ADHESIVE FORMULATIONS UTILIZING MICROSPHERES FOR HIGH ADHESION BUT LONG-TERM REMOVABLE APPLICATIONS

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Abstract

Water-borne microsphere adhesive technology is seeing a boom in the pressure sensitive adhesive (PSA) market as technologies, such as variable information linerless labels, logistics, and removable wallpapers and graphics are seeing CAGRs (compound annual growth rate) approaching double digits. Microspheres are much larger in size than typical water-borne emulsions, which allow them to be almost infinitely removable due to the low contact area between the sphere and the substrate. However, microspheres have very low tack and peel adhesion, making them unsuitable for applications requiring more adhesion. Microspheres can be used in adhesive formulations meet these demanding applications because, while the adhesive generally needs to be aggressive in terms of tack and peel adhesion, it also must maintain clean removability long term. Additionally, in self-wound constructions, the microspheres are needed to aid in facile release from the release coating. Understanding the interactions between the microspheres and other formulations components, including emulsion PSA binders, is critical for making successful formulations for these demanding applications and will be explored.

I. Introduction

Acrylic microsphere technology is heavily utilized when long-term, ultra-clean removability is needed for a given application.[1] A key difference between an acrylic microsphere adhesive and an acrylic emulsion adhesive is the particle size.[2] The particle size of a microsphere is generally between 10 and 50 µm whereas a standard emulsion has a particle size in the 200-800 nm range.[2] The large particle size of the microspheres lends the adhesive unique properties, such as decreased contact area with the binding substrate limiting adhesion and increasing removability, elastic deformation of the sphere upon application and removal so that the adhesive is "infinitely" repositionable, and very little adhesion build as the adhesive and/or construction ages.[3,4] Additionally, due to the large particle size of a microsphere adhesive, a non-continuous film is formed where there are areas of little to no adhesive in the interstitial spaces between the particles, which increases the ultra-clean removability of the construction.[5] There is also some thought that microsphere adhesives are "self-cleaning" with any dust or debris getting stuck in the interstitial spaces between the particles.[4] Therefore, the adhesive surface stays free of contamination and maintains its adhesive properties.

While microspheres offer excellent clean removability and repositionability, they have extremely low adhesion and tack.[2] In many applications, such as masking tapes and linerless receipt tapes, clean removability over a variety of sensitive and difficult-to-bond-to substrates is a pre-requisite but the adhesion and tack need to be higher than a microsphere alone can provide. To maintain clean removability and repositionability, but increase the adhesion, acrylic emulsion adhesives, often referred to as binders, can be formulated with the microsphere adhesive.[1, 6, 7] Except in rare circumstances, the binder needs to be chemically and physically compatible with the microspheres.[1, 8, 9] Aspects such as particle size and molecular weight of the binder versus the microspheres are key in creating a well dispersed adhesive and thus a homogeneous film. Essentially, there should be very limited areas of sequestered microspheres versus emulsion particles. In addition to increasing adhesion and tack, the binder can also improve the anchorage of the microsphere to the facestock. In this case, the binder is between the facestock and microsphere interface. In direct coat applications, the binder coats the facestock and engulfs part or all of the sphere effectively tying the 2 together.[9] This can be especially important on low surface energy facestocks. The ratio of the binder to the microsphere is key in providing superior anchorage to the facestock, maintaining clean removability, and repositionability while simultaneously increasing adhesion and tack.[1, 10]

At times, it can be necessary to transfer coat a microsphere-based adhesive. In this case, a binder is almost always required. Regardless, this is a very challenging endeavor as there is a vastly different density between a microsphere and an emulsion particle. During transfer coating, a release liner is coated with the adhesive. Because the emulsion binder is denser than the microsphere, the emulsion coats the liner, and the microspheres “sit” on top of the emulsion as described above for the direct coat applications.[11] However, when material is transfer coated, the laminate is “flipped” upside down, so the emulsion tends to bury the microsphere.[11] When this occurs, the anchorage to the facestock suffers because the microspheres, which have limited affinity for most facestocks, are now virtually the only thing in contact with the facestock. Likewise, the binder instead of the spheres, tends to come into contact with the adhering substrate, which limits clean removability and repositionability because the spheres are rendered ineffective due to the film morphology. To mitigate these issues, binders and other formulation ingredients, as well as total adhesive construction, must be chosen very carefully to ensure that, upon transfer coating, the spheres protrude from the film and the binder more fully coats the facestock.[12, 13]

Microsphere adhesives can be very versatile as one microsphere type can be formulated into many different adhesives ranging the gamut of adhesion properties while still maintaining long-term clean removability and repositionability by carefully choosing emulsion binders and other formulating ingredients. Formulated microspheres can be utilized across broad market segments including linerless receipt tapes, masking tapes, wall graphics, children’s stickers, and resealable food packaging.

II. Experimental

II.1 Microsphere Preparation

All microspheres were synthesized using a batch suspension polymerization process. A production grade reactor equipped with an agitator and thermocouple. All raw materials were placed in the reactor and the polymerization was performed in an inert atmosphere. After an extended reaction period, the reactor was cooled down and formulating ingredients were added to achieve appropriate physical properties. The final product was filtered through a proper filter size to ensure the microspheres were not filtered from the suspension.

II.2 Emulsion Binder Preparation

Emulsion binders were prepared at the industrial scale with reactors equipped with an agitator, condenser, and thermocouple. The monomer/surfactant pre-emulsion and initiator solution were fed into the reactor at controlled rates. At the conclusion of the feeds, the polymerization was allowed to finish until residual monomer levels were in acceptable ranges. The reactor was then cooled down and filtered. In some cases, additional formulating ingredients were added to achieve the desired physical properties.

II.3 Microsphere/Emulsion Binder Formulations

Microsphere/emulsion binder formulations were prepared by adding the emulsion binder to the microsphere under constant agitation. Other formulating ingredients to obtain the needed physical properties may have been added to the final formulation. All ingredients were added under constant agitation.

II.4 Direct Coat Performance Testing

Unless otherwise noted, all performance testing was completed using a 1 mil mylar facestock with a 0.5 mil (14 gsm) coat weight coated via a Meyer rod. Films were dried at 82°C for 30 minutes. Before any testing was performed, the films were conditioned in a controlled temperature and humidity room with a temperature setting of 70 ± 3°F and a humidity setting of 50 ± 2% relative humidity. Peel testing was performed using PSTC-101 Test Method A using various dwell times, and the substrates included stainless steel with a 304 finish, corrugated cardboard, and high-density polyethylene. A peel angle of 180° was used in all direct coat performance testing. Loop tack testing was performed using PSTC-16. All test panels except for corrugated cardboard were prepared according to the cleaning guidelines presented in Appendix B of the PSTC Test Methods manual. All testing was performed in the controlled temperature and humidity room with the settings described above.

II.5 Transfer Coat Performance Testing

Unless otherwise noted, all transfer coated performance testing was completed using a paper facestock or 6 mil vinyl facestock with a 0.8 mil coat weight. The formulation was coated on a siliconized release liner, dried, and then married to the paper or vinyl facestock via a compression roller; thus, transferring the adhesive film to the paper or vinyl. The samples were tested as outlined in Section II.4 with the exception that a peel angle of 90° and 180° was used.

III. Results and Discussion

III.1 Effect of Emulsion Binder on Microsphere Adhesive Properties

The adhesion of the microspheres synthesized in this study have very low adhesion on all substrates where the average is 0.02 pli, 0 pli, and 0.01 pli on stainless steel, corrugated cardboard, and high-density polyethylene (HDPE), respectively. In order to make a microsphere based adhesive relevant to multiple applications, the microspheres need to be combined with an acrylic emulsion binder. Figure 1 presents the 180° peel adhesion at a 1 min dwell time (A) and a 30-minute dwell time (B) for microspheres formulated with only an emulsion binder. The test specimens were direct coated using the coating methods described in the Experimental Section. For almost all binders, as the binder concentration increases, the adhesion increases no matter the substrate because all the binders have much higher adhesion than the microsphere. Similar to the 180° peel data, the loop tack data presented in Figure 2 shows that as binder concentration increases, the tack increases. However, for the binder with high adhesion but long-term removability and the binder that builds to permanent, the tack decreases at the highest concentration of binder. This is because these binders need more than 1 second to wet out the bonding substrate. These two binders tend to have a higher glass transition temperature than the two cold temperature binders, so it takes a bit longer to form a strong bond. This problem is mostly mitigated by allowing the adhesive to dwell for 1 min on the bonding substrate as shown in Figure 1A.

The binder chosen can impart varying properties other than just variable adhesion. For example, the microspheres were combined with an acrylic binder specifically made to operate in cold (5-10°C) temperatures and to have high adhesion to low surface energy substrates (LSE, navy bars in Figure 1). These formulations would be useful in variable information tapes that adhere to refrigerated food, such as packaged meat. Additionally, even at room temperature, the formulated microsphere adhesive with the cold temperature, LSE adhesion binder has high adhesion on corrugated cardboard and HDPE at approximately 0.7 pli and 0.5 pli, respectively, with the highest concentration of binder. This formulation also has stable adhesion across multiple substrates with varying textures and surface energies. This binder has high tack (0.3-0.5 lbf) on corrugated cardboard, likely because it has a low glass transition temperature and flows and wets the bonding substrate very quickly. This allows the adhesive to flow into the highly textured surface of the corrugated cardboard and form a strong bond. On the non-textured surfaces, such as stainless steel and HDPE, this phenomenon is less noticeable.

The formulated microsphere with the freezing temperature binder has relatively weak adhesion (<0.3 pli except for the higher concentration of binder on stainless steel) across all substrates at room temperature (Figure 1, blue), but the adhesion holds when the temperature decreases (data not shown). This formulated microsphere adhesive is well suited to freezing (< 0°C) temperatures, which are useful in walk-in freezer shelf marking labels, Additional applications include logistics in frigid climates when long-term removability is necessary, but the label or tape cannot fall off the substrate in extremely cold environments. At room temperature, the formulated microspheres with the freezing temperature binder tend to have the lowest tack until the highest loading of binder is achieved. This is partly due to film morphology changes as the binder content is increased. Because this binder operates well in freezing temperatures, it tends to want to bond well to high surface energy substrates, such as stainless steel, over low surface energy substrates. This is a sacrifice for this adhesive to maintain strong adhesion even at temperatures below 0°C.

The “Goldilocks” adhesive in this set of data is the formulated microsphere with the high adhesion, long term removable binder. This adhesive can be useful in variable information tapes that are utilized in quick service restaurants across a wide variety of temperature ranges. It has very high adhesion as shown in Figure 1 (light blue), but can cleanly remove across stainless steel, corrugated cardboard, and HDPE for extended periods of time. There is also a substantial increase in adhesion when the concentration of the high adhesion, but removable, binder is increased from the lowest to the middle concentration. There is far less adhesion gain when increasing the high adhesion but removable binder from the middle to the highest concentration except on the corrugated cardboard. This is likely due to the difference in how the binder arranges itself around the microspheres as the binder content is increased thus affecting the morphology of the film. The high adhesion binder has one of the highest tacks (0.25 to 1.3 lbf) on stainless steel and HDPE making it ideal for quickly grabbing the bonding substrate no matter the surface energy. However, on highly textured surfaces, such as corrugated cardboard, this adhesive has to be formulated with additional ingredients to achieve high, which will be discussed in Section III.2.

The most aggressive formulated microsphere adhesive development for this study was made with a binder that allows the formulated microsphere to maintain short term removability, but the adhesive does become permanent and will have a destructive bond upon removal after a few hours. Achieving greater than 0.8 pli on all tested substrates for a microsphere-based formula and maintaining some level of clean removability (Figure 1, gray), even if it is short term, is highly difficult to do. Even though this adhesive only has short term removability, it is useful in tamper evident application. In these applications, short term removability is key in case the specimen needs to be repositioned or stuck to and removed from multiple substrates within a few hours. However, when the adhesive is left on a substrate for an extended period of time, it will cause substrate destruction, alerting the consumer that the item has been tampered with. The tack on the formulated microsphere with the short term removable but ultimately permanent binder has very high tack on all substrates, especially corrugated cardboard. The film morphology of this microsphere formulation is different than all of the other microsphere/binder combinations (data not shown) rendering it able to quickly grab both smooth and rough surfaces at a variety of surface energies. However, this adhesive can be too aggressive for many microsphere applications and is a niche adhesive.

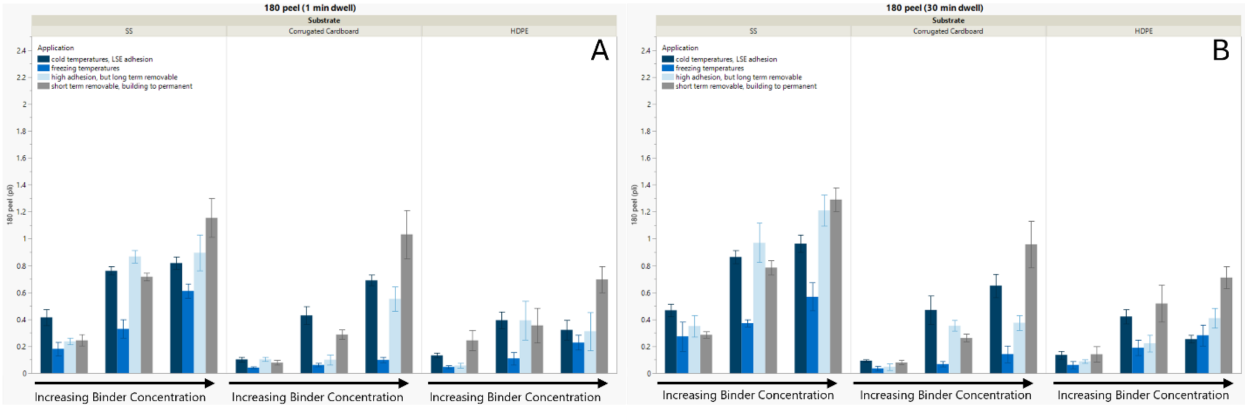

Figure 1: 180° peel testing results at (A) 1 min of dwell time and (B) 30 minutes of dwell time. For each peel testing condition, three testing substrates were used stainless steel (SS, left), corrugated cardboard (middle), and high-density polyethylene (HDPE, right). Four different binders were blended with the microsphere and tested at varying binder concentrations with increasing binder concentration going from left to right. The binders include a cold temperature binder with superior low surface energy adhesion (navy), a binder for use in freezing temperatures (blue), a binder with high adhesion though it remains removable long term (light blue), and a binder with very high adhesion that maintains short term removability but builds to permanent adhesion (gray).

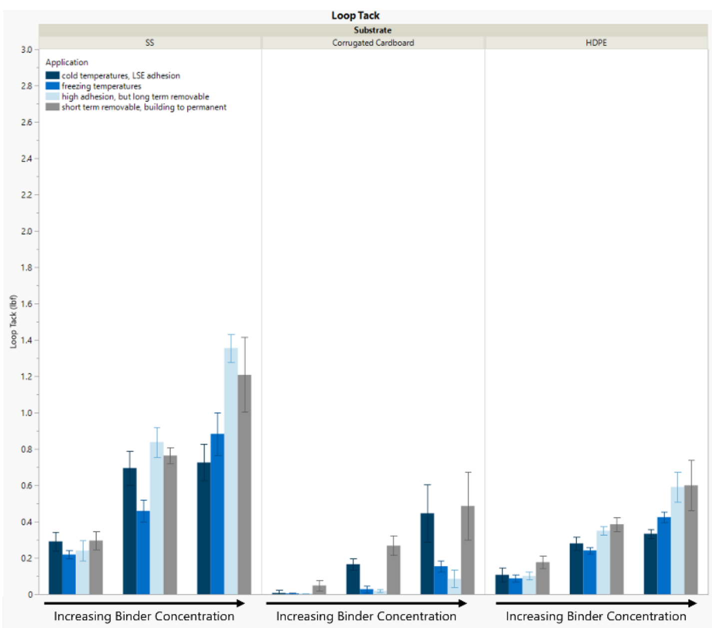

Figure 2: Loop tack testing results on stainless steel (SS, left), corrugated cardboard (middle), and high-density polyethylene (HDPE, right). Four different binders were blended with the microsphere and tested at varying binder concentrations with increasing binder concentration going from left to right. The binders include a cold temperature binder with superior low surface energy adhesion (navy), a binder for use in freezing temperatures (blue), a binder with high adhesion though it remains removable long term (light blue), and a binder with very high adhesion that maintains short term removability but builds to permanent adhesion (gray).

III.2 Effect of Additional Formulating Ingredients on Microsphere/Binder Adhesives

The adhesion of the microsphere/binder formulations can be further increased, without destabilizing the microsphere, by adding additional adhesion promoting formulation ingredients. Many applications of formulated microsphere adhesives require high adhesion on difficult-to-bond-to substates, such as HDPE, high recycled content corrugated cardboard, and treated papers. Figure 3 presents the 180° peel for both a 1 minute and 30 min dwell time. For most of these adhesive formulations, increased dwell time does not greatly increase the adhesion value, and some remain within standard deviation of one another. Essentially, the time it takes to fully bond to the substrate has vastly decreased from the microsphere/binder only formulations to these formulations with additional ingredients. This is very important for formulations that require “quick grab” in their application, such as linerless tape receipts.

For both low temperature binders, the adhesion is increased by approximately 2 times (at a minimum, some formulations are higher). In fact, at the one minute dwell, the adhesion of both low temperature binder formulations are much more equalized than in the binder only microsphere formulations. There is one fluke in the data with the freezing temperature binder where the adhesion drops significantly for the highest concentration of binder on the corrugated cardboard. This could be due to the considerable variation in cardboard surfaces as the recycled content, texture, and fiber content can be different among the panels. The panels in these studies all came from the same source, but there is no PSTC standard corrugated cardboard panel. It must be noted that having these substantially higher adhesive values with the low temperature binders does make their low temperature performance suffer, so this may not be an ideal formulation for adhesives used in low temperature environments. Additionally, the peel adhesion of the formulated microspheres with the freezing temperature binder decreases as dwell time increases on corrugated cardboard and HDPE. This behavior is unexpected but may be due to film morphology changes as the adhesive wets out, or lack thereof, the substrate. This could also be due to slight incompatibility between the extra formulating ingredients and the freezing temperature binder; the incompatibility would have to come from the binder rather than the microsphere because the same microsphere is in all the formulated adhesives, and this behavior is not observed in the formulations with other binders. The formulations with the freezing temperature binder have a mode of failure switch from adhesive to ghosting (or stain) on the stainless steel and HDPE panels, and an adhesive to fiber tear mode of failure switch for the corrugated cardboard, with the additional formulating ingredients.

By adding more adhesion promoting formulation ingredients to the microsphere/high adhesion, long term removable adhesive, the adhesion at both 1 min and 30 min dwell times are increased, on average, by 4 times across all substrates. Some of the formulations with the highest binder concentration only increase by approximately 2 times. Even with this substantial increase in adhesion, these adhesive formulations still maintain their clean removability. Additionally, these formulations do not cause destruction, not even fiber pick, on the corrugated cardboard. This makes this adhesive ideal for applications that require a quick grab onto the substrate without destruction after removal of the adhesive item.

The adhesive formulation that is the least affected by the additional adhesion promoting formulating ingredients is the microsphere formulated with the short term removable, but permanent binder. This makes sense as this neat microsphere/binder formulation had the highest adhesion across all testing substrates, so it is difficult to further increase the adhesion. Additionally, the mode of failure changes from adhesive to ghosting (or stain) with the increasing amount of binder causing more severe ghosting. These formulations lose their clean removability quickly and will ultimately cause cohesive failure, making them applicable only in very niche applications.

The tack of the adhesive formulations, presented in Figure 4, show similar trends to the 180° peel data at a 1 min dwell time. The formulated microsphere with the high adhesion, removable binder is the superior formulation in terms of tack as it provides very high tack while maintaining clean removability. The low temperature binder microsphere formulations tended to have staining or ghosting on the panel, while the microsphere formulation with the permanent binder needed more time to wet out the substrate before a strong bond can be formed. This is especially notable on the corrugated cardboard panel and is likely due to the highly textured surface of the corrugate.

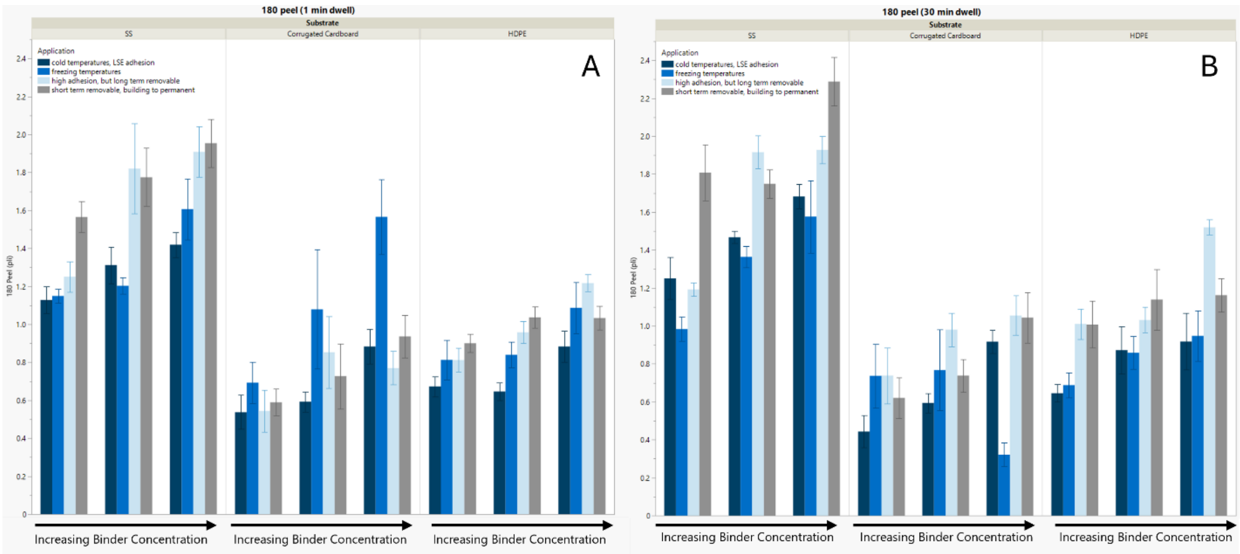

Figure 3: 180° peel testing results at (A) 1 min of dwell time and (B) 30 minutes of dwell time. For each peel testing condition, three testing substrates were used stainless steel (SS, left), corrugated cardboard (middle), and high-density polyethylene (HDPE, right). Four different binders were blended with the microsphere and tested at varying binder concentrations with increasing binder concentration going from left to right. The binders include a cold temperature binder with superior low surface energy adhesion (navy), a binder for use in freezing temperatures (blue), a binder with high adhesion though it remains removable long term (light blue), and a binder with very high adhesion that maintains short term removability but builds to permanent adhesion (gray). These formulations have additional adhesion promoting ingredients. For all formulations the amount of adhesion promoting ingredients is kept constant on a weight-to-weight basis.

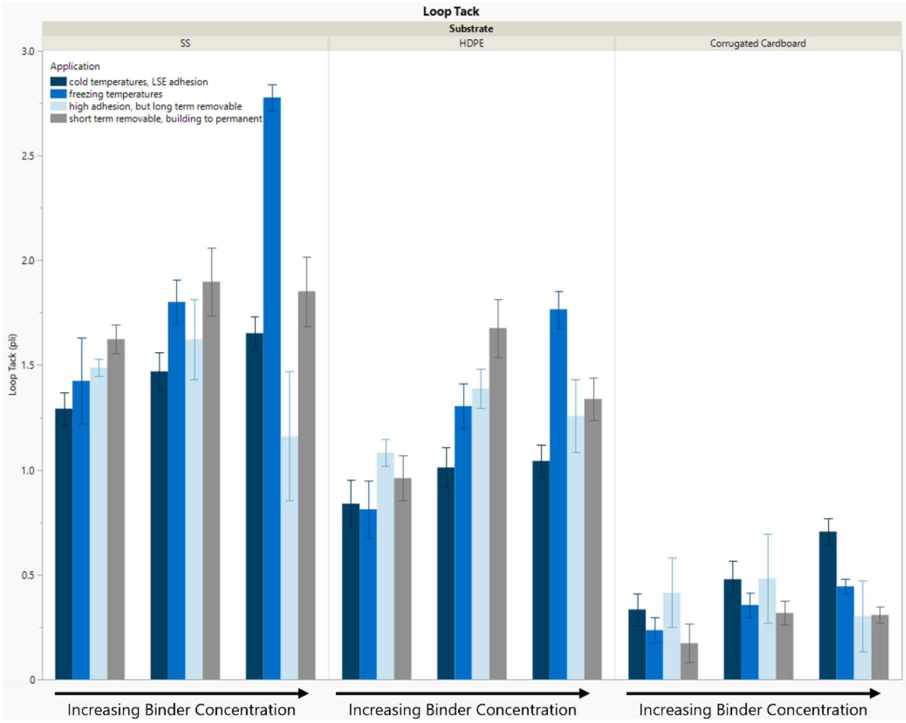

Figure 4: Loop tack testing results on stainless steel (SS, left), corrugated cardboard (middle), and high-density polyethylene (HDPE, right). Four different binders were blended with the microsphere and tested at varying binder concentrations with increasing binder concentration going from left to right. The binders include a cold temperature binder with superior low surface energy adhesion (navy), a binder for use in freezing temperatures (blue), a binder with high adhesion though it remains removable long term (light blue), and a binder with very high adhesion that maintains short term removability but builds to permanent adhesion (gray). These formulations have additional adhesion promoting ingredients. For all formulations the amount of adhesion promoting ingredients is kept constant on a weight-to-weight basis.

III.3 Effect of Transfer Coating on Microsphere/Binder Adhesives

The formulated microsphere/binder adhesives, both with and without additional formulating ingredients, can be made into transfer coatable versions by adding other formulation ingredients. As described above, it is difficult to make a microsphere transfer coatable due to the morphology of the film. Figure 5 shows the 90° peel adhesion of Product A and B as a direct coat formula and a transfer coat formula on 3 different testing substrates: stainless steel, corrugated cardboard, and HDPE. It should be noted that these materials were coated on direct thermal paper. On stainless steel, the adhesion of both products roughly doubles when the product is transfer coated. This is solely due to the transfer coating process as the spheres become buried in the emulsion binder. The adhesion is less affected on corrugate and HDPE though the adhesion does increase. While the adhesion increased, it is important to note that the failure mode remained adhesive.

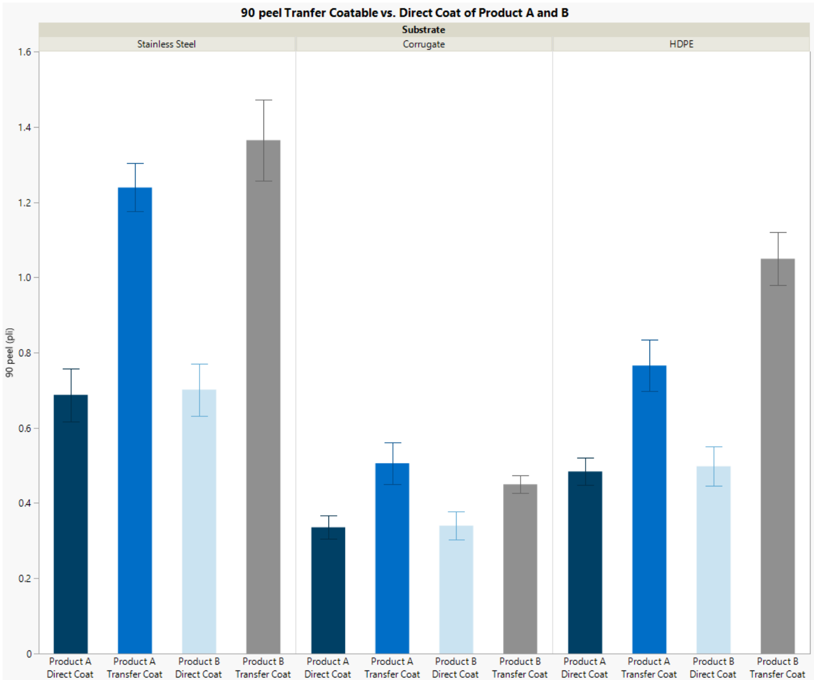

Figure 5: 90° peel testing results for two formulated microsphere products both as a direct coat option (Product A, navy and Product B, light blue) and as a transfer coat option (Product A, blue and Product B, gray). Products were coated on direct thermal paper at a coat weight of 0.5 mil.

The adhesion of the adhesives presented in Figure 5 is, generally, too high for many transfer coatable microsphere applications, such as wall graphics or masking tape. Figure 6 presents the 180° and 90° peel adhesion of a transfer coatable microsphere (Product C) that is more suited to wall graphics and masking tapes. Product C was tested on stainless steel, glass, and acrylic panels to mimic glass windows and acrylic painted drywall as that is the application surface of most graphics and masking tapes. Product C has consistent adhesion across multiple substrates and reaches >85% of its ultimate adhesion within 24 hours, which makes it suited for long-term removable applications. This is possible because the morphology of the film is controlled, and the microspheres protrude more at adhesive/air interface rather than the facestock/adhesive interface.

The application of most transfer coatable microspheres includes adhering to painted drywall or glass windows. Figure 7 presents 1-month real time aging of Product C on 3 different painted drywalls as well as interior and exterior glass windows. Product C was tested on a total of 12 different paints and 3 different glass windows with a 1- and 3-month real time dwell. Product C removed cleanly, without any sticky residue or paint damage, after 1-month and 3- month, making it ideally suited for ultra removable applications on sensitive and difficult to adhere to substrates. For reference, Product A and B left some residue on some of the painted drywall samples and damaged some paints after a 1-month dwell.

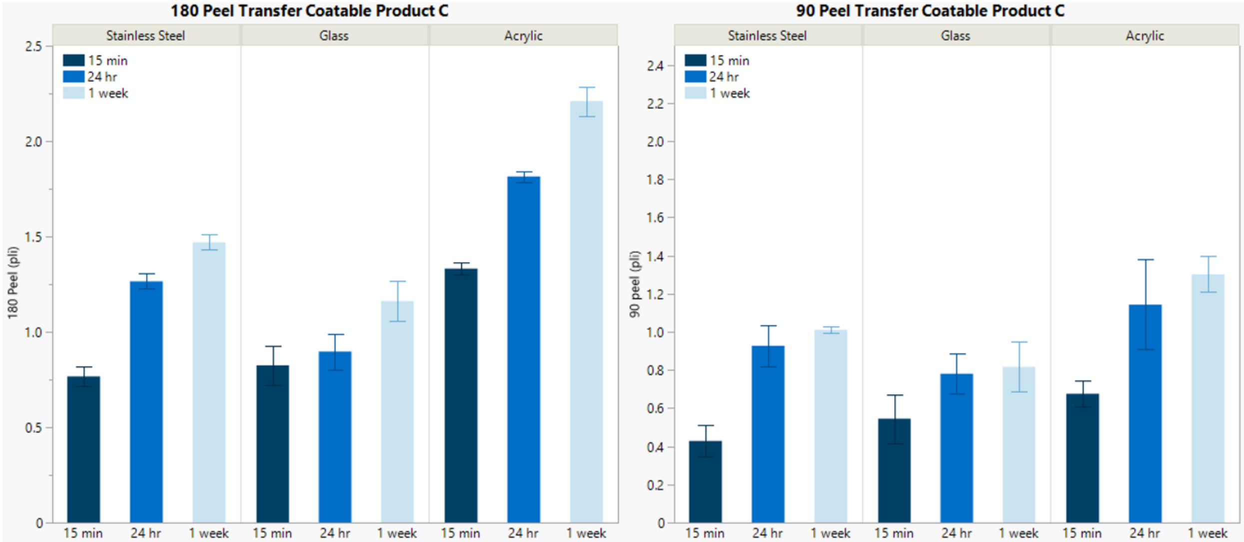

Figure 6: 180° (left) and 90° (right) peel testing results on stainless steel (left, each graph), glass (middle, each graph), and acrylic (right, each graph) of transfer coatable Product C. Product C was coated at a 0.8 mil coat weight on a 6 mil vinyl facestock. The figure shows the adhesion at 3 different dwell times: 15 min (navy), 24 hr (blue), and 1 week (light blue).

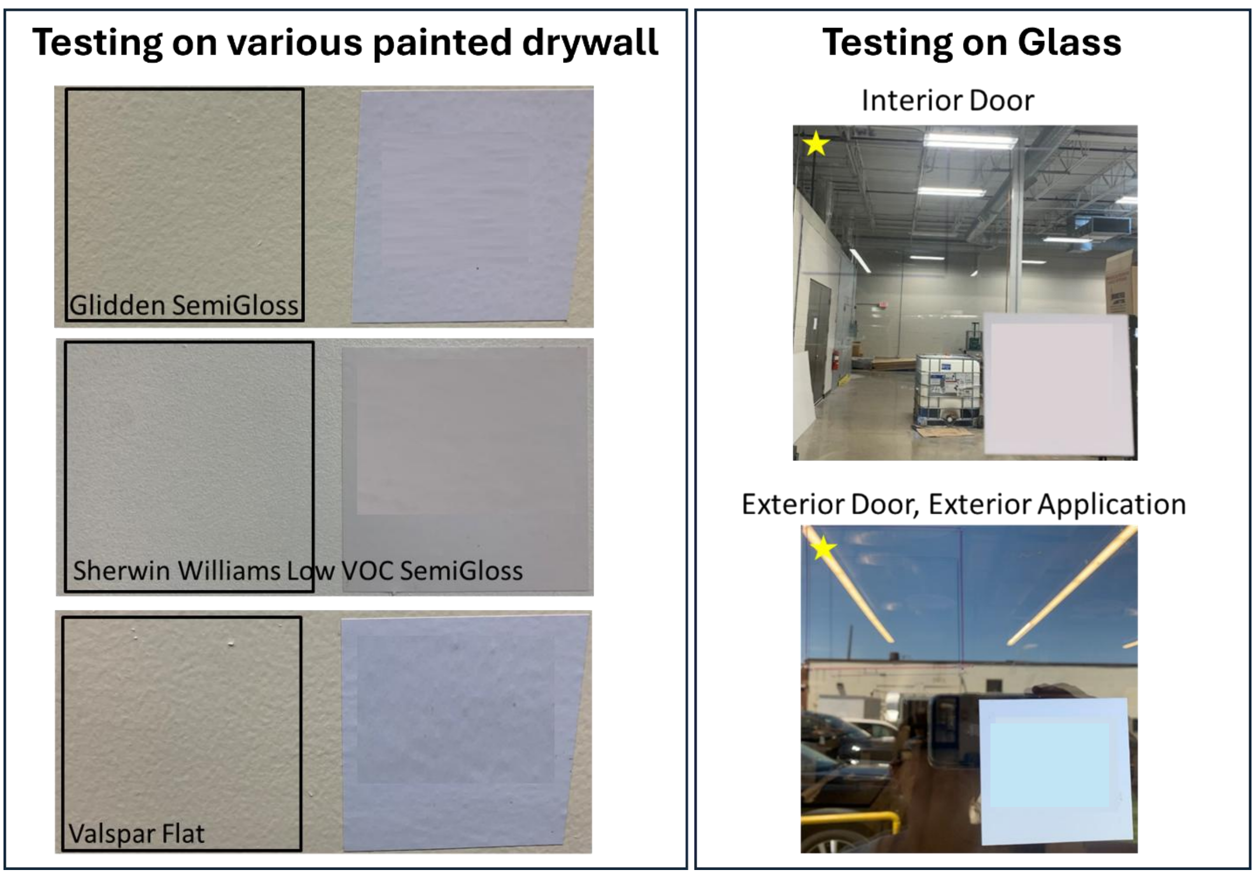

Figure 7: Product C applied to painted drywall (left) with a Glidden semi-gloss paint (top), a Sherwin Williams low volatile organic compound (VOC) semi-gloss paint (middle), and a Valspar flat paint (bottom). In each panel, the black box indicates where the adhesive sample was applied and removed (left of each panel) after a 1 month real time dwell. For reference, in each panel, the right gray/white square is a sample of the adhesive that was left on the drywall. On the right, Product C was applied to an

interior glass window (top) and an exterior door with the adhesive sample applied to the exterior of the door (bottom). The yellow star indicates where the adhesive sample was removed after a 1 month real time dwell (top left of each image). The white/blue square on the bottom right of each glass image is a sample of the adhesive that was left on the glass as a reference.

IV. Conclusion

Water-borne microsphere adhesives are challenging to make and formulate into a wide variety of applications, such as linerless receipt tapes, wall graphics, and masking tapes. Issues such as chemical and physical compatibility must be at the forefront of the design process. Additional design requirements such as acrylic emulsion binder properties, not only adhesion but also other “intangible” attributes, they can give the overall adhesive formulation must be considered to make a successful, stable adhesive for a given application. Indeed these “intangible” attributes are often the most important, and additional formulating ingredients can be added to a base formulation to increase properties such as adhesion and quick tack. Lastly, formulated microsphere adhesives can be made into transfer coatable versions, but their properties may change due to the inversion of the film. Careful consideration of the binder properties and the physics of the adhesive film, including drying dynamics, is key in generating a transfer coatable formulation that maintains all the desirable qualities that a direct coat formulation has, such as long-term clean removability and almost infinite repositionability. One neat microsphere adhesive can be formulated into a multitude of adhesives for a variety of adhesion levels and end use applications.

V. References

1. Smith, D. E. and Conover, M. A (2003). Microsphere adhesive formulations. WO Patent No. 03/035789 A1.
2. Silver, S. F. (1972). Acrylate copolymer microspheres. US Patent No. 3691140.
3. Delgado, J. (1991). Hollow acrylate polymer microspheres. US Patent No. 5053436.
4. Delgado, J. (1991). Hollow acid-free acrylate polymeric microspheres having multiple small voids. US Patent No. 4988567.
5. Mallya, P. (1996). Adhesive microspheres prepared by suspension polymerization. EP Patent No. 0710678A2.
6. Silver, S. F., Leinen, R. W., and Delgado, J. (1992). Pressure-sensitive adhesive comprising solid tacky microspheres and macromonomer-containing binder copolymer. US Patent No. 5118750.
7. Morris, T. L., Lu, Y., Parker, M. M., and Delgado, J. (1996). Feminine hygiene pad. US Patent No. 5514122.
8. Merrill, R. F. Jr. and Courtney, H. R. (1974). Acrylate microsphere-surfaced sheet material. US Patent No. 3857731.
9. Miyasaka, H.; Kitazaki, Y., Matsuda, T., and Kobayashi, J. (1988). Removable adhesive sheet. US Patent No. 4735837.
10. Bohnel, B. and Schlosser, D. L. (1991). Aqueous, repositionable, high peel strength pressure sensitive adhesives. European Patent No. 0439941B1.
11. Gosnell, J. D., Jordan, G. R., and Kennedy, C. B. (2021). A process for transferring microstructures to a final substrate. Australian Patent No. 2019229332.
12. Bilski, L. A., Bailey, D. O., Vogel, M. S., and Gustafson, F. J. (2010). Method of making a microsphere transfer adhesive. US Patent No. 7645355B2.

13. Mazurek, M. H., Galkiewicz, R. K., and Benson, G. M. (2002). Pressure-sensitive adhesives having microstructured surfaces. US Patent No. 6440880B2.

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