WATER-BASED ADHESIVES

SOLVENTLESS LAMINATION REDUCES FLEXIBLE PACKAGING VOCS

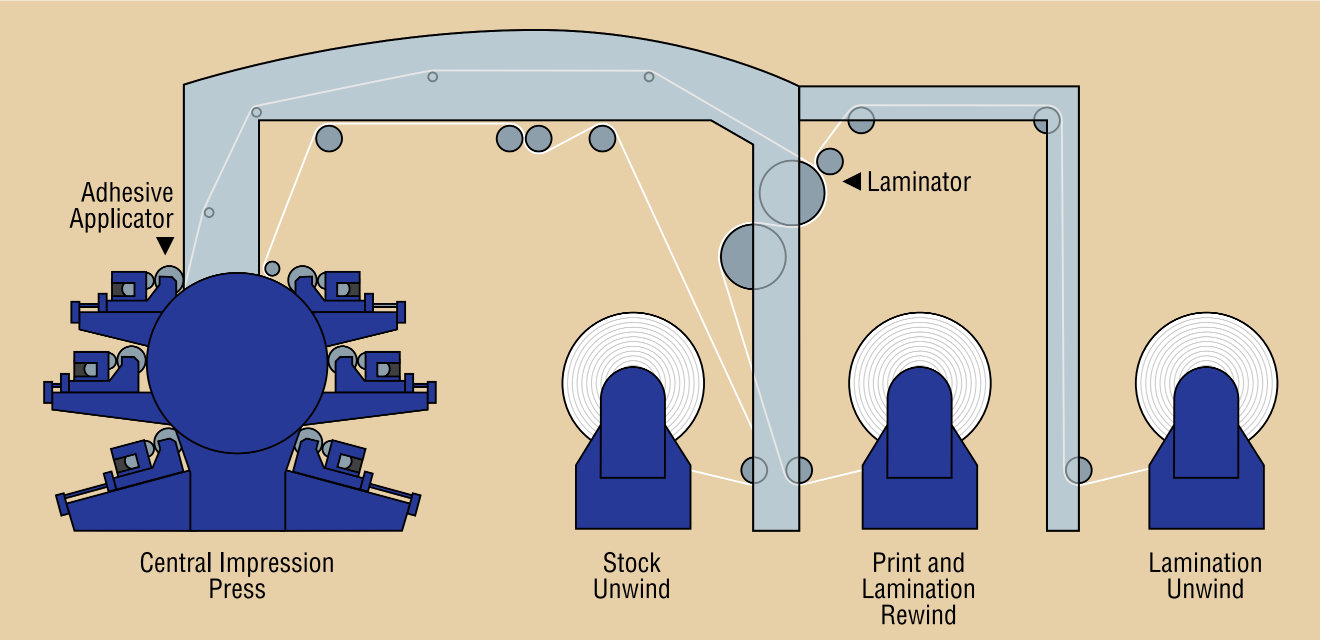
By Peter A. Voss

Editor's Note: The following article is based on a presentation given by Peter A. Voss, Global Program Manager-Flexible Packaging, H.B. Fuller Co., at a "Flexo on Unsupported Film" seminar in Spring 2001. The seminar was sponsored by Akzo Nobel Inks at the company's Center for Technical Excellence in Plymouth, MN. For more information on Akzo Nobel Inks seminars, contact Emily Horn at (800) 328-7838, ext. 326.

In light of ever-tightening governmental and environmental legislation to reduce volatile organic compound (VOC) emissions, the flexible film and paper laminating industry is rapidly changing from solvent-based adhesives to new water-based polyurethane adhesives and acrylic emulsions for dry-bond laminating. In addition, very low residual monomer 100 percent solids systems are rapidly gaining acceptance as an alternative technology to traditional dry-bond laminating techniques.

Dry-bond laminating is the process of coating either a solvent-based or water-based adhesive to a substrate, drying the adhesive with heat and airflow and then laminating the adhesive to a second substrate via a heated compression nip that mates the films together. Solventless laminating, on the other hand, involves metering a low-viscosity adhesive onto a multiple-application roll configuration that applies the adhesive to the first substrate, which is then mated to a second substrate using a heated nip. Whether the laminating technique is dry-bond or solventless, adhesive coating weights are typically 1.0 –1. 5 lbs. per 3,000 ft., requiring a relatively small adhesive coating weight to meet the finished laminate performance requirements.

A typical laminating converter's product line is composed of structures using polyolefinic films such as polyethylene terephthalate, polypropylene and polyethylene



This six-color central-impression press has been modified for laminating after printing.

as well as paper and aluminum foil. The finished laminations can be used for a variety of end-use applications, although food packaging consumes the largest portion of these laminations.

While there are many applications for flexible packaging laminates, there are relatively few key performance requirements that they all share. The adhesives must have excellent clarity and bond strengths as well as be resistant to extremes of heat and humidity. In addition, the adhesive must be resistant to tunneling. Tunneling is the localized separating or delamination of the two substrates being bonded together. Tunneling often occurs when the two films differ in extensibility, and stretch or relax at different rates. These localized delaminations can have a detrimental effect on package appearance and a potentially damaging effect on the package contents, and remains the major concern for most converters.

Water-Based Adhesives

The flexible packaging adhesive market is estimated at $130 million, of which approximately only 25 percent is supplied by either acrylic emulsions or polyurethane dispersions (PUDs). Aside from governmental pressure for laminating converters to switch from solvent-based products to waterborne, there has been little incentive for these converters to make a change. The introduction of improved crosslinkers (catalysts to increase the performance of the adhesive) — such as dispersible isocyanates, polyfunctional aziridines and polyfunctional carbodiimides — enables the water-based adhesives to meet many of the performance criteria when the lamination is subject to extremes of heat and humidity and is narrowing the performance gap between solvent-based and water-based adhesives.

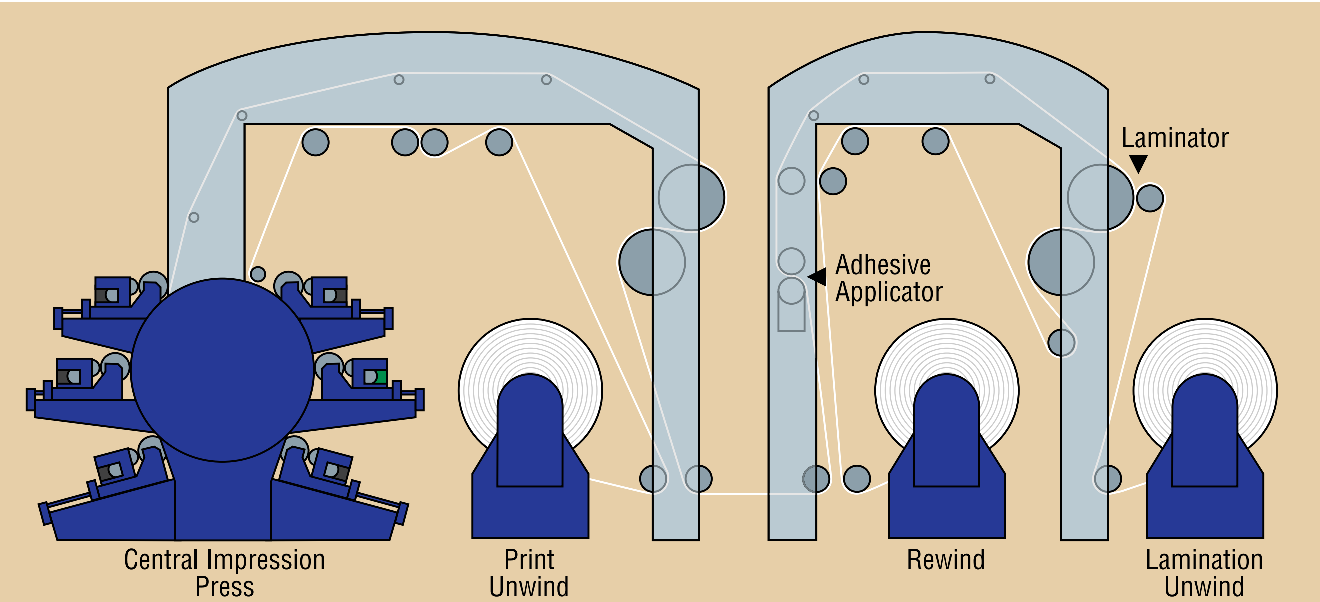
Polyurethane Dispersions. In comparison to conventional solvent-based polyurethanes, PUDs are the closest performing water-based polymers in terms of adhesion and resistance properties that are commercially available. PUDs typically have very low solution particle sizes (<75nm). The particle size of a water-based adhesive directly relates to the machinability (how well the product runs on the equipment) of the adhesive on laminating equipment and the ability to operate at maximum line speeds. In addition, the low particle size enhances the dried adhesives' clarity to a level comparable to solvent-based products. The main drawback to PUDs is cost. PUDs are based on aliphatic diisocyanates such as isophorone diisocyanate and tetramethylxylene diisocyanate, which are significantly more expensive than toluene diisocyanate, which is used in most solvent-based polyurethanes.

Acrylic Emulsions. Acrylic emulsions offer the laminating converter a low-cost product with moderate performance properties, which often meets their requirements for less stringent applications. In some cases, acrylics do not meet converter requirements, in that the adhesion and resistance properties are less than those of PUDs and conventional solvent-based products. In addition, acrylic polymers historically used in dry-bond laminating had very poor machinability and required chilling the roll to prevent the adhesive from coagulating.

These acrylics also suffered from a tendency to foam, which, in combination with the machining issues, severely limited the speed at which a converter could run the laminator. Thus, much of the price advantage gained by using a low-cost acrylic was erased by the decreased efficiency of the laminating equipment.

New commercially available acrylic polymers are available with excellent machining properties that can be used

This in-line laminating setup incorporates a separate and self-contained laminating machine in-line with the flexo press.



at maximum dry-bond laminator line speeds of 700-800 fpm. In addition, when it is crosslinked with either a polyfunctional aziridine or dispersible isocyanate, the adhesive system meets many of the heat and humidity resistance properties that only a PUD could achieve.

Crosslinking Chemistry.
Crosslinking a water-based adhesive imparts a lamination with the necessary resistance properties to maintain the package integrity when hot-filled, boiled or stored in a refrigerated case. In addition, crosslinking the adhesive significantly increases bond strengths and reduces the possibility of tunneling.

There are several commercially available crosslinkers for water-based polymers, each differing in reactivity, pot life (the length of time the adhesive can be used after a crosslinker is added) and effect on final properties. It should be noted that the adhesive polymers used with these crosslinkers are anionic (stable in water), having carboxylic functionality in the backbone (reacts with the crosslinker), which is neutralized with a volatile tertiary amine or ammonia. The presence of the carboxylate salt renders the polymer dispersible or emulsifiable in water.

Pot life is always a consideration with any two-component ambient cure system. Reactions that occur through the carboxylic acid functionality tend to have an excellent pot life of eight to 10 hours because these reactions are typically alkali-hindered. Polymers neutralized with ammonia or an amine routinely have a pH >7.5. As the ammonia or tertiary amine volatilizes during the drying process, the carboxylic acid functionality becomes available to react with the crosslinker. The isocyanate-hydroxyl reaction is common for solvent-based adhesive systems, resulting in exceptional properties. When dispersible isocyanate crosslinkers are used with water-based polymers, the systems are plagued by the isocyanate-water side reaction. As a result of this reaction, dispersible isocyanate systems are limited to pot lives of four to six hours in order to maintain performance properties.

Although the water-based adhesives are dried at elevated temperatures of up to 200 degrees F., due to short dwell times of two to four seconds in the drying ovens it is believed that the majority of the crosslinking reaction takes place in the finished lamination at ambient temperatures, which are usually 77 degrees F. Heat-aging a dry-bond lamination is not always required. In most cases, a lamination can be cut or slit to its final size almost immediately after laminating. Even though the crosslinkers have not fully reacted with the base polymer, there is still enough laminate integrity for the slitting operation. This in turn enables a laminator to produce material on a "just-in-time" basis. Aside from the actual equipment used in production, the rapid turnaround time of dry-bond laminating is the most critical difference between dry-bond laminating and solventless laminating.

Solventless Adhesives

First-Generation Adhesives. The first solventless laminating adhesives developed were polyurethane moisture-curing products. These adhesives are made from isocyanate prepolymers, the reaction product of a polyol with excess isocyanate. The prepolymers are high in viscosity, which gives excellent initial bond strengths; however, they require an application temperature of 90 to 100 degrees C. The adhesive is coated onto the primary film and atmospheric moisture reacts with the excess isocyanate groups to crosslink the adhesive after the secondary film has been mated to the primary film; slitting can usually take place in 24 to 72 hours.

First-generation curing mechanism:

R-NCO + H2O _ R-NH2 + CO2

R-NH2 + R'-NCO _ R-NHCOHN-R'

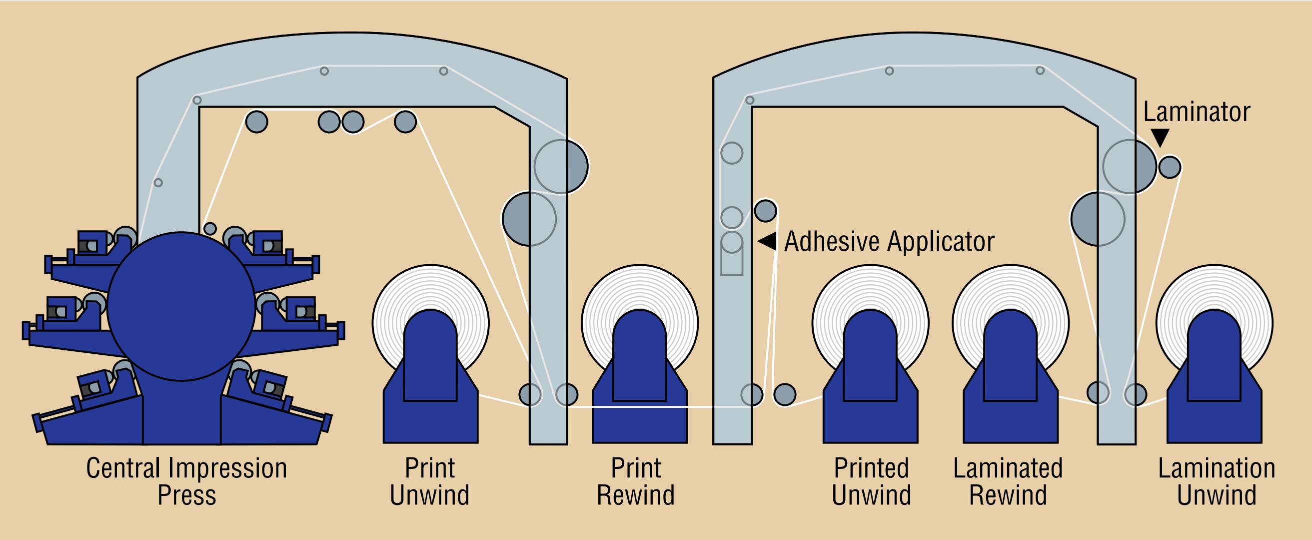
The problems encountered with using these first-generation adhesives are bubbles in the lamination, a cloudy appearance in clear films and inconsistency of the cure rate. The bubbles are produced by the by-product carbon dioxide of the curing reaction, and can be trapped when high-barrier films are laminated. The amount of atmospheric moisture that comes in contact with the adhesive as it is coated can lead to a cloudy appearance in clear films and an inconsistency in the cure rate. Moisture is often added to the primary film by means of a spray boom just prior to nipping the secondary film. This will increase the rate of cure, but it also reduces the clarity of the laminated film by leaving a cloudy appearance. This cloudy appearance can readily be seen in clear laminations and in clear package window areas of printed structures.

Second-Generation Adhesives. The next major advancement in solventless laminating adhesives was the development of two-part polyurethane adhesives. These products are comprised of a polyurethane prepolymer and a polyol, both low in viscosity. The components are mixed together with a meter-mix-dispensing unit at room temperature and pumped onto the coating station of the laminator through an in-line static mixer. The meter-mix in combination with the static mixer ensures that the proper ratio of adhesive components is present and completely mixed, resulting in a consistent cure rate.

Second-generation curing mechanism:

R-NCO + HO-R' _ R-NHCOO-R'

The problems encountered with using these second-generation adhesives are low initial bond strengths and the presence of high residual monomer. The low initial bonds are a result of the low viscosity of both adhesive components, which means tighter laminator controls are needed to prevent laminations from tunneling before the adhesive has a chance to properly cure. Slitting the lamination can only take place after a 12- to 48-hour cure time. The high residual isocyanate monomer causes a phenomenon known as anti-seal. This occurs when the isocyanate



A flexo press with a separate laminator allows the converter to use both machines in tandem or independently, thus offering a wide variety of applications.

monomer migrates through a soft sealant film such as polyethylene and reacts with atmospheric moisture. This reaction creates a very hard and thermally stable polyurea layer that renders the laminate unsealable. In addition to the anti-seal problems, there are possible health risks due to worker exposure from the high-residual monomer. Finally, the presence of isocyanate monomer requires EPA documentation and reporting, which can be a time-consuming burden for any laminating converter.

To address the problems associated with using first- or second-generation solventless adhesives, third-generation two-part polyurethane adhesive systems that have a consistent cure rate, low residual monomer and increased initial bond strengths have been developed.

Third-Generation Adhesives. Typical third-generation adhesives are based on moderate-viscosity polyurethane polymers that require a 50-degree C. to 70-degree C. application temperature. The increased viscosity of the third-generation versus second requires a 12- to 24-hour cure time before slitting. The third-generation adhesives are made from a process that removes nearly all of the excess isocyanate monomer from the prepolymer component, consistently resulting in a blended adhesive system with less than 0.08 percent free isocyanate. The low residual isocyanate monomer eliminates the anti-seal issue, health concerns from worker exposure to isocyanate monomers and the regulatory documentation associated with isocyanates.

Third-generation curing mechanism:

R-NCO + HO-R' _ R-NHCOO-R'

The majority of solventless laminators in the United States are still applying a second-generation adhesive system. The meter mix dispensing units are not generally equipped with heating capabilities. In order for a laminating converter to begin using a third-generation adhesive, a capital expenditure to update their meter-mix-dispensing unit with heating capabilities is necessary. This capital expenditure can often delay the conversion to a third-generation adhesive or altogether discourage a converter from changing to a third-generation system.

To overcome this hurdle and keep the equipment expenses associated with using a third-generation adhesive system minimal, a third-generation adhesive has been developed that can be pumped and mixed at room temperature through existing meter-mix dispensing units used with second-generation products. This system gives a laminating converter the many benefits of using a third-generation adhesive without any expensive meter-mix dispensing equipment upgrades.

Conclusion

As the government regulations to reduce VOC emissions become more and more stringent, film-laminating converters are faced with several choices that enable them to comply with the new laws. Polyurethane dispersions and acrylic emulsions are very viable alternatives to conventional solvent-based products; when they are reacted with crosslinkers such as polyfunctional aziridine or dispersible isocyanate, they have properties that often exceed the solvent-borne systems. In addition, third-generation solventless adhesives are an alternative technology to dry-bond laminating that also enables a converter to meet the rapidly changing environmental and performance standards.

About the Author…
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