter of the silica is approximately 7 nm. However, the silica agglomerates into particles having diameters of between approximately 30 and 50 nm. Assuming spherical particles of equal mass to the actual ground particles, the quantity of silica was chosen so that the weight percent of silica would give a constant surface area coverage of silica particles for all five volume-weighted diameters of the particles. Estimates of the percent of the surface area covered by silica, which were confirmed by SEM micrographs of similar silica-coated particles, suggest that, at the highest surface treatment levels, approximately 75% of the toner surface was covered with silica. The particles were deposited onto the substrate in a manner analogous to the deposition of toner in an electrophotographic engine. The particles were first mixed with larger, magnetic ferrite particles, which served to tribocharge the particles. This mixture was, in effect, quite similar to a so-called "two-component" electrophotographic developer.

Particle charge was measured using the techniques described elsewhere [23]. A uniform deposition of the particles, with about 30–40% of the substrate covered, was made using a sumpless magnetic "development station," similar to the one described by Miskinis [24], in a linear breadboard, described elsewhere [19]. In this technique, the magnetic particles remain with the "development station" and serve only to transport and tribocharge the actual particles of interest. The substrate consisted of a commercially available composite organic photoconductor, comprising a polyester binder, produced by Eastman Kodak (Rochester, NY, USA). This substrate was chosen because it readily allowed the particles to be electrostatically and uniformly deposited. Contact angle measurements done with distilled H_2O and CH_2I_2 gave a surface energy of approximately 43–45 mJ/m^2. This surface energy is consistent with typical values for polyester and shows an absence of low surface energy contaminants such as silicone oils that are often used as coating surfactants.

The force needed to detach the toner particles from the photoconductor was determined using a Beckman ultracentrifuge (Beckman, Fullerton, CA, USA) with a rotor having a radius of 6.45 cm and rotational speeds up to 70,000 rpm. The procedure for determining the detachment force was as follows: The initial number of deposited particles was determined by counting with a microscope and using Image-Pro software (Media Cyberneties, Silver Spring, MD, USA). The samples were then mounted on appropriate holders and inserted into the rotor. The rotor was placed into the centrifuge and the centrifuge was evacuated to a pressure of 10^{-2} Torr. The rotor was then spun at the desired speed, the substrate removed, and the particles remaining were again counted. Deposition of the particles onto the substrate and all centrifugation and counting was done on the same day to minimize increases in the detachment forces caused by adhesion-induced plastic deformations.

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The applied force was determined from the centripetal acceleration and by calculating the mass of a single particle assuming that the particles were spheres having an equivalent diameter to the number average diameter of the particles. This diameter, as opposed to the volume-weighted diameter, was chosen because the procedure used counts the number of particles present on the substrate.

The detachment force was taken to be that force where half of the initial toner particles were removed. This value is commonly chosen because it is representative of the average detachment force, rather than the force needed to detach the statistical outliers. Because of the theta function-type, also known as the Heaviside or unit-step function behavior of the percent detached *versus* the applied force, estimating a mean detachment force by extrapolating the detachment force of the statistical outliers is not valid. Similarly, requiring that most, if not all, the particles be removed skews the results to the most tightly bound particles, which are also statistical outliers.

Five nominal particle diameters, with number-average diameters between 3.6 μm and 8.5 μm were chosen for this study. The distributions in particle diameter about these means effectively span the entire size range, with a certain degree of overlap of one size into the next. Accordingly, attempts to generate additional sizes within this range would not have been effective. The use of smaller particles would be problematic because of difficulties encountered in trying to detach such small particles with this centrifuge. In addition, there would be problems grinding and classifying toners to smaller sizes. The properties of the particles used in this study are summarized in Table 1. The reader is reminded that the difference between the volume-(D_V) and number-(D_N) averaged diameters of the particles is representative of the size distribution of the particles and approximately tracks with the full width at half maximum.

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RESULTS

Figures 1a–1e show the percent removed as a function of particle diameter, at each level of silica, for the 3.6 μm through 8.5 μm diameter particles, respectively.

Several features can be seen from the graphs shown in Figure 1. First, it is apparent that the higher the silica concentration, the higher the percentage of particles that are removed at a given detachment force. Moreover, the applied force at which half of the particles are removed decreases with increasing silica. It should be noted that it was not possible for this centrifuge to remove half of the 3.6 μm, 5.5 μm, and 6.4 μm particles with no silica. It was barely possible to

TABLE 1 Properties of the Particles

Particle number	D_N (μm)	D_V (μm)	q/m (μC/g)	Silica (wt%)
1	3.6	5.0	−51	0
2	3.6	5.0	−93	2.48
3	3.6	5.0	−63	1.66
4	3.6	5.0	−41	1.16
5	5.5	6.2	−37	0
6	5.5	6.2	−54	1.90
7	5.5	6.2	−36	1.27
8	5.5	6.2	−32	0.89
9	6.4	8.2	−28	0
10	6.4	8.2	−39	1.46
11	6.4	8.2	−24	0.97
12	6.4	8.2	−17	0.68
13	6.6	7.0	−14	0
14	6.6	7.0	−50	1.61
15	6.6	7.0	−35	1.08
16	6.6	7.0	−7	0.75
17	8.5	10.5	−26	0
18	8.5	10.5	−28	1.14
19	8.5	10.5	−22	0.76
20	8.5	10.5	−16	0.53

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remove half of the 6.6 μm particles with no silica. Finally, it is apparent that the detachment force tends to increase with increasing particle diameter.

In order to determine the actual detachment force, a spline-fit curve passing through each set of data was created. As is commonly done in particle-detachment force measurements, the point where half the particles had been removed was designated as the detachment force. This is because it is incorrect to ascribe the adhesion properties of the particles to the detachment percentages either at significantly lower or higher percentages than 50%, as the lower or higher values would be determined by the statistical outliers and, thus, do not represent the average force needed to separate the particles from the substrate. The particles used in this experiment were produced by grinding and classifying, which results in significant distributions in both size and shape. Therefore, requiring that essentially all the particles be removed or, alternatively, extrapolating detachment forces from a small percentage of the toner being removed, would result in erroneous conclusions. Furthermore, it is also recognized that more data to better define the curve would have been preferred. However, considering aforementioned distributions in the size and shape of the particles, it is unlikely that more points would have significantly

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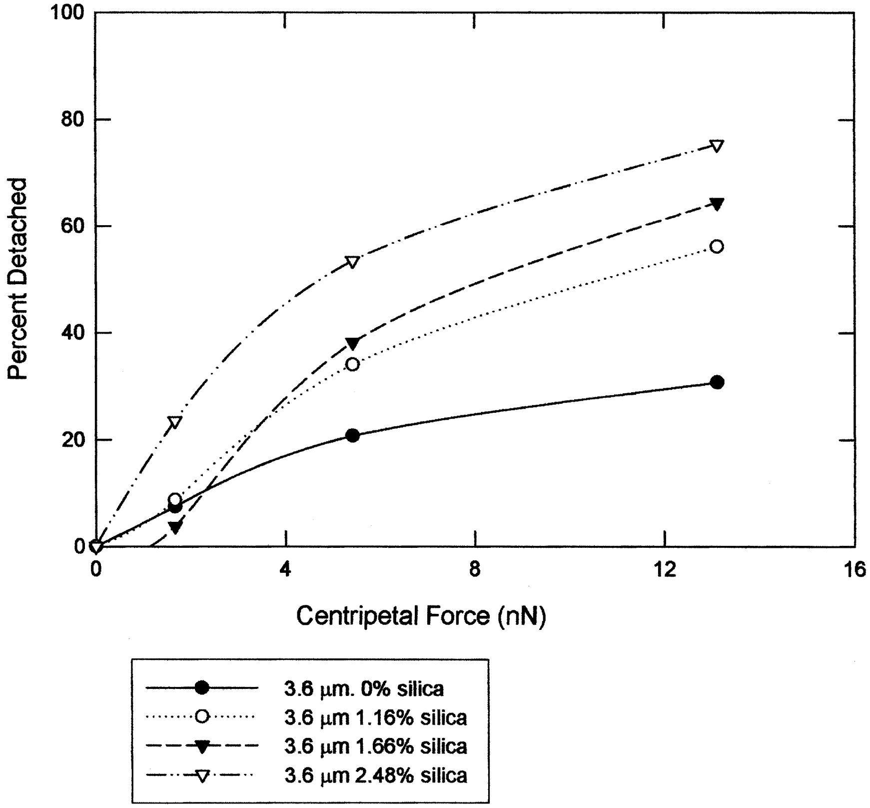
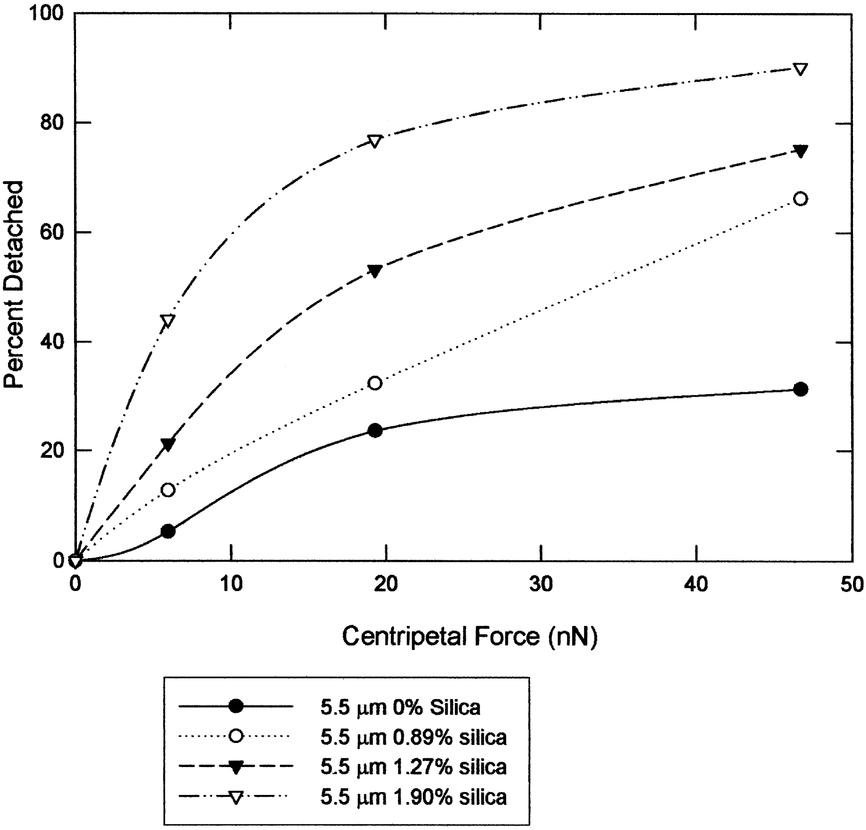


(a)

FIGURE 1 The percentage of particles detached as a function of the applied centripetal force for (a) 3.6 µm, (b) 5.5 µm, (c) 6.4 µm, (d) 6.6 µm, and (e) 8.5 µm diameter particles. (*Continued*).

altered the determination of detachment forces. It should be emphasized that, as previously discussed, the number-average diameter was used to calculate the mass of the particles and, therefore, the detachment force. This was done because the percent removed was determined by actually counting particles. Similarly, the charge per particle was also calculated using the number-average diameter and assuming that the particles were spherical with that diameter. As the actual mass of silica was, at most, less than 2½% of the particles, no corrections were made for the mass differences of surface-treated particles in calculating either their detachment force or their charge.



(b)

FIGURE 1 (*Continued*).

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The detachment force and particle charge are given in Table 2 for each particle listed in Table 1.

As is well known to electrophotographic scientists and engineers [17, 18], the addition of silica to the surface of toner particles reduces the forces needed to detach toner particles from a photoconductor. This effect is also noted in for each classification of particle used in this study, as seen in Figure 2.

As can be seen, the detachment force decreases monotonically with increasing silica concentration. The only instance where this did not appear to happen was with the 6.6 µm diameter particles with 0.75 wt% silica. In this case, the percentage of particles detached at a given centrifuge speed seemed very similar to what was observed

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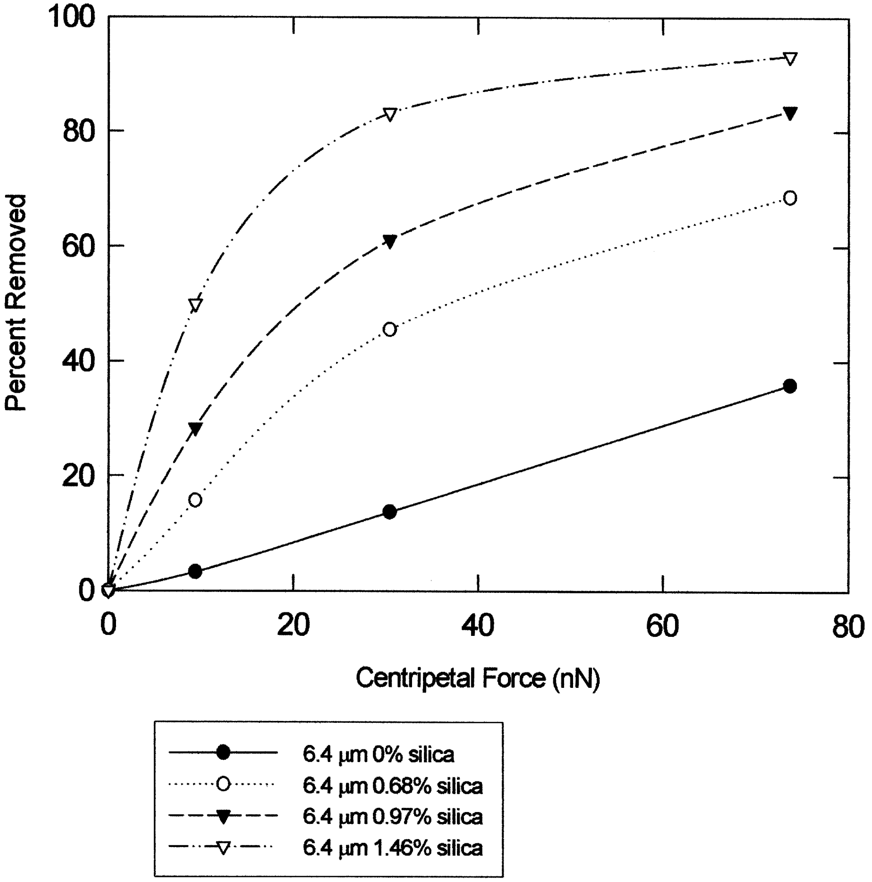

(c)

FIGURE 1 (*Continued*).

for the uncoated particles of this size. This suggests that, for some unknown reason, the silica may not have become attached to the surface of this particular set of particles during the blending to make this particular surface concentration. However, since this is not established and there is no positive reason to exclude the data obtained for this size particle with the nominal 0.75% silica, it is presented. However, this datum is a consistent outlier throughout this study and probably should be ignored.

As previously mentioned, it is well established that increasing the silica concentration on micrometer-size particles decreases the force

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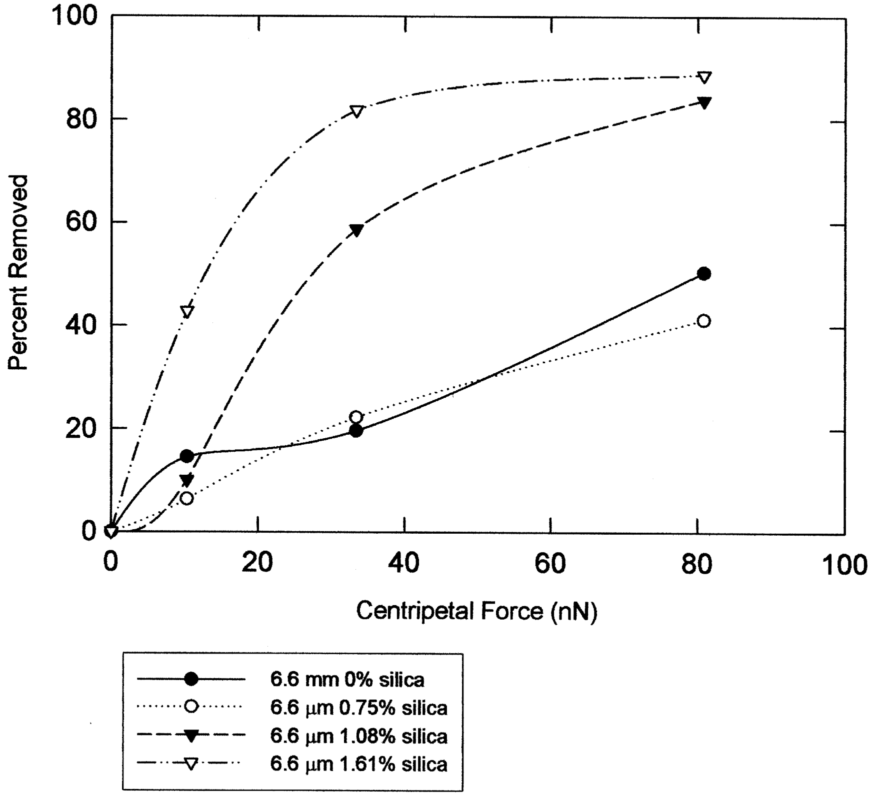

(d)

FIGURE 1 (*Continued*).

that needs to be applied to detach those particles from a substrate. However, the role played by the silica has been the subject of some dispute in the literature. Specifically, whether the presence of the silica alters the role of electrostatic or electrodynamic interactions has been the subject of controversy. Specifically, there are those who argue that silica effects the detachment force by altering the charge distribution of the particles. For example, Iimura *et al.* [17] attempted to explain their observations by invoking the charged-patch model of Hays [11]. Specifically, Iimura *et al.* argued that, by increasing the silica concentration, the number of sites upon which charge could reside would increase. This would result in a lower charge per site, assuming the net charge on the particle did not change, thereby reducing the charged

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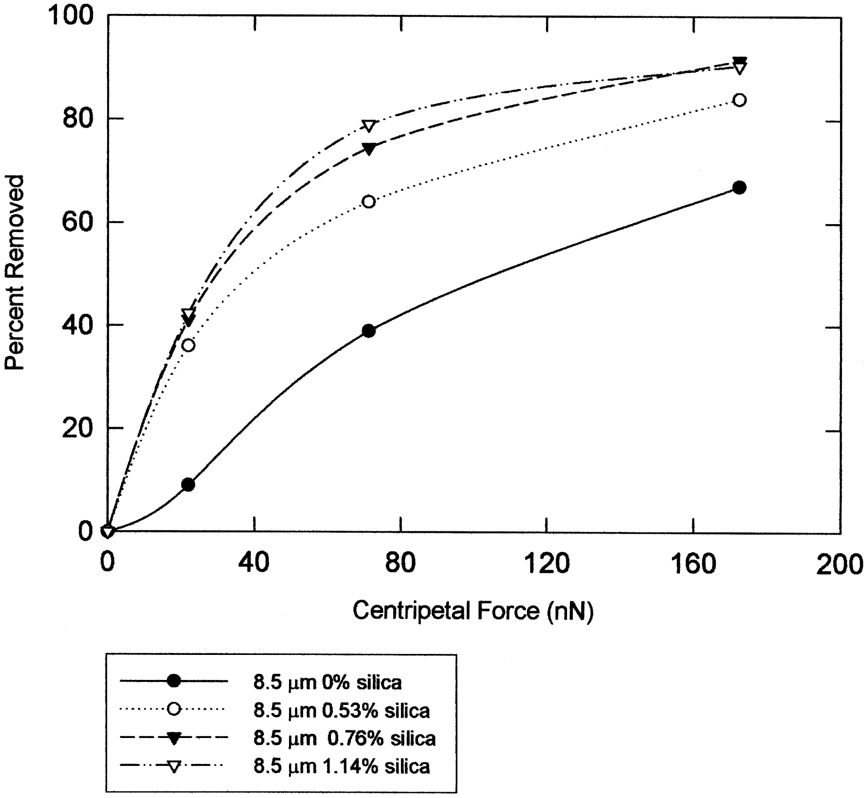

(e)

FIGURE 1 (*Continued*).

patch attraction. Unfortunately, it is not presently possible to measure the charge distribution on the surface of a toner particle. Moreover, how the aggregate charge over all the contacting sites would affect particle detachment is a more complicated problem than that assumed by Iimura *et al.* and a quantitative determination has not been made, nor are the results of such a calculation obvious.

Conversely, electrodynamic interactions, such as those giving rise to van der Waals forces, have also been invoked to explain the effect of silica. For example, Gady *et al.* argued that the presence of silica would decrease the effective particle radius by elevating the particle above the surface of the photoconductor. Since the range of van der Waals forces is of the order of a nanometer and the agglomerate diameter of the silica is of the order of 50 nm, the silica would, for all

TABLE 2 Detachment Force and Charge for Each Type of Particle

Sample number	Detachment force (nN)	q per particle (10^{-15} Coul)
1	*	−1.5
2	4.7	−2.7
3	8.3	−1.8
4	11.0	−1.2
5	*	−3.8
6	7.5	−5.6
7	17.5	−3.7
8	34.0	−3.3
9	*	−4.6
10	9.0	−6.4
11	21.0	−3.9
12	37.0	−2.8
13	80.0	−2.5
14	13.0	−9.0
15	27.0	−6.3
16	*	−1.3
17	105.0	−10.0
18	28.0	−10.8
19	30.0	−8.5
20	40.0	−6.1

*Could not remove at least half of the particles with the centrifuge.

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intents and purposes, place the main body of the particle at an infinite distance from the substrate. Accordingly, this would change from a simple particle–substrate adhesion problem to one of interactions between rough surfaces, as discussed theoretically by Fuller and Tabor [25] and experimentally by Schaefer *et al.* [26].

The role played by asperities in controlling the detachment force between particles and substrates is quite complex compared with the planar substrates considered in the paper by Fuller and Tabor [25]. In their model, Fuller and Tabor assumed a Gaussian distribution of asperity heights and postulated that contact between the smallest asperity and the mating surface would be the first to break. They did not have to consider the role played by the geometry of a particle. The role played by the asperities is greatly complicated even for spherical particles, as the radius of curvature of the particle also contributes to when the contact between an asperity and the substrate would be broken. For irregular particles, as is the case here, the effect of the asperities is, again, further complicated. Not only does one need to consider the shape of the particle and the size distribution of the asperities in determining the detachment force, but one needs to consider just how the asperities elevate the particle. Specifically, in the

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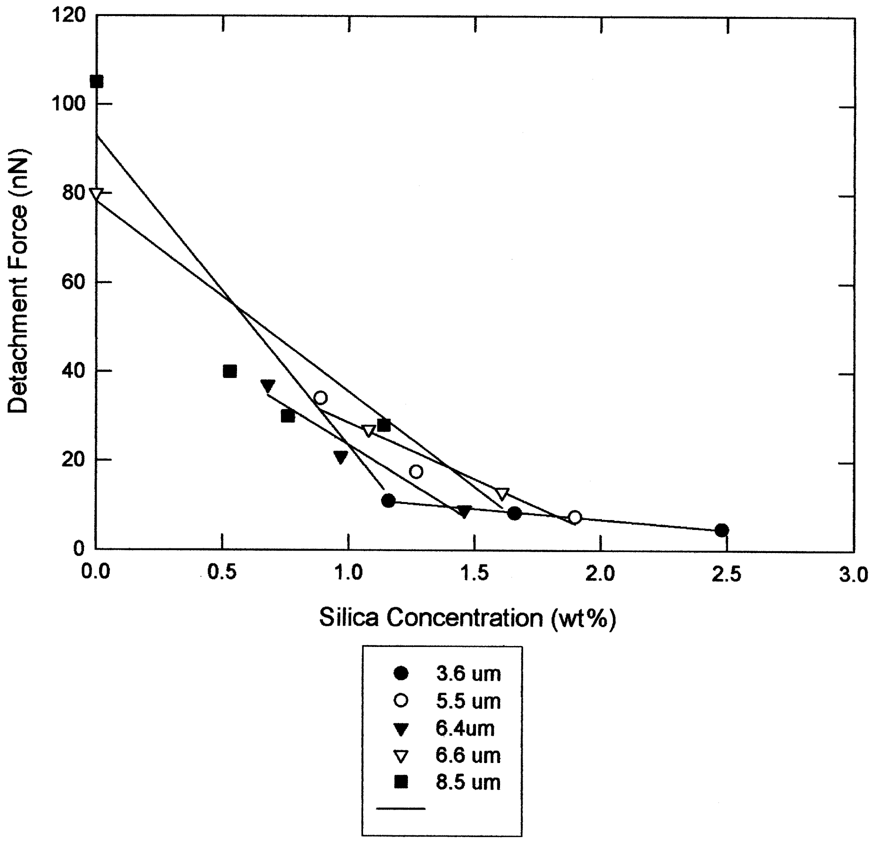

FIGURE 2 The detachment force as a function of silica concentration.

case of irregularly-shaped particles, the asperities can serve to pry the particle from the substrate without fully elevating the particle. In such a case, the contact between the particle and the substrate is not completely broken, but is simply reduced. The problem of calculating the detachment force in such a case has not yet been done. Intuitively, one might expect that, if the surface of the particle were flat and the asperities all were of the same size, the particle-to-substrate detachment force would be minimized if only three asperities, or, in this instance, silica particles, were present. Additional particles would merely serve to increase the number of contacts, thereby increasing the detachment force. However, the asperities created by the presence of the silica are not all the same size and, therefore, should be expected to detach separately, as discussed in the Fuller and Tabor model. Moreover, as the particles do not have flat surfaces, geometric effects arising from the shape of the particle confounding the role of the asperities must also be taken into account. Naturally, the particle itself has asperities even in the absence of the silica, and that further complicates adhesion. Finally, due to the irregular shape of the particles, the presence of the silica does not necessarily cause the particle itself to break contact with the substrate. Rather, the silica would more likely partially separate the particle from the surface as if the particle were being pried from the surface. As more silica particles are introduced, enhanced separation of the bulk of the particle from the substrate is achieved. The reader is referred elsewhere [27] for a more in-depth discussion of asperity effects. Suffice it to say, roughness remains an ongoing topic of adhesion-related research.

It might be reasonable to expect that the role of the silica in reducing particle adhesion might reach a limit with increasing silica concentration as the surface becomes coated with the silica. This, however, is more complicated than it might appear. The irregular shape of the particles causes the particle-to-substrate contact to be quite varied. The silica could elevate one portion of the particle without affecting the contact elsewhere. The silica particle heights would vary due to both size variations and curvature of the particle, resulting in further reduction of adhesion, as discussed by Fuller and Tabor [25]. Finally, as the silica concentration is increased, there is a probability that the silica would attach to other silica already on the particle, effectively altering the size of the silica particle and further complicating analysis.

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It might be argued that the decrease in the detachment force with increasing silica is due to the silica increasing the effective hardness of the particle. However, according to the JKR theory, the detachment force is independent of Young's modulus. It should be apparent from the preceding discussion that a quantitative theoretical understanding of the role(s) of van der Waals on particles that have been overcoated with nanometer-size particulate addenda is not presently possible. Similarly, without a method of precisely specifying the charge distribution on particles, it is not possible to calculate the role played by electrostatic charge patch forces. It is worthwhile to look for experimentally determined trends suggestive of either or both types of interactions.

Let us first examine the effects of charge on the force needed to detach the particles from the substrate. It should be noted that, in this experiment, particle charge was not controlled in the manner reported in a previous paper [28]. In the earlier paper, the particle charge was controlled by changing the triboelectric properties of the magnetic particles that were initially mixed with the particles of interest. At first, it was not possible to detach a significant portion of the particles used in that study. However, only after reducing the van der Waals forces with an application of zinc stearate upon the substrate, Rimai *et al.* [28] found that the detachment force depended upon the square of the particle charge, suggestive of an electrostatic image-force interaction between the particles and the substrate. However, in the absence of zinc stearate, the van der Waals forces appeared to dominate over the electrostatic forces.

In the present instance, variations in particle charge are due to changes in the silica concentration. As can be seen from Table 1, the change in q/m is not a monotonic function of the silica concentration. Rather, for every size particle, the magnitude of the charge-to-mass ratio initially decreases with increasing silica concentration and then starts to increase. The reason for this behavior is not presently understood. Suffice it to say, particle charge is definitely affected by the presence of silica and effects of the charge on the measured detachment force are confounded by the varying concentrations of the silica. Accordingly, any assumption regarding the effect of the silica simply spreading localized charge to more patches [17] would require experimental verification, which presently has not been accomplished.

Let us now examine the apparent effects of particle charge variations due to changes in silica concentration. As previously discussed, these effects on the particle detachment forces are confounded by the varying concentrations of silica. Thus, an analysis of the effects of charge variations on particle adhesion is more complicated in this situation than it would be if the charge were varied by other means. However, any trend in the detachment force observed while changing the charge by changing the silica concentration would shed light on the role of electrostatic interactions, especially as they relate to the effects of electrostatically charged patches, in the adhesion of particles with distinct asperities in general and surface-treated toners in particular. The dependence of the detachment force on the particle charge for the five different size particles used in this study is shown in Figure 3.

It might, from Figure 3, appear that the detachment force decreases monotonically with increasing charge for the 3.6 μm, 5.5 μm, and 6.4 μm diameter particles. However, such an appearance is not quite correct. In all three instances, the detachment force was higher than could be achieved with the ultracentrifuge at 0% silica and, therefore, could not be determined. However, in these instances, the charge of the particles with 0% silica was higher than in some cases involving

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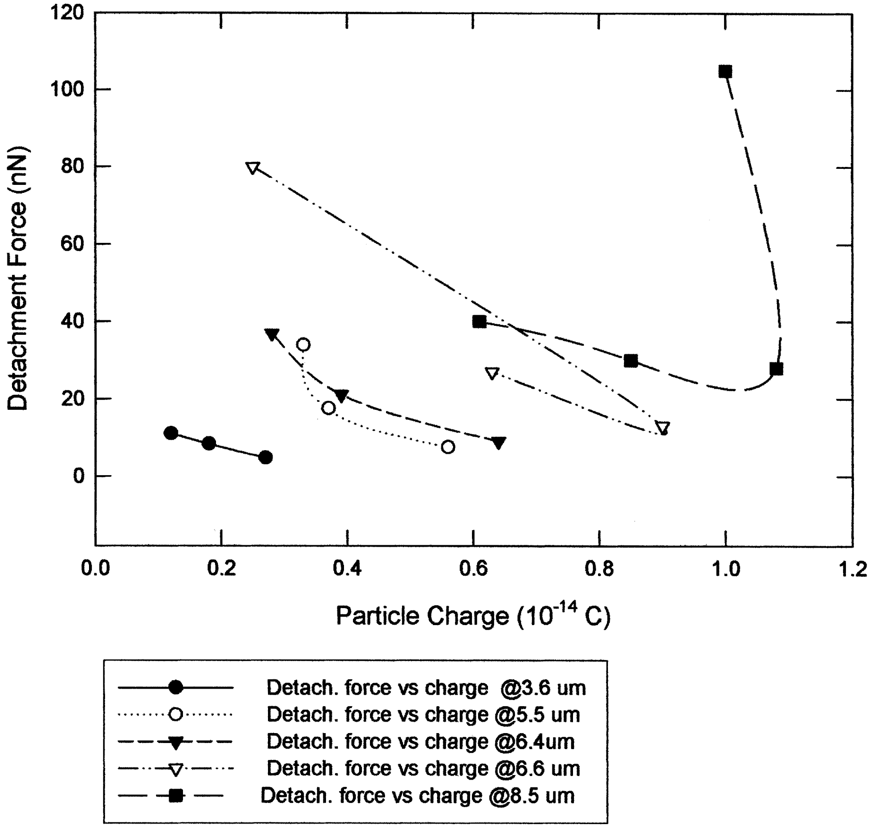

FIGURE 3 The detachment force as a function of particle charge.

the same size particles with silica present. If those data were to be included, it would be clear that the detachment force would exhibit no apparent functional dependence on particle charge. The complicated behavior of the detachment force as a function of charge is clearly seen by examining the curves of the 6.6 and 8.5 μm particles. Mathemaztically speaking, the lack of a unique value for the detachment force on particle charge means that the detachment force cannot even be considered a function of the particle charge. Physically speaking, this, of course, is nonsense, as it is obvious that electrostatic attraction has to contribute to the adhesion between the particles and the substrate. These results do suggest, however, that other confounding factors may dominate over the electrostatic attraction. Specifically, the effect of

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charge in this study is confounded by the variations of the silica concentrations.

To enhance further our understanding of the role of particle charge, it is worthwhile to consider the attractive, rather than just the detachment, force between the particles and substrate used in this study. To do this, let us first assume, as Hays [11] did, that a particle comprises a dielectric sphere with the charge uniformly distributed over its surface. (Subsequently, we will examine the case of localized charged patches.)

Furthermore, the substrate is treated as a grounded conductor, which would be a reasonable approximation for the substrate used in this study. In this case, the electrostatic attraction can be calculated using the method of images. The attractive force F_I due to the presence of such an image charge is given by

$$F_I = -\frac{\alpha}{4\pi\varepsilon_0}\left(\frac{q}{d}\right)^2, \tag{1}$$

where ε_0 is the permittivity of free space, q and d are the particle charge and diameter, respectively, and α is a polarization constant, whose value is between 1 and 2. The detachment forces are plotted as a function of the attractive force, calculated assuming that $\alpha = 1$, in Figure 4.

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As is apparent from Figure 4, the detachment force is almost independent of the electrostatic attraction. If there is any correlation, it is slightly negative. The one outlying datum, with a detachment force of 100 nN and an electrostatic attraction of approximately 27 nN, is the same outlier discussed earlier. While using a higher value for α would increase the calculated attractive force, it would not alter the measured detachment force. Accordingly, the shape of this curve would be unaltered if a different value of α were chosen.

If, on the other hand, it is assumed that the electrostatic attraction is dominated by localized charged patches rather than a constant surface charge density, the attractive force F_E should vary as [11]

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

where σ is the localized charged density and A_C is the contact area. It should be emphasized that the charge distribution on particles has not ever been measured. However, for the sake of present discussion, let us consider two possibilities. First, let us assume that the total charge varies directly with the surface charge density. This would be the case for either σ being constant, which is the case of a uniform charge

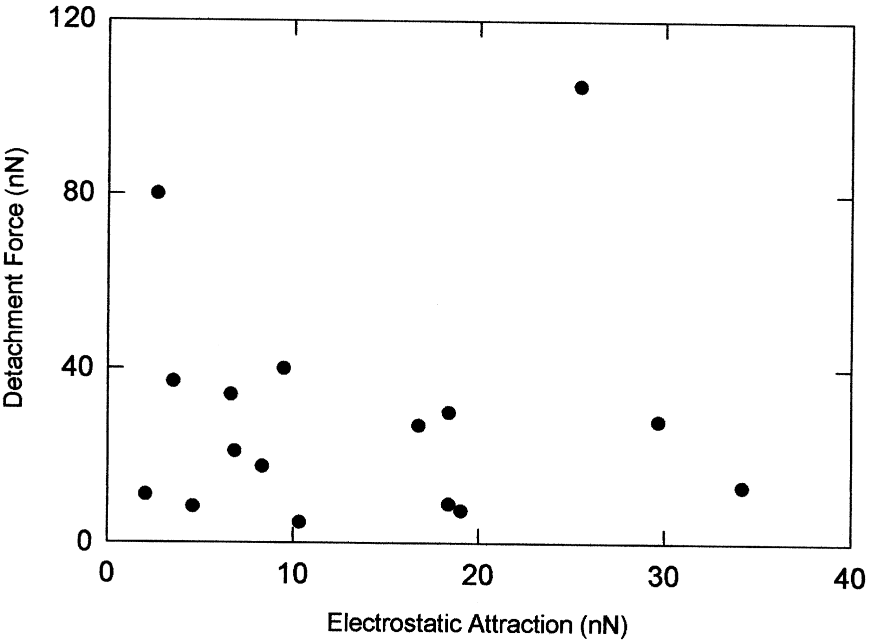

FIGURE 4 The detachment force as a function of the electrostatic attractive force.

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distribution, or σ being a function of position, which is a basic tenet of the charge patch model. In either instance, the total charge would simply be the integral of the surface charge density over the area of the particle. As such, the attractive force would be expected to scale with the square of the charge.

Alternatively, the function describing the surface-charge density may, itself, be a function of the amount of charge present. In other words, the form of the surface-charge density function may vary with the particle charge, *i.e.*, charge densities can vary for reasons other than simply the presence of high spots on the toner. An example where this is possible is with silica-coated toner particles, similar to the ones used in this study, in which the triboelectric properties of the toner and silica are different. If this were to occur, any assumption that the observed decrease in detachment force with increasing silica concentration arises from the presence of more localized patches that lower the localized charge per patch would be incorrect. In either case, if variations in electrostatic charge distribution with increasing silica concentration played a significant role in the adhesion of these particles, there should be some sort of scaling between the detachment and attractive forces. Again, as can be seen from Figure 4, no such scaling is apparent, suggesting that the role played by the silica in reducing particle adhesion is due to variations in other factors. These will be discussed forthwith.

Again, it should be emphasized that the experimental results reported herein should not be construed to mean that electrostatics does not play a significant role in particle adhesion under any circumstances. Rather, these results argue that asperities on particles in this size-range do not appreciably affect adhesion by redistributing the charge on the particles. Rather, the silica-generated asperities affect particle adhesion by nonelectrostatic interactions. One such interaction could arise from surface forces such as those arising from van der Waals interactions.

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According to the JKR theory [29], the force F_{detach} needed to detach a spherical particle from a planar substrate is given by

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

where w_A represents the work of adhesion and R the particle radius. Assuming that w_A does not vary for a series of spherical particles, the ratio of the detachment force to particle radius should be constant and not depend on any other factors such as particle charge.

Complications are introduced when one has to consider the effects of asperities, such as those generated by the silica on the surface of the particles [27]. Specifically, the detachment force does not simply scale as the ratio of the asperity-to-particle radii times the number of contacts. Rather, as discussed by Fuller and Tabor [25], the detachment force generally would be lower due to the statistical variation in the size of the contacts, causing the asperity-to-substrate contacts to break sequentially rather than simultaneously. In other words, to separate two materials, it is only necessary to exert a sufficient force to break the contacts corresponding to the highest asperities. This would be the peak detachment force needed, as it represents the greatest number of asperity contacts. It should be noted that the model proposed by Fuller and Tabor focused on the effect of asperities on the detachment force of two planes, not the detachment force between a particle and a plane. The latter is more complicated because the curvature of the particle would combine with the number and size distribution of the asperities in determining the detachment force. This problem has not yet been solved.

As is apparent from the preceding discussion, the effect of asperities created by the silica on the adhesion of irregularly-shaped particles to a planar substrate is a complex, unsolved problem. However, in order to gain some understanding of the underlying mechanism giving rise to the adhesion of such particles, it is worthwhile to go back to the basic JKR model. As is apparent from Equation (3), the detachment force of an ideal, spherical particle in which adhesion is dominated by van der Waals interaction varies linearly with the particle radius. Accordingly, it is reasonable to plot the detachment force as a function of particle radius, at constant surface silica concentration, to see if the present system can be approximated by the JKR model, which had been derived assuming that the particles were spherical. Accordingly, Figure 5 shows the detachment force as a function of the number-average toner diameter at constant surface silica concentration.

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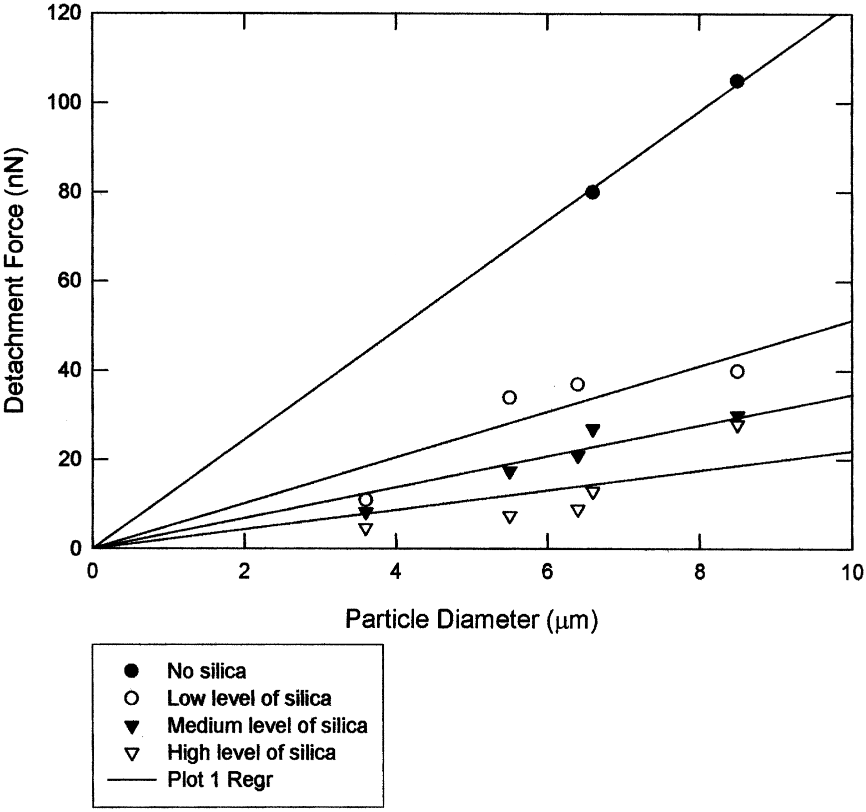

FIGURE 5 The detachment force as a function of particle diameter at constant surface silica coverage.

As can be seen from this figure, the detachment force appears to increase monotonically with increasing particle diameter for each silica surface concentration. Moreover, as can be seen from the least squares fit line through each set of data, the detachment force appears to vary linearly with particle diameter. The work of adhesion for the particles without silica, calculated from the slope of the curve in Figure 5 using Equation (3), was found to be approximately 5 ergs/cm^2. This result is comparable with that reported elsewhere for monodisperse beads [19] and is a reasonable value for these materials, especially when one takes into account the irregular shape of the particles.

As a digression, it is worthwhile to discuss the ramifications to the present analysis if the DMT [30], rather than the JKR, model were to be used to analyze the effect of adhesion on the particles caused by the presence of the nanometer-size silica. As discussed elsewhere [31], the work of adhesion, as predicted by the DMT model, is only 3/4 that predicted by the JKR model at constant detachment force. This, obviously, would not amount to a significant discrepancy in the present study. Maugis [32] also considered the effect of asperities on the adhesion of two planar substrates. His work differed from the earlier work of Fuller and Tabor [25] in that Maugis assumed the validity of the DMT theory, whereas Fuller and Tabor used the JKR formalism. Maugis found that there was little difference between the detachment forces predicted by the two theories except when the ratio of the standard deviation of the asperity to the penetration depth approached zero. At that point, the Maugis model predicted a detachment force that could actually exceed that for two atomically smooth planes. Suffice to say, it would appear that either model would be adequate in analyzing the present results.

As previously discussed, for ideal spherical particles for which adhesion is dominated by van der Waals interactions, the ratio of the detachment force to the particle diameter should be constant. For irregularly shaped particles, such as those formed by grinding, the theoretical relationship between the particle diameter and the detachment force is not intuitively obvious. This is even more so when the particle has asperities such as those introduced by the presence of silica on the surface of the particle. To that extent, the linear relationships shown in Figure 5 for each set of particles at constant surface coverage by the silica are, perhaps, somewhat surprising. Moreover, these results suggest that the effect of asperities on particle adhesion may be significantly more complicated than that between two planes, as discussed in the models of Fuller and Tabor [25] and Maugis [32]. This is most likely because the silica can “wedge up” the particle, thereby reducing the van der Waals interactions, at the

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same time that it changes the orientation and contact of the particle to the substrate. In other words, the effect of the silica, or more generally asperities on particle adhesion, may be more complicated than modeling of the contact between a substrate and an irregularly shaped particle that had been coated with silica and is beyond the scope of this article.

Figure 6 shows the detachment force, normalized to the particle radius, as a function of the surface concentration of the silica. It is readily apparent from this figure that the normalized detachment force tends to form four clusters with one cluster for each surface concentration of silica. The scatter within each cluster presumably comes from the statistical variations in particle shape and silica coverage within each sample. That the normalized detachment force should be constant is not intuitively obvious. This is because the larger particles contain more silica on their surfaces. As a result, it would be expected that the standard deviation about the mean diameter of the silica should decrease with increasing silica concentration. One might expect this, based on either the Fuller-Tabor or Maugis model

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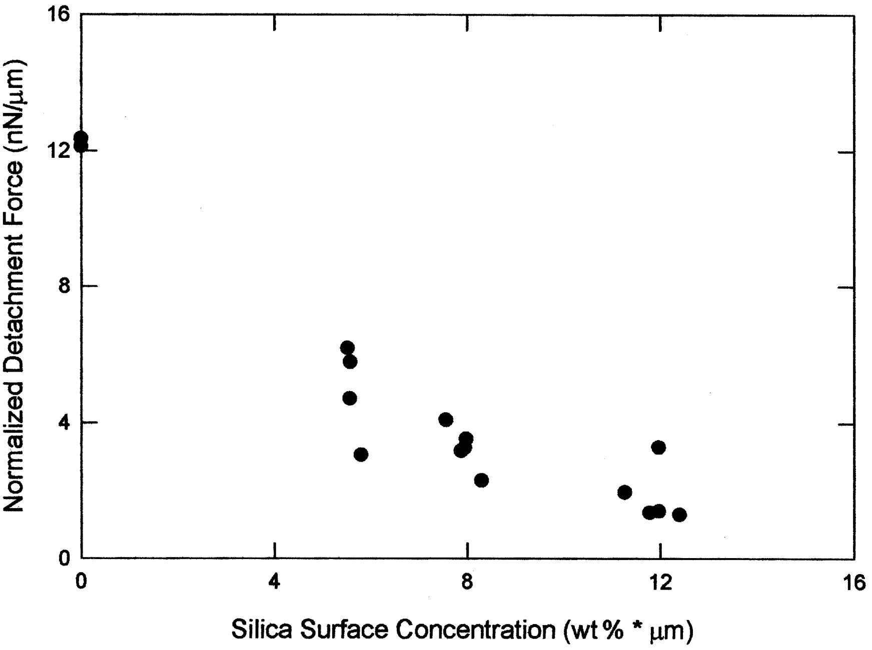

FIGURE 6 The normalized detachment force as a function of the surface concentration of silica.

of asperity adhesion, to cause the detachment force to increase with increasing particle size. Again, there might be differences between the role of asperities on particle adhesion and their corresponding effects on the adhesion of parallel planes. Further mathematical analysis and modeling appears necessary to resolve these apparent discrepancies.

CONCLUSIONS

The force needed to separate irregularly shaped, ground particles in the micrometer-size range from a planar polyester substrate was determined using ultracentrifugation. In most cases, asperities were introduced on the surfaces of the particles by coating the particles with nanometer-size silica particles. The detachment force was then determined as a function of particle size, electrical charge, and silica concentration. The detachment force was found to increase with particle diameter and decreasing silica concentration. The correlation between the detachment force and the particle charge was weak and, if anything, tended to decrease with increasing charge. It should be noted that the charge was not an independent variable, but, rather, was confounded by the silica concentration. It was also found that the detachment force, normalized to the particle diameter, appeared to be constant at a given surface area coverage of silica and to decrease with increasing silica concentration.

The results obtained in this study suggest that asperities in general, and silica in particular, decrease particle adhesion for particles in this size range by reducing the van der Waals interactions rather than by redistributing the charge *via* the charged-patch model.

There is still much work that needs to be done in order to understand fully the interactions that give rise to the adhesion of silica-treated particles. For example, these experimental determinations hold for particles having diameters between about 3.6 μm and 8.5 μm on a polymeric substrate that was carefully prepared to exclude the presence of low surface energy or release agents such as silicone oils, zinc stearate, or Teflon®. Moreover, the charge range was relatively restricted, although realistically chosen to reflect the charges commonly obtained on toner particles. Finally, only one type of silica was used in this study, rather than studying the effects obtained with various functional groups appended to the silica. In addition, other types of particulate addenda, such as strontium or barium titanate, commonly used in the formulation of toners, were also not studied. Measurements of the effects of variations in these parameters would be valuable and straightforward to perform.

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Perhaps of more value (and more difficulty) are measurements that would quantitatively map the charge distribution on the surface of particles. Determinations of the particle–substrate contact as a function of silica concentration would also be of value. Finally, the development of a holistic model of how the silica particles charge and interact with both the particles and the substrate would be of immense importance in understanding the adhesion of surface-treated particles and would help shed light on the role played by asperities in particle adhesion.

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