One Part Adhesives for Protective Masking

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Introduction

Surfaces often can be scratched, marred, or abraded during routine production as well as shipping to a point of distribution or purchase. More delicate or highly valued surfaces are often covered with a protective film to minimize damage caused by routine handling. Such films are generally comprised of a polyolefin face stock coated with a pressure sensitive adhesive. The face stock provides the actual protection whereas the adhesive ensures that the film sticks to the surface prior to reaching a final destination. Once the item is at its final destination, the film must be removed cleanly and easily without leaving any residue whatsoever. Hence, the adhesive must have good anchorage to the face stock, not exhibit too high a peel build, and not have any lower molecular weight components that can migrate to the surface and leave a residue.

One approach to ensuring the adhesive adheres to the face stock and not to the substrate of interest is to formulate the adhesive with crosslinkers. Not only does the crosslinker diminish the peel force, but it also improves anchorage to the face stock through covalent chemical bonds that are formed. However, the crosslinkers that impart these properties are reactive in nature, must be added as a two part system, and have a limited pot life. Recently, it has been found that formulating with select polyolefin dispersions (POD's) results in adhesives that are suitable for protective film applications without the need for a two-part reactive system.

Legacy Approaches

Pressure sensitive adhesives for protective film applications fall within the general class of removable adhesives that have relatively low adhesion to a broad range of substrates. Unfortunately, they can also have poor adhesion to a face stock, so over time the adhesive may adhere better to the substrate than the face stock, especially to more polar substrates. When the protective film is removed, the adhesive can then transfer to the article that is being protected, leaving an unacceptable level of residue. In cases where the face stock is a polyolefin film, corona treating the film can improve anchorage to some degree, but solely corona treating the film is often met with limited success. Priming the film can substantially improve anchorage; however, this approach requires a two pass operation which increases costs. In addition, if the primer is a PSA, rewinding and recoating can be troublesome.

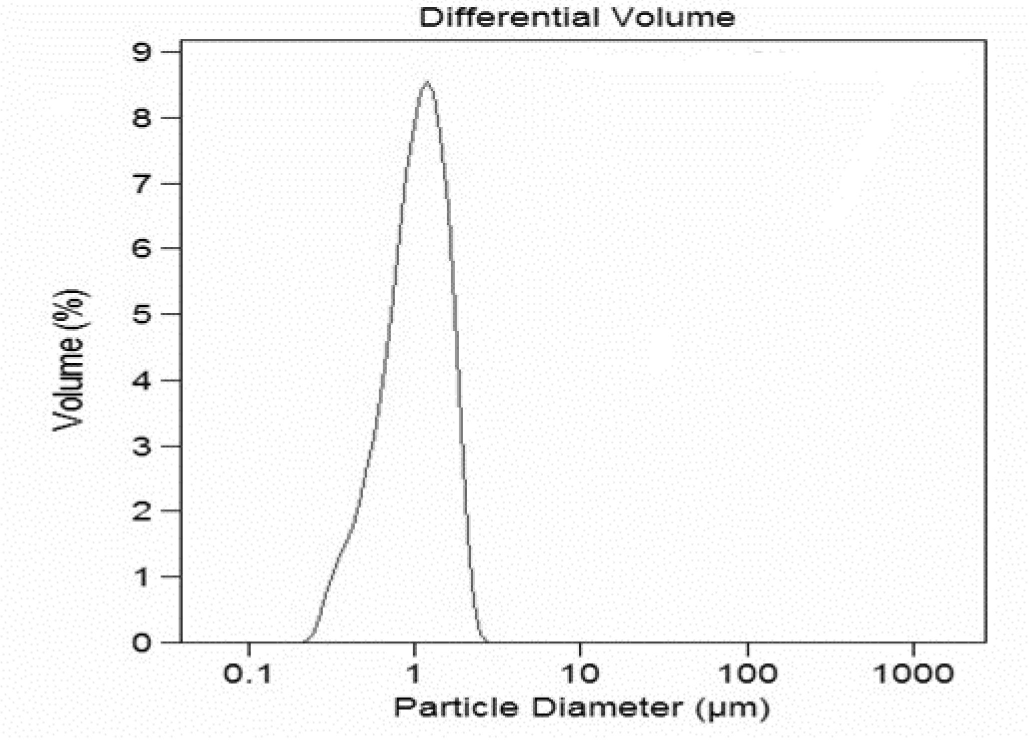
If the face stock is to be coated in a single pass, one must employ a technology that enhances anchorage. Predominately, this is achieved by selecting a reactive chemistry that can covalently bond the pressure sensitive adhesive to the face stock [1]. Corona treating a polyethylene face stock adds functionality to the surface including species such as alcohols and carboxylic acids. Analogous functionalities also may be polymerized at the surface of a latex particle. By mixing in an appropriate multifunctional crosslinker into the latex, its particles can be crosslinked to the film as the latex is coated and dried thereby yielding excellent anchorage to the face stock.

Because these are reactive systems, they have certain limitations. Owing to limited pot life, materials must be formulated and coated within a finite time, typically on the order of a day or two. Also, there are only a finite number of reactive sites on the acrylic particles. Once consumed, it is no longer possible to further react these crosslinkers with the adhesives. Thus, if sufficient crosslinker is added to an emulsion and the system is permitted to completely react prior to coating, the system cannot be rejuvenated by dosing additional crosslinker. The adhesive must then be discarded as waste.

Polyolefin Dispersions

Until recently, dispersing higher molecular weight polyolefins in water was not practical due to the high temperatures required to surpass the melt temperature of the polyolefin. These were well in excess of the boiling point of water. Dispersions were limited to waxy, lower molecular weight polyolefins or compositions that included a substantial level of a water soluble monomer, such as acrylic acid, within the polymer chain. Unlike more polar polymers, the polymerization of high molecular weight polyolefins directly in water to produce stable lattices is quite limited in scope.

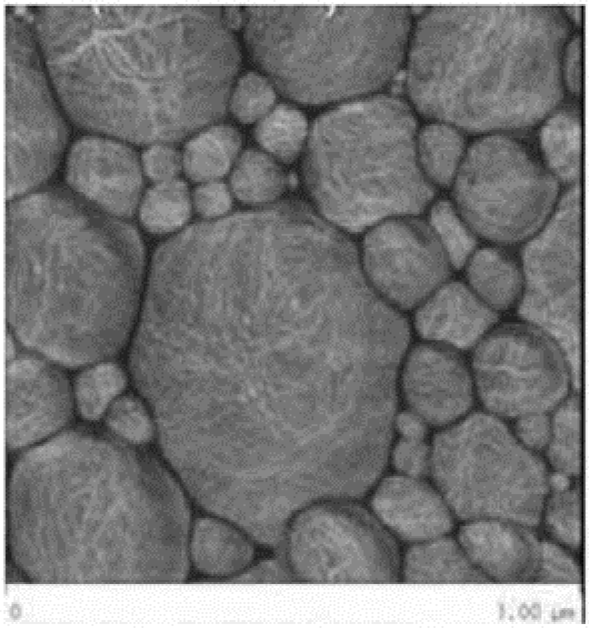
Figure 1. Particle Size Distribution of Polyolefin Dispersion



Recently, a new dispersion technology has been patented that combines dispersants and polyolefin polymers and produces stable lattices of a sufficiently small particle size distribution. In fact, dispersions can be made with shelf stability in excess of 6 months and in even cases where there is striation within a sample, material may be stirred to readily regain uniformity. As can be seen in Figure 1, particle size is higher than typical acrylic emulsion (~0.2 to 0.6 microns).

Owing to the density of polyolefins and the structure of the dispersant, settling is not an issue. A micrograph showing individual particles is shown in Figure 2.

Figure 2. Micrograph of Dried Polyolefin Dispersion



Polyolefins with a wide variety of various chemistries can readily be polymerized via non-aqueous approaches. This technology enables dispersing polyolefins that can vary in composition, crystallinity, melting point, molecular weight, morphology, and functionality directly into water at solids well in excess of 40%. Having these materials in an aqueous median permits them to be coated at lower coat weights with higher line speeds than if they were 100% solids. They also can find applications in paper coatings (moisture and oil resistance), carpet backing, heat seal applications, and personal care items (absorbency/softness). Additional background describing these attributes in more detail can be found elsewhere[2,3].

Protective Film Formulations

An ideal adhesive for protective film applications should meet the targeted peel value for the substrate of interest, have little change in adhesion with respect to time, and have good anchorage to its face stock. Changes in peel force with time can be caused by the natural peel build process as the adhesive wets the substrate. In addition, any changes within the adhesive caused by oxidation or UV degradation are undesirable. In cases where a clear face stock is used, the adhesive should also have good optical characteristics. Thus, acrylic pressure sensitive adhesives are a good choice for the base of any formulation.

At lower peel values that are commonly required for protective films applications, neat acrylic adhesives generally have unacceptable anchorage to polyethylene face stocks even when the face stock is corona treated. As mentioned above, anchorage can be improved by covalently bonding the adhesive to the face stock. An alternate approach would be to identify a material that has an exceptionally strong interaction with polyethylene. Simply applying the principal that “like likes like,” polyolefin dispersions (POD) offer the potential for interactions that are difficult to engineer in other chemistries. However, neat polyolefins of high molecular weight do not have acceptable quick stick. Blending the two has the potential to achieve the targeted balance.

For the present study, a water-borne acrylic pressure sensitive adhesive that is used in protective film applications was selected as one component. POD’s of various compositions were selected as the other. Samples were prepared by simply mixing with an overhead stirrer and directly coated onto polyethylene film. Solids were adjusted so that 10 g/m^2 dry coat weight was achieved using a bar applicator. Samples were oven dried at 80^o C for five minutes. 180^o peels were measured from various substrates according to test method PSTC-101.

Stainless Steel Substrates

Initial experiments were conducted on stainless steel substrates. Peel was measured at designated times on samples held at standard CTR test conditions. In order to accelerate aging and peel build effects, a sample was placed in 50^o C oven. As an additional control, a high Tg acrylic polymer (hard filler) was also included in the series to illustrate that the addition of the POD differs from a hard filler material. Initial results of these experiments can be found in Table 1.

Table 1. Stainless Steel Peel Build Profile

-	**180° Peel, SS (oz/in)** 20 Min	**180° Peel, SS (oz/in)** 24 Hr Dwell	**180° Peel, SS (oz/in)** 7 Day Dwell	**180° Peel, SS (oz/in)** 7 Day Dwell, 50 °C
Neat Acrylic	7 A	14 A	22 A	41 C
Acrylic + Isocyante	6 A	8 A	8 A	4 A
50 Acrylic/50 POD #1	6 A	9 A	9 A	6 A
50 Acrylic/ 50 POD #2	5 A	7 A	7 A	8 A
50 Acrylic + 50 Hard filler	2 A	4 A	4 A	6 G

A = Adhesive Failure
C = Cohesive Failure
G = Ghost/Residue on Panel

Most acrylic pressure sensitive adhesives have good affinity to stainless steel and tend to increase adhesion with respect to time, particularly if they are not significantly crosslinked. Therefore, the increase in peel force for the neat acrylic is to be expected. Crosslinking the acrylic with a multifunctional isocyanate reduces the peel build to an acceptable level and data for this formulation is analogous to commercially available products. The addition of the POD substantially reduces the peel build with time and accomplishes much of the same effect as the isocyanate. Although it flattens the peel build, the addition of hard filler causes the sample to leave a haze on the panel after heat aging. Also, tests for anchorage to the polyethylene face stock demonstrate that the anchorage is improved with the POD formulation over the filler approach.

Other Substrates

Stainless steel data can be used to predict how pressure sensitive adhesives perform on metallic surfaces, but in real life situations, surfaces of different chemistry and polarities are commonplace. Substrates were identified that would represent a cross section of surface energies. A methyl methacrylate sheet (Acrylic) was selected since the surface energies of an acrylic based adhesive should match well with the acrylic sheet. A panel coated with an automotive clear coat (Paint) was selected as another common chemistry. Finally, high density polyethylene (HDPE) panels were use to represent a non-polar surface. As can be seen in Table 2 below, most of the data mimics the stainless steel results except for the HDPE where lower peel is measured.

Table 2. Peel Build on Common Substrates

	180° Peel, Paint (oz/in)				**180° Peel, HDPE (oz/in)**				**180° Peel, Acrylic (oz/in)**			
	20 Min		7 Day Dwell		20 Min		7 Day Dwell		20 Min		7 Day Dwell	
Acrylic + Isocyante	9	A	10	A	3	A	3	A	9	A	12	A
50 Acrylic/ 50 POD #1	8	A	12	A	1	A	2	A	9	A	12	A
50 Acrylic/ 50 POD #2	7	A	12	A	1	A	1	A	9	A	13	A

Once again, all surfaces appear clean and without any visual residue after testing.

Conclusion

One part pressure sensitive adhesives can be formulated by blending an acrylic pressure sensitive adhesive with a POD. When coated on polyolefin films, these mixtures have good anchorage to the film and properties suitable for removable adhesives. Performance can be achieved that is comparable to formulations that require the addition of a reactive crosslinker. This simplified approach can reduce waste and remove potentially hazardous ingredients from the formulation. Extending these studies to broader compositional space, other acrylics and PODs, should permit additional optimization of the formulation.

References

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Acknowledgements

The authors would like to thank Melissa Lane for her assistance in designing and conducting adhesive analyses and Paul Nedwick for his discussions on polyolefin dispersion technology.