Letter to the Editor
Comments on "Adhesion of Silica-Coated Toner Particles to Bisphenol-A Polycarbonate Films"

The paper "Adhesion of Silica-Coated Toner Particles to Bisphenol-A Polycarbonate Films" by Dejesus, Rimai, Stelter, Tombs and Weiss [J.Imaging Sci. Technol. 52(1), 010503–010503–6 (2008)] is among the latest in a large group of publications in journals and book chapters from Rimai and co-workers claiming that adhesion of toner is due predominantly to van der Waals rather than electrostatic forces. In the present work the authors measured the adhesion force using a centrifuge. The average value remained constant as the polymer thickness separating the toner and the ground plane is varied. Since they claim that the adhesion should decrease with separation if electrostatics is dominant assuming sufficient toner spacing, van der Waals forces must logically be the main contributor. Although this argument appears sound, we suggest a more cautious take on the conclusion.

Adhesion of toner has been studied extensively for a half century. Throughout this period much of the discussion centered on whether van der Waals or electrostatic forces dominate. Among the earlier results only one group supplied proof that van der Waals forces are important. This was done by Mastrangelo[1] and his colleagues. The other often cited work is that of Krupp and co-workers[2–4] where the theory behind van der Waals forces was discussed.[2,3] In their one experimental article, adhesion of toner to selenium photoconductor, was described.[4] Here the authors claimed verification of their van der Waals thesis. But their centrifuge data actually showed that the adhesion was a strong function of toner charge, typical of electrostatic dominance. The authors' explanation for the dependence centered on asperities on the toner particles, which they surmised must have crushed when the toner was higher charged. Hence these toners had the contact radius of the particle rather than that of the asperities. By judicious choice of radii, they even showed calculated values matching their very limited experimental data. To the neutral observer, however, this argument hardly supports van der Waals. Rather, it appeared that the authors maintained their stand despite strong evidence to the contrary. Indeed it is now tacitly assumed by all, including Rimai and his colleagues,[5] that such dependence would likely indicate a strong electrostatic component.

Shortly after Krupp's papers, Donald and Watson countered that toner adhesion is mainly electrostatic with little van der Waals contribution.[6,7] They examined toner on carrier beads and found that centrifuge data were strongly dependent on toner charge for a wide range of values. They further showed that toner adhesion can be significantly influenced by an electric field, a feature not possible with van der Waals domination.

Goel and Spencer did both theoretical and experimental comparisons of toner.[8] Their centrifuge results showed that electrostatic forces overwhelmed van der Waals for 18–47 μm toner. At the next smaller size, 3.6 μm, a van der Waals contribution at the lowest charge level seemed evident. But during that era 3.6 μm was considered "toner fine," which likely had a composition that varied widely and deviated from that of the average toner. Thus a low average did not guarantee that individual particles had low charge of the same sign. Since the adhesion result for the 3.6 μm was unreliable, a conclusion one can draw from Goel and Spencer is that any van der Waals contribution had not been conclusively demonstrated.

The one credible case for van der Waals was made by Mastrangelo.[1] Using a centrifuge, he examined the force necessary to remove toner of varying charge. Their Fig. 5 is especially striking. Here the charge increased by more than an order of magnitude, but the adhesion force at 50% removal increased to no more than 1.6× that at the low charge. He did a number of other supporting measurements as well. So van der Waals dominance seemed possible, at least for the conditions he tested. But the actual situation is much more tenuous.

We had become interested in the toner adhesion problem just as Dr. Mastrangelo changed to another field within IBM. He was kind enough to give us his centrifuge and all related equipment. So in fact we used his rotor, his sandwich sample holders, and even cellulose tubes that he described in detail. We had fully expected to duplicate his trends and support the van der Waals thesis. But we quickly found that this setup significantly distorted the results. The rotor and other necessary parts were remade with the problem removed for all our adhesion publications.[9–11] Our results strongly supported Donald's electrostatic thesis and the suggestion by Hays that toner particles must be nonuniformly charged.[12] We found no noticeable contribution from van der Waals forces. In our first adhesion publication[9] we used the line, "Toner adhesion forces were measured with a method similar to that of Mastrangelo using a Beckman Airfuge® ultracentrifuge." This statement was intentionally vague because we felt no need to mention Mastrangelo's oversight. Indeed our results appeared so overwhelmingly convincing for electrostatics domination that further comments on papers supporting van der Waals seemed superfluous.

While many early, publishable adhesion studies used the centrifuge, other methods were tried as well. Some of these

were mentioned in Goel and Spencer.[8] We ourselves found that looking directly at toner interactions was immensely useful for "seeing" adhesion. The technique was described in an unrelated paper[13] where we used a video camera to observe toner movement from a conductive magnetic brush. A permanent magnet holding the carrier chains could be dragged across an indium tin oxide (ITO)-coated glass or moved in and out using micromanipulators. The camera recorded the event from the back side. We mentioned a number of observations including toner flying to the glass under developing conditions.[13] These were recently confirmed in experiments and computer simulations by Thompson and co-workers.[14]

The toner adhesion observations, which had not been previously described, were made using an insulative magnetic brush with 20 μm toner. At a low development field, removing toner was quite difficult, unlike for the conductive magnetic brush discussed above. As a toner particle on the carrier was dragged along the ITO surface, nothing happened except on rare occasions. If a particle was slightly displaced from the bead, one of two things occurred. One, the toner went straight back to the carrier. Two, the toner particle rotated so that the side originally facing the bead headed toward the ITO ended up flat against it and was thus "developed." This was consistently seen with different carrier chains and toner particles. If one believes in van der Waals, there is no asymmetry from one surface to an adjacent one. Hence no rotation of the toner should be necessary for development once the toner is loosened from the carrier bead.

The result was just as stunning if the voltage was reversed. Here we tried to remove toner from the ITO using the voltage. A toner particle can be pushed by the bead from any direction, and the particle typically got moved along without being picked up. Occasionally the toner was slightly lifted from the ITO. Then if the toner rotates so the surface that used to be on the ITO turned all the way to the bead, it stuck to the bead and was thus removed from the ITO. Without rotation, the particle went back to the ITO. Sometimes toner turned partially so that, say, only one corner that used to be on the ITO was against the bead surface. In that case the toner stuck on both the ITO and the bead and could be dragged along indefinitely. Where the particle ended up depended on which way it ultimately turned.

The most logical conclusion is that the most highly charged region always faces the photoconductor or other surfaces on which the particle sticks. Our observations are consistent with the concept presented in Fig. 6 and the (SEM) results in Fig. 7 of Ref. 9. More interestingly we note that the carrier beads used in the video studies were not highly loaded with toner. This means that the charging pattern was close to that of Fig. 6 bottom. This speaks volumes on the nature of toner adhesion. While toner reorientation does not in itself suggest that van der Waals forces are insignificant, it certainly confirms the patch hypothesis of charging, which is a linchpin of the electrostatic adhesion model. This seeming proof of patch charging also renders moot the contention that adhesion must be due to van der Waals because the measured force is too large to be explained by electrostatic forces on a uniformly charged particle. For a patch distribution, the expected electrostatic attraction is more than sufficient to cover the experimental results.[9] Incidentally, our video observations readily explain the need for contact in toner transfer, an effect Rimai and co-workers attributed to van der Waals forces.[15]

If we discount the Mastrangelo[1] result and Krupp's[4] conclusion, all the early centrifuge toner papers point to electrostatic adhesion as essentially dominant. Recent advances in toner fabrication and the move to smaller particle could change that picture. But, aside from the publications from Rimai and co-workers, newer work by Takeuchi[16] and Iimura[17] generally finds the same tendency for electrostatics. They actually see a likely van der Waals contribution, but its effect is readily swamped by the usual charge on the particle. Iimura showed for a 9 μm bare conventional toner that the adhesion is nearly five times higher for a 20 μC/g charge (470 nN) compared to the uncharged (0 net charge) version (101 nN).[17] For sufficient (25%) surface extraparticulate coverage, the uncharged adhesion drops to 10 nN. Takeuchi[16] found adhesion for bare spherical 10 μm toner to be just 80 nN at 10 μC/g. In contrast Rimai suggested that the adhesion force should be about 1100 nN for similar size uncharged, bare conventional toner and has experimental data confirming this.[5,18] That is an order of magnitude higher than the estimates of the other two investigators who used different centrifuges but came up with similar results. With sufficient extraparticulates, Rimai found forces as low as 39 nN for 2% silica-coated particles.[18]

Extraparticulates can significantly suppress the van der Waals component. Using electric field detachment measurements, Hays and Feng[19] calculated a non-electrostatic force contribution of $\sim$1 nN for 11.4 μm ion charged toner deposited on a conductive substrate. In similar measurements, Hays and Sheflin[20] reported a non-electrostatic force of only $\sim$2 nN for 8.3 μm toner with surface additives. The question, however, is whether van der Waals can ever be important. This returns the focus to bare toners.

Back when toner adhesion was of significant interest to the electrophotographic community, the experiments were always somewhat ambiguous due to toner limitations. Conventional toners are irregular and rough, making it impossible to know the exact contact area or radius. The size spread was large even after classification. The blending of multiple components in the melt mix resulted in surface compositions that could vary after toner fabrication. Hence the charging was expected to have a wide spread among particles. Toner adhesion was shown to be very strongly dependent on toner charge by multiple groups of workers. Indirect proof was offered for the charge patch in Fig. 7.[9] Yet sufficient hand waving was often needed to quantitatively explain the measured forces. That left wiggle room for those who believe in van der Waals. But of course the latter proponents had the same problem in that much hand waving was also needed to support their case because the possible contact radius had a wide range.

Today the same problem remains for quantitatively proving electrostatic dominance since the charge magnitude and location cannot readily be determined for individual toner particles in an ensemble. On the other hand, the definitive experiments for the van der Waals case can actually be done. With the advent of chemical toners, spherical particles with uniform surfaces can be made if desired.[21] Rimai and co-workers have relied extensively on the Johnson–Kendall–Roberts (JKR) equation[22]

$$F_S = -\frac{3}{2}\omega_A \pi R,$$

where ω_A depends only on the surface free energies of the toner, photoconductor (or relevant surface) and the interfacial energy. R is the particle radius. Since the JKR equation has no adjustable parameters, the adhesion force should be exactly the same for all round particles of the same size. Furthermore, the 1100 nN has been repeatedly cited for particles in this size range. To prove that van der Waals is the dominant force, all one needs to do is to show that adhesion force is a δ function at 1100 nN with minimal spread for all particles irrespective of charge level using such round particles, which are now available.

We can gauge the prospects of a successful confirmation by looking at his already published centrifuge data. But there is more. Rimai co-authored a paper where the JKR theory was discussed and actually tested using an atomic force microscope (AFM).[23] There 8 μm spherical glass, tin, and polystyrene particles on atomically flat pyrolitic graphite and mica surfaces were studied. Polystyrene can be considered a model toner. The results showed the JKR theory gave adhesion forces roughly 50 times the actual measured ones. For the polystyrene the ratio is at least 68. To explain the large discrepancy, the particle surfaces were profiled and found to have asperities. By applying the asperity radii, the JKR theory was found to be just three times that of the measured but the remaining gap could not be closed.

The casual observer may wonder why Rimai does not quote an expected van der Waals contribution of 400 nN rather than 1100 nN since JKR seems to overestimate the adhesion force by a factor of 3. But that misses the bigger picture. The particles tested in Ref. 23 were chosen to be close to perfectly smooth spheres. There is no reason to believe that different toners fabricated by various techniques over several decades should all have surfaces that are significantly smoother atomically than the polystyrene used for the AFM test. At most one may guess a comparable smoothness. So for real-life particles the JKR theory actually overestimates the van der Waals contributions by around 50 times under the best circumstances. This means that the van der Waals contribution is likely to be closer to 20 nN rather than 1100 nN. Indeed, 20 nN was the value obtained by Rimai and co-workers for adhesion of a 7 μm polystyrene sphere using AFM[24] in a paper published before Ref. 23. They also found that a smaller 5 μm polystyrene sphere had an adhesion of 100 nN, hardly an endorsement of JKR's R dependence and nowhere near 1100 nN; 100 nN is in line with Takeuchi[16] and Iimura[17] for slightly charged and 0 net charge toner, respectively.

Despite overwhelming evidence to the contrary in Refs. 23 and 24, Rimai still persists on two basic points about van der Waals forces. First, toner is sufficiently smooth and the nominal radius can be used to calculate the van der Waals contribution. Second, the JKR theory correctly finds this value. The case was detailed in a recent publication.[25] But the question is why. If all toners are essentially atomically smooth (but no smoother than the spherical polystyrene in Ref. 23) in his view, then the JKR theory must be wrong by nearly two orders of magnitude. Just because something is in print does not make it true. If he insists on using the asperity argument for the polystyrene, then he should accept the same for toner. In that case the van der Waals contribution is much smaller even assuming JKR. Maybe Rimai had to account for the large force measured from his centrifuge even though his values are so much larger than those obtained by so many others for low charge toner. But centrifuge results are not infallible as we found with Mastrangelo.

Perhaps we can anticipate another line of argument. In Ref. 24 Rimai and co-workers hinted that the 20 nN adhesion force was likely low compared to other measurements, presumably centrifuge, because of the short contact time of several seconds compared to measurements that take much longer. But the residence time for toner on photoconductor or transfer belt is typically less than several seconds. Hence no case can be made for claiming that his centrifuge technique, with a much longer measurement time, should be more relevant for determining toner adhesion during operation of an electrophotographic engine.

The analysis above suggests little independent support for the van der Waals thesis and plenty of opposing evidence, including those from Rimai's own publications. That leaves just some of Rimai's work in its defense. The neutral observer must be wondering about the strength of this evidence. It is beyond the intent of this letter to examine his large body of work other than to point out a few relevant ones. Nevertheless, we can perhaps get some idea of their quality based on the present paper. Here half of its experimental data centered on considering the effect of corona charging the dielectric on the toner adhesion force. By the authors' own admission, a parallel plate capacitor has no electric fields outside. But they suggested non-uniformities in the deposited charge distribution could help eject the toner if adhesion were electrostatic. But unless the distribution is very non-uniform, there would have no effect once the toner is moved off the dielectric by much more than the average spacing between the charges, around 7 nm at the higher 500 V. Since the countercharge is on the ground plane 4.5 μm away according to the authors, the difference in electrostatic adhesion between a uniformly charged 7.1 μm toner being on the surface and even 20 nm farther away is under 2%, much less than the experimental uncertainty.

Even more disconcerting is the claim of a non-uniform charge distribution on the polycarbonate when Rimai continuously argues against non-uniformity of charge on the toner. The toner charging process is inherently non-uniform due to the specific contact needed with carrier beads or other surfaces to tribocharge. Corona charging is inherently more uniform because it is a random, in-filling process depositing charge an average several nm apart. Even taking the most optimistic scenario of similar non-uniform distributions for both toner and surface, the higher charged regions of the toner would certainly avoid the more charged surface areas when the toner was being deposited if stray fields were actually important. So there would unlikely be any enhancement of rejecting forces. Hence these data cannot prove or disprove the electrostatics hypothesis, making half the experimental section irrelevant.

We have compared the case for van der Waals versus electrostatic domination in toner adhesion and found that essentially all results point to electrostatics aside from Rimai's work. While there appears to be some support for van der Waals in the present publication, we believe such a conclusion is not warranted based on the totality of the available evidence. Nevertheless, we have indicated a path for Rimai to prove his case with further experiments. For another perspective we suggest the recent comprehensive comparison of the two forces on powder adhesion by Feng and Hays.[26]

REFERENCES

[1] C. J. Mastrangelo, Photograph. Sci. Eng. **26**, 194 (1982).
[2] H. Krupp, Adv. Colloid Interface Sci. **1**, 111 (1967).
[3] H. Krupp and G. Sperling, J. Appl. Phys. **37**, 4176 (1966).
[4] W. Kottler, H. Krupp, and H. Rabenhorst, Z. Angew. Phys. **24**, 219 (1968).
[5] D. S. Rimai, M. Ezenyilimba, W. K. Goebel, S. Cormier, and D. J. Quesnel, J. Imaging Sci. Technol. **46**, 200 (2002).
[6] D. K. Donald and P. K. Watson, Photograph. Sci. Eng. **14**, 36 (1970).
[7] D. K. Donald and P. K. Watson, IEEE Trans. Electron Devices **ED-19**, 458 (1972).
[8] N. S. Goel and P. R. Spencer, Polym. Sci. Technol. **9B**, 763 (1975).
[9] M. H. Lee and J. Ayala, Acta Protozool. **11**, 79 (1985).
[10] M. H. Lee and A. B. Jaffe, in *Particles on Surfaces*, edited by K. L. Mittal (Plenum, New York, 1988), pp. 169–178.
[11] M. H. Lee, Curr. Appl. Phys. **16**, 238 (1985).
[12] D. A. Hays, Photograph. Sci. Eng. **22**, 232 (1978).
[13] M. H. Lee and G. Beardsley, J. Imaging Technol. **13**, 29 (1987).
[14] M. D. Thompson, P. W. Morehouse, P. Ramesh, and G. W. Shaw, *Proc. IS&T's NIP23: Inter. Conf. on Digital Printing Technol.* (IS&T, Springfield, VA 2007), pp. 48–52.
[15] G. Wright, T. N. Tombs, A. Chowdry, D. S. Weiss, and D. S. Rimai, J. Imaging Sci. Technol. **49**, 531 (2005).
[16] M. Takeuchi, K. Noguchi, M. Anzai, and R. Kojima, *Proc. IS&T's 11th Inter. Cong. on Adv. in Non-Impact Printing Technol.*, (IS&T, Springfield, VA 1995), pp. 169–172.
[17] H. Iimura, H. Kurosu, and T. Yamaguchi, *Proc. IS&T's NIP15: Inter. Conf. on Digital Printing Technol.* (IS&T, Springfield, VA 1999), pp. 535–538.
[18] B. Gady, D. J. Quesnel, D. S. Rimai, S. Leone, and P. Alexandrovich, J. Imaging Sci. Technol. **43**, 289 (1999).
[19] D. A. Hays and J. Q. Feng, *Electrostatics 2003*, Inst. Phys. Conf. Ser. (IoP, Bristol, 2004), Vol. **178**, pp. 77–82.
[20] D. A. Hays and J. C. Sheflin, J. Electrost. **63**, 687 (2005).
[21] C. K. Hong, M. Y. Cheong, Y. Shin, and K.-Y. Yon, *Proc. IS&T's NIP22: Inter. Conf. on Digital Printing Technol.* (IS&T, Springfield, VA, 2006), pp. 184–187.
[22] K. L. Johnson, K. Kendall, and A. D. Roberts, Proc. R. Soc. London, Ser. A **324**, 301 (1971).
[23] D. M. Schaefer, M. Carpenter, B. Gady, R. Reifenberger, L. P. Demejo, and D. S. Rimai, J. Adhes. Sci. Technol. **9**, 1049 (1995).
[24] D. M. Schaefer, M. Carpenter, R. Reifenberger, L. P. Demejo, and D. S. Rimai, J. Adhes. Sci. Technol. **8**, 197 (1994).
[25] D. S. Rimai, D. S. Weiss, and D. J. Quesnel, J. Adhes. Sci. Technol. **17**, 917 (2003).
[26] J. Q. Feng and D. A. Hays, Powder Technol. **135–136**, 65 (2003).

—M. Lee