Film and foil lamination with ultraviolet curable adhesives

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UV adhesives are winning acceptance as alternatives to existing technologies in the packaging and plastic card industries.

Historically, multilayer laminating processes, such as those used by manufacturers of blister packs and credit cards, have utilized solvent-based pressure-sensitive adhesives (PSAs) as the means of bonding the laminations. Developments within the last 10 years, driven by EPA and OSHA requirements, have focused on elimination of the solvents by conversion to water-based analogs or change-over to thermoplastic hot melts. Although these technologies have enjoyed limited success in that they reduce overall solvent emissions, they have not allowed the typical end user to increase productivity. In some instances, they have caused slowdowns in production. The extended time necessary for water flash has not satisfactorily been resolved, nor have the melt temperatures of hot melts been lowered enough to allow hot-melt usage on temperature sensitive substrates. Much more development is necessary with these two technologies before they can claim to be universal replacements for solvent-based PSA technology.

Coincidentally, with the reduction of solvent-based PSAs, there has been a great deal of focus on the use of a wider spectrum of substrates. These new substrates have allowed laminators to produce end products exhibiting better environmental resistance, flexibility, appearance, and overall product quality at theoretically higher production rates.

A major problem is that the evolution of the new generations of substrates has outpaced that of the evolution of new generations of adhesives.

A group of 100% solid ultraviolet (UV) curable laminating adhesives—basically one-component acrylic functional materials— offer the advantage that various chemistries, mainly epoxy and polyurethane, can be formulated into the backbone of the acrylic oligomer. Using this category of adhesives allows the laminator:

- To eliminate the need for drying and curing ovens
- To remove solvent recovery systems
- To use a wide variety of heat sensitive substrates
- To greatly increase production speeds.

Photoinitiation and photopolymerization

UV-curable adhesives and coatings can be broadly classified into two categories: free radical polymerized and cationic polymerized. The interest in cationically cured adhesives has grown recently, but for purposes of this paper the focus will be free radical initiated polymerization.

Polymers formed by free radical polymerization are generally based upon acrylic monomers or oligomers. These monomers are typically 100% solids. They are converted to high molecular weight polymers with varying degrees of crosslink density upon exposure to ultraviolet radiation.

Free radical polymerization

The process of polymerization of UV-curable adhesives consists of four steps. This process is initiated when the liquid sample is exposed to a light source. The first step of the process is the excitation of the photoinitiator to a singlet or triplet state. The area of the electromagnetic spectrum which is responsible for exciting the photoinitiator is typically 200-400 nm.

The excited state photoinitiator can undergo two possible reactions. The type 1 process involves a cleavage of the photoinitiator into two molecular radicals. In the type 2 process, the triplet excited photoinitiator abstracts a hydrogen from a labile donor molecule, such as a hydrogen on a carbon adjacent to an oxygen or nitrogen. This results in the formation of an initiator radical and a radical site on the donor molecule.

The next step is the initiation step. The efficiency of this step is determined by the structure and stability of the free radical species formed. The third step is propagation or growth. During this step, the formation of the polymer network is occurring through the addition of monomer radicals.

The final stage is termination. The method in which termination occurs ultimately affects the performance of

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the resultant polymer. There are several possibilities for the termination reaction. The first possibility is the most desired—the combination of two polymer radicals, resulting in a high molecular weight polymer. Chain transfer occurs when a growing polymer radical abstracts a labile hydrogen from a chain terminating agent. This results in a lower molecular weight polymer.

Oxidation is responsible for the third termination mechanism. Oxygen reacts rapidly with a growing chain to form an alkyl peroxyradical. This radical can undergo further chain extension, although typically the process is orders of magnitude slower than the normal polymerization. In practical terms, it is too stable to initiate further reaction. Therefore, formation of the peroxyradical terminates the reaction.

Free radical photoinitiators

There are various types of free radical photoinitiators. The three major classes are benzophenone-amine, alpha-substituted acetophenone, and amino acetophenone. Each has various advantages and disadvantages.

Benzophenone-amine. This is probably the most widely studied and best understood of the major photoinitiators. The benzophenone extracts a hydrogen from the amine, leading to the formation of two free radicals, each of which is excellent at initiating the polymerization process. Secondarily, the amine radical is an efficient oxygen scavenger. It has primarily found use in thin film coatings and varnishes because of its excellent surface cure and high crosslinking capability. Its present use in adhesives is limited.

Alpha-substituted acetophenone. This class of photoinitiator involves a homolytic cleavage reaction. The electron-rich nature of this initiator species accounts for its high efficiency. The most common member of this class is α hydroxy cyclohexylphenylketone (HCPK). The advantages of HCPK are excellent cure through, low odor, and good formulation color stability.

Amino acetophenone (AAP). The major advantage of this class is the speed in which formulations containing it cure. It has found significant usage in applications where thin film curing is necessary (similar to benzophenone-amine applications). The advantage over alpha-substituted acetophenones is that there is no need to use highly volatile amines.

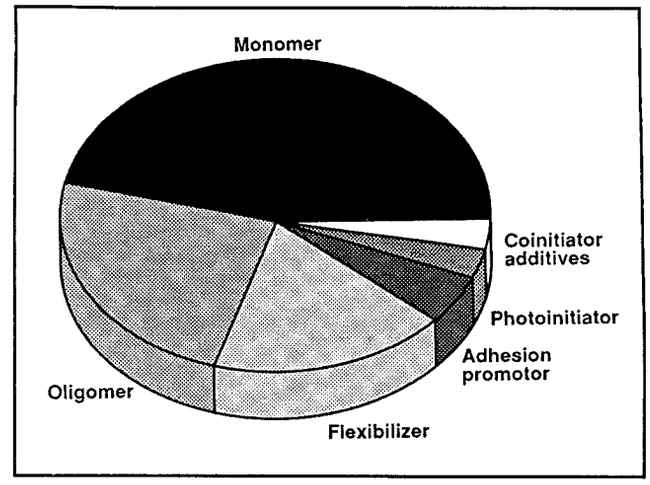
One of the drawbacks to the introduction of UV technology has been the issue of user safety, due to the absorbance range (far UV-200-370 nm) of the photoinitiators mentioned above. This drawback has been partially resolved through the combined use of a photoinitiator with isopropyl thioxanthone (ITX). This allows an increase in the depth of cure obtained from a photoinitiator which by itself gives a good surface cure. The sensitizing effect of ITX on the photoinitiator, with the resultant shift, makes the use of near visible and potentially visible light a reality. The importance of this effect will become apparent later in the article.

UV adhesives—formulation and applications

Adhesive formulation

UV-curable adhesives offer a number of advantages over other types of adhesive systems. Most important among these are the capability to use them on heat-sensitive substrates, their speed of cure, absence of volatiles, and in-line testing.

1. Basic UV-curable adhesive formulation



Other advantages of UV curing include:

- Rapid cure—within 1 to 30 s
- Substrate versatility
- Minimal heat generation
- One-component formulations
- Fewer fixtures and less part handling
- Possibility of in-line quality control
- Possibility of shadow curing.

As with any class of adhesives, there are also limitations, the key one being that there must be a UV transparent substrate when using a free radically cured system. Other potential limitations are the limited depth of cure (0.25 in.) and the surface tack of some acrylics.

UV-curable adhesives offer a wide range of formulating possibilities. **Figure 1** shows a breakdown of a typical UV-curable adhesive formulation. Each of the materials is important in the ultimate performance of the end product, but the key is the nature and concentration of the photoinitiator. Unlike thermal initiators, where an increase in concentration typically leads to an increase in reaction rate uniformly throughout the bulk material, varying the concentration of the photoinitiator affects where the radiation is absorbed. This in turn determines where the initiating species are generated, with the result that increasing or decreasing the photoinitiator will affect properties such as depth of cure.

Optimization of photoinitiator levels has historically been a matter of trial and error, with a formulator using a personal databank of past experiences for future formation and product modification. The following factors will play a role in selecting the optimum photoinitiator for a particular application.

UV light source. There are a multitude of bulbs available, each with a specific fingerprint of wavelength emission. The choice of a photoinitiator becomes dependent upon the bulb chosen and its respective fingerprint. Thus, in selection of a photoinitiator, one should match the major

energy absorbance to the lamp spectra.

Intensity of UV light source. The intensity of the radiation source will directly affect the rate of generation of the initiating species as described by the equation below:

$$d(P)/dt = \phi_p I_a \quad (1)$$

where:

$d(P)/dt$ = rate of formation of initiating species

ϕ_p = quantum yield

I_a = intensity of radiation absorbed

Therefore, the use of a photosensitive catalyst may be necessary when using a bulb of low intensity. This is especially important in areas such as foil laminations, where lower intensity light sources may be used to prevent distortion of heat-sensitive substrates.

Another consideration of intensity is the life of the bulb. Bulb life varies from 300 h to 1000 h of use. As bulbs age, they typically begin to lose intensity.

Substrate being bonded. Depending upon the end application, the substrate may need to have UV resistance. If that is the case, the substrate typically will have a UV absorber added to screen the shorter wavelengths of radiation from the adhesive. In those instances, a photosensitizer such as ITX will be necessary to utilize the longer wavelength radiation which does penetrate the substrate.

Joint design. The typical UV adhesive must receive direct irradiation by UV light. Steps must be taken to eliminate the need for "shadow curing" or the curing of material not directly exposed. If there is a need for shadow curing, the formulator may need to use a secondary curative system, such as a cationic catalyst, which may require some type of post cure. This necessitates further processing which in turn decreases production rates.

Additional key ingredients in formulation

Other key ingredients in UV adhesives include acrylic monomers, acrylic oligomers, flexibilizers, adhesion promoters, and fillers. They function in the manner described below.

Acrylic monomers. These materials have a significant influence on the application and performance traits of the end product. Features such as adhesive viscosity, crosslink density, and functionality are the building blocks around which the other ingredients are chosen.

Acrylic oligomers. These are typically the proprietary ingredients in the formulation. They are usually created by end-capping other polymers, such as epoxies or polyurethanes, or by partially reacting acrylic monomers to a controlled endpoint based on molecular weight or molecular structure.

Flexibilizers. These materials impart a higher degree of flexibility to the adhesive. Typically, they are nonreactive materials such as thermoplastics, which are solvated by the acrylic materials or dispersed throughout the formulation by high shear.

Adhesion promoters. It may be necessary to add an adhesion promoter in some cases to attain adhesion to difficult-to-adhere-to substrates such as polyethylene or polypropylene.

Fillers. These may be as simple as mineral fillers or as complicated as colorants and dyes.

Although these appear to be the same basic ingredients as in any adhesive formulation, the choice is more critical in UV curables because each ingredient will have a direct effect on the cure of the final material. Most additives will interfere with the photoinitiation by absorbing variable amounts of the available energy. Thus, even the addition of 0.05% of an adhesion promoter may change a formulation from a rigid cured material to a material that will not cure.

Processing

In choosing the application equipment for utilization of UV technology, the same considerations must be given as to any other adhesive application. The product should be formulated with handling characteristics which fit the application and curing equipment to be used. This allows the adhesive to be formulated to the necessary viscosity for the application equipment, color for the end product, cure response of the equipment to be used, and adhesion characteristics of the substrates, or it allows the equipment to be manufactured to match the adhesive and the desired process.

The basic component of the UV-curing system is the irradiation source. As previously noted, there are many types of bulbs available with specific wavelength fingerprints. The most common in use are the D-Bulb, the V-Bulb, and the H-Bulb or Hg-(mercury) arc Bulb. A by-product of the light source is heat, evolved from the infrared portion of the electromagnetic spectrum. This heat is generated by the vaporization of Hg in a vacuum-sealed bulb containing an inert gas. Two methods of accomplishing this are presently available. One involves the vaporization of Hg by passing an electric current (arc) through the sealed bulb. Because of the bulb design, the bulb must be allowed to cool off (up to 15 min between use cycles) each time it is turned off to avoid thermal shock to the glass bulb. There is also a lag time caused by the delay necessary to re-arc the mercury, which makes instant on/off impossible. As a result, the bulb is typically left running. Even when operating at a reduced power level, this results in the following drawbacks:

- A decrease in useful bulb life
- The necessity for shielding to dissipate heat. Typically a water-cooled shield is used.

A second technology is based upon the use of microwave energy to excite the Hg to a vapor. Due to the capability of the Hg to act as an "antenna," it vaporizes much faster when exposed to microwave radiation than when exposed to an electrical arc, creating an instant on/off bulb. This feature, coupled with an improved bulb design, means such bulbs can be turned off during breaks and powered up to use within 30 s.

Another advantage of the second technology is that the bulbs operate at lower temperatures due to the built-in air cooling systems supplied by the manufacturer, which allow use at higher intensities without distortion of the substrates. These lower temperatures result in significant increases in production rates, cure through substrates with

I. Line speed vs. bulb intensity

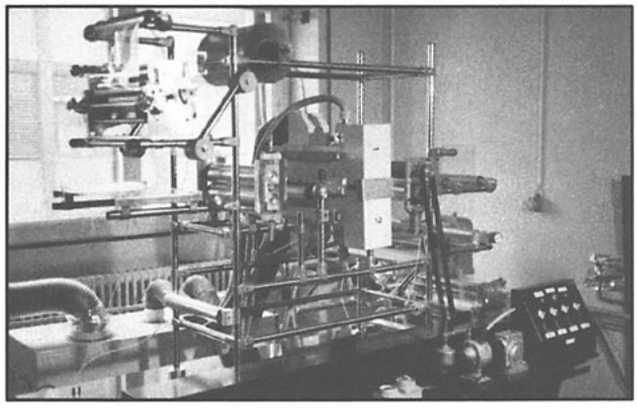
Bulb type	Output	Black ink max. line speed, ft/min	White ink max. line speed, ft/min
D-Bulb	300 W/in.	35	
H-Bulb	300 W/in.	70	50
D-Bulb	600 W/in.	70	
H-Bulb	600 W/in.	140	115
Hg Arc	300 W/in.	20	30
Hg Arc	400 W/in.	35	40

II. Bulb intensity vs. cure depth

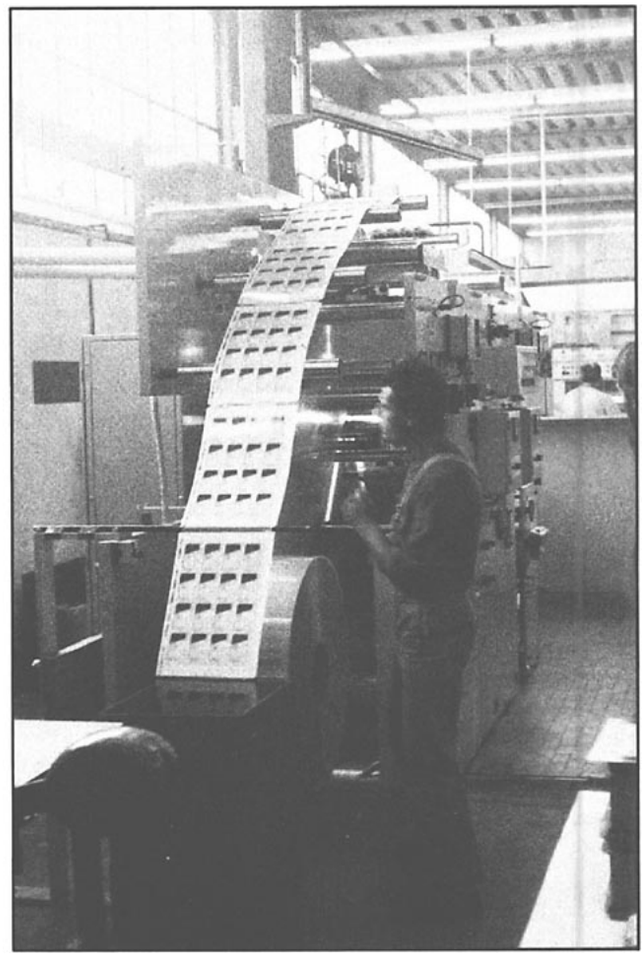
Bulb type	Intensity	Depth of cure, mils
H-Bulb	300 W/in.	1.55
D-Bulb	300 W/in.	3.0
H-Bulb	600 W/in.	14.0
D-Bulb	600 W/in.	21.0
Hg Arc	300 W/in.	2.0
Hg Arc	400 W/in.	6.0

Polymer was a clear thiolene-based photopolymer.

3. Foil laminating equipment



2. Blister packaging equipment



some UV blockers added, deeper throughcure, and cure through heavily colored adhesives. These bulbs still generate heat, however, and in large applications, shielding is typically required.

Table I compares the maximum line speeds offered by using a D, H, or Hg (arc) bulb at various intensities. **Table II** shows the effect of increasing intensity on the depth of cure. As can be seen, a significant increase can be achieved by increasing the intensity of the light source.* This performance is key in laminating technologies where high production rates, typically > 100 ft/min, are the general rule.

Applications

The following three examples of in-process applications illustrate the utility of UV adhesives in the packaging industry. Prototypes of machinery were developed with participation of the end user.

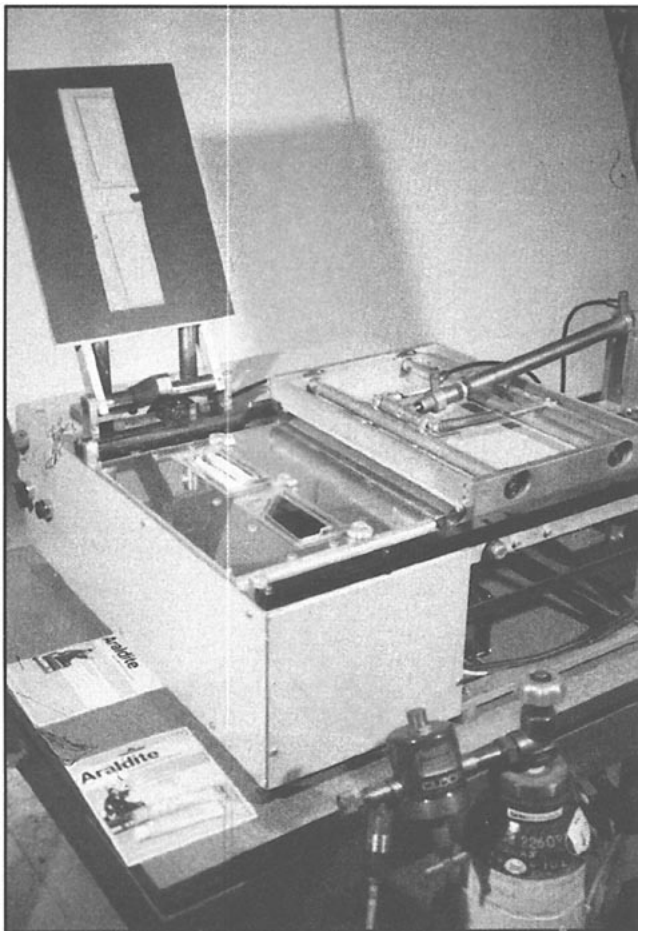
Blister packaging

This form of packaging is used for fast processing of sealed packages for retail marketing. The major advantage is that small parts can be locked in place by the bonding of a formed thermoplastic top (blister) to a backing, typically a cardboard piece coated with a thermoplastic hot melt. Adhesion is accomplished through a heat cycle of 5-7 s at 150-180°C.

The standard substrate at the present time is PVC, 400 μm thick film. For toxological reasons, alternative materials are actively being sought. These alternative materials—polystyrene (PS), polyamide (PA), polyacrylonitrile (PAN), polycarbonate (PC), and polyethylene terephthalate (PET)—have increased melting temperatures and poorer adhesion traits. When used in a conventional manner, the conversion to these newer substrates results in decreased production rates from the higher temperatures and longer cycle times needed.

*Schaeffer, W., Resins and Pigments Catalogue, "UV curable materials and its relationship to the power levels and lamp spectra," Oct. 3, 1990.

4. Card lamination equipment



These limitations can be overcome by the use of evolving UV adhesive technology. Almost all plastic foils usable for blister packaging are suitable for use with UV technology.

Application of the UV adhesive to the border of the blister pack can be accomplished through silk screening, relief and gravure printing, roll coating, or spraying. The blister is then positioned onto the backing with low pressure. Production equipment is illustrated in **Fig. 2.** The part is then irradiated for as little as 0.2 s, thus eliminating the potential for heat deformation of the blister. Postcuring and cooling are unnecessary. Attempts at destroying the bond immediately after UV fixturing results in tearing the carton backing.

Another advantage of this technology is the ability to use lower-cost carton papers. All common papers, even corrugates, are usable with UV technology due to the excellent adhesion characteristics of the adhesive to those substrates. Testing has also shown that diverse substrates such as metalized paper, wood, or plastics also are adhered to satisfactorily.

Lamination of multilayer foils

Multilayer foils are widely used in the packaging industry. Often more than two layers of different materials are laminated simultaneously. The industry standard is to use solvent-based two component polyurethane adhesives.

UV-adhesive technology currently provides a viable alternative with significant advantages in this niche of the packaging industry as well. Trials on laboratory pilot equipment, as shown in **Fig. 3,** demonstrate the utility of this process. Production units currently using alternative technologies can readily be converted to commercial UV-processing equipment. Because of the increase in production speeds, elimination of solvents, and elimination of drying ovens and mixing equipment, cost savings, and improvements in product quality are easily realized.

Multilayer plastic card laminations

Plastic cards have shown a phenomenal growth rate over the last five years due to the advent of such applications as hotel cards, personal ID cards, and access cards for telephone systems, banking, airlines, and other services. The largest increase has been due to the rapid growth in the credit card industry. Despite this growth surge, the methods of production have basically remained constant.

A PVC core material carrying the relevant information is laminated with either one or two layers of a thin PVC film. The lamination is then accomplished in a heated press at 120–150°C for up to 20 minutes. Disadvantages of the process include the potentially damaging effects of the heat and delays in production due to loading, unloading, and cure times for the process.

Technical problems also arise from obtaining correctly dimensioned sheets and a defined melt profile of the PVC. In order to achieve acceptable adhesion, it is also necessary to have a specific, controlled surface roughness. Finally, the PVC presents toxicological problems. Therefore, an alternate technology is necessary for the industry to continue to service the growing marketplace.

The major advantages of using UV adhesives for plastic card bonding are the increase in production speed from 1700/h to 50,000/h, the reduction in necessary manpower and, most importantly, the increase in product quality. An added advantage with this technology is that falsification or modification of the cards is virtually impossible. With hot-melt technology, it may be possible to melt, modify, and reseal the card. **Fig. 4** shows a current in-production unit with the capability of producing more than 50,000 cards per hour.

Summary

This article introduces the basics of UV-adhesive technology and its utility in the packaging industry. With an understanding of the photochemistry involved, the end user will better be able to understand the overall process when considering the change to UV. The examples provided show how the technology is adaptable to the packaging/foil laminating marketplace and illustrate the range of versatility in using UV-curable adhesives.□

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