


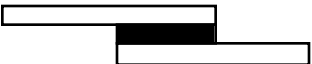

UV Structural Adhesives and Sealants

How They Are Unique In The Larger Universe Of Photocuring Resins

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UV structural adhesives and sealants exhibit some unique characteristics within the universe of photocuring resins. With the rapid expansion of new photocuring applications (as well as resin and equipment products), a better understanding of some of the broad differences separating structural adhesives from other photocuring resins can assist potential users in determining whether or not their application is suitable for photocuring.

Photocuring resins can be broadly divided into thick and thin layer curing applications. Essentially, all of the structural applications fall into the "thick layer curing" group with the vast majority of other photocuring resins falling into the "thin layer curing" category.

Thin Layer Curing Resins	Thick Layer Curing Resins
Inks, clear overprint coatings, floor coatings, photoresists and decorative coatings	Structural adhesives, sealants and encapsulants
	
<p align="center"><u>Typical Thickness</u> 5-50 microns</p>	<p align="center"><u>Typical Thickness</u> .003 to .250 inches typical</p>
<p>(*special applications to 300 microns)</p>	

By segregating thick layer bonding, sealing and coating applications from thin layer applications, some distinguishing characteristics of each group emerge. For purposes of this discussion, thin layer applications will be defined here as those applications in the thickness range of 5 to 50 microns. This includes most of the ink and decorative coating applications summarized in the following discussion. In contrast, thick layer photocuring applications generally fall within the range of 75 to 6250 microns (.003 to .250 of an inch). This is sometimes measured from a single surface application, but often between two bonded surfaces.

I. Introduction And History

Thin Layer Resins - UV Inks And Coatings

UV inks and coating applications have grown and diversified since the early 1970's when they were first introduced in response to the energy shortage, and primarily, as cost effective solvent free alternatives to solvent-based inks for the graphic arts. By 1995, the estimated use for products for these applications was >45,000 metric tons per year for the North American Market with a total value of some \$300,000,000. With approximately 10% per year projected growth, the amount used in North America by 1998 would be 60,000 metric tons. Major uses for thin layer resins include clear overprint coatings for paper and paperboard, photopolymer printing plates, clear floor coatings, lithographic inks, screen print inks, electronics, photoresists, metal deco coatings, clear coatings for plastics, pigmented paper coatings and wood other than flooring products.

Thick Layer Resins - UV Adhesives And Sealants

The earliest applications for UV adhesives during the late 70's were in glass assembly and stemware applications. The broad commercial acceptance of UV adhesives and sealants in industry was spurred by technological advancements in the late 1970's and early 1980's. Perhaps the most important of these was the development of aerobic acrylic adhesives that offered materials which were essentially non-flammable and solvent free. As with the thin layer photocuring inks and coatings, environmental acceptability was a key driver for growth. Interest in the technology grew rapidly as the manufacturing and productivity advantages of this technology became better understood. During the 80's and 90's, UV adhesives and sealants reached into most industry developing a wide range of uses as summarized in Table I. Today, the North American market for UV adhesives and sealants in these applications is estimated to be between 300-500 metric tons annually.

Though very small in volume in relation to the inks and coatings industry, the diversity of new application possibilities and rapid acceptance of photocuring across the industrial spectrum promises to greatly accelerate future growth.

Table I

Typical Thick Layer Applications
Glass and plastic headlamp assembly
Electrical sealing and tacking
Optical assembly
Microelectronic assembly
Dome coatings
Conformal coatings
Medical Disposable Device assembly
Coil terminating
Tamper proofing
Fingernail coating
Formed-In-place gaskets

II. Thin Versus Thick Layer Resins - Major Differences

Thin layer resins provide a striking contrast to thick layer resins in almost all respects. Their typical uses, application equipment and facilities required to apply them, as well as the physical properties and the range of application requirements which must be met, are different. The typical end uses for thin layer resins as summarized above can be seen to vary dramatically from those listed for thick layer curing resins in Table I.

Application/Market Driven Differences

To generalize, typical uses of thin layer curing resins involve either printing inks, or the covering large surfaces with very thin layers of resin. These applications utilize large volumes of resin on very large surface areas. Floor coverings, cans, newspapers, wood products, etc., are good illustrations of this point. The combination of high volume, large surface area and a thin layer resin results in a relatively low value-added profile for the ink or coating in relation to the cost per square foot of the item being produced. Thick layer resins, in contrast, are used for applications where much smaller amounts of adhesive or sealant are used. In this case, the adhesive or

sealant is usually replacing an alternative, non-photocuring technology. It may even be replacing an adhesive tape or fastening technique, such as mechanical fasteners. The selection of a thick layer UV curing resin, in either case, is intimately tied to a combination of value added issues which provide significant cost savings due to such things as process step elimination, increased productivity, etc. Thick layer coatings are often a custom solution which offers a very high value added to the end user. See general application types listed in Table II.

**Table II
Typical Application Types Based on Coating or Sealant Geometry**

	Thin Layer Resins	Thick Layer Resins
Bonding plastic, metal & glass (to 4,000 psi)	No	Yes
Coatings 5 to 50 microns on porous surfaces, metal glass, plastic and floor coverings; inks, laminating	Yes	No
Sealing seams to .125"	No	Yes
Tacking to .125 inch drop	No	Yes
Potting to .250 inches	No	Yes

Differences In Properties

It takes little imagination to understand that the range of resin properties necessary to coat paper, metal cans and wood products is significantly different from those required in the bonding of medical disposable devices, sealing of metal motor housings, or the bonding of automotive head lamps. Some of the properties include: viscosity, adhesion (exceeding the strength of various substrates), abrasion resistance, clarity, surface dryness or slickness, environmental resistance, dishwasher resistance, resistance to severe thermal shock, solvent resistance, and hardness. A closer look at the physical and chemical properties of thick and thin layer resins in Table II reveals some of the more important differences in typical properties.

**Table III
Typical Properties Chart for Thin and Thick Layer Resins**

Ranges For	Thin Layer Resins	Thick Layer Resins
Cure depth	1-100 mils deep layers not easily available	1-100 mils typical thickness used
Cure speed	Fractional second cures	1 to many seconds cures "typical"
Viscosity	500 - 1500 cP	10 - 200,000 cP
Adhesion to metals, plastic & glass	Pass industry cross hatch testing-30 PLI	4,000 psi or substrate destruction
Abrasion resistance	Good to excellent	Fair to good
Clarity	Water white to pigmented	Water white to straw, or translucent
Surface dryness/slickness	Excellent dry surfaces	Dry surface cures

Moisture resistance	Poor to excellent	Good to excellent
Hardness (Shore A&D)	D 70 - D 90	A 30 to D 80
Ranges For	Thin Layer Resins	Thick Layer Resins
Resistance to thermal shock under load	Poor	Good to excellent
Solvent resistance	Good to excellent	Good to excellent

Processing Differences

Thin and thick layer resins vary most in their processing requirements. Because of the great speeds at which printing presses and other large commodity printers and coaters must run, speed of dry surface cures for typical inks and coatings must be as fast as possible. Run rates from several hundred to 1200 feet per minute are common. Therefore, with these run rates, chemistry must be optimized to cure as fast as possible in thin layers. Usually large Conveyor/ Curing systems requiring substantial capital investment for high speed printing are needed.

The dispensing equipment required for thin film resins varies from large screen printers to sophisticated spraying and curtain coating systems. Four foot wide web presses that are 20-50 feet long are typical. Because exposure to the UV light is only fractions of a second, highly focused lamps of maximum intensity are required. Workers need to be screened from the high intensity lamps by the design and length of the conveyor system. It should also be noted that in thin film coating, cure is sometimes effected by exposure to electron beam radiation. In this case, these otherwise similar formulations do not need photoinitiators. The capital costs associated with EB (electron beam) however, are significant and very application specific. Thus, they are only justified by high volume applications and very high run rates (line speeds).

In contrast to the very fast thin layer curing resins, their thick layer cousins typically creep along at 1 to 20 feet per minute in their typical cure depths. Importantly, with this slower run rate and curing speeds from 1 to 30 seconds upon exposure to moderate and high intensity UV lamps, productivity is typically greatly enhanced over other assembly or coating methods. See Chart I, Typical Thick Layer Adhesive and Coating Cure Rates with a Range of UV Lamps.

Thick layer industrial applications have given rise to a UV equipment industry all their own. This has been most noticeable in the last ten years with the development of high intensity spot, or wand style curing lamps designed to cure small, relatively thick spots of adhesive. These advancements in equipment technology have been directly attributed to the rapid growth in end use applications and the need for more custom manufacturing solutions (rather than just new adhesives or sealants) to meet customer needs in the assembly of their products. Such responsiveness to individual end user manufacturing needs through the engineering of equipment systems that take full advantage of UV technology will continue to support application growth in the future.

Many applications require only lower intensity curing lamps. Bonding between surfaces, one of which allows light to pass, is one of the applications where resin may be effectively cured with lower intensity, lower cost lamps. Most UV formulations are capable of curing within 1 to 30 seconds through clear glass or plastic parts under lower intensity lamps. Because the inhibiting effect of oxygen is not present, cures are relatively fast. Bond lines are usually fairly thin - .001 to .125 inches.

The lamps shown below represent the range of equipment available for curing thick layer resin applications.





Conveyors with Lamps Mounted



Custom Curing Chambers

Custom Curing Chambers



UV Spot (Wand Lamps)



Moderate Intensity Flood Lamps



Hand Held Lamps

Chart I
Typical Thick Layer Adhesive And Coating Cure Rates With A Range Of UV Curing Lamps

Lamp/Type	Moderate Intensity UV Flood	Higher Intensity UV Flood	High Intensity UV Spot	Very High Intensity UV Spot	Conveyorized Beam 2 x 1200-EC High Intensity	Conveyorized Electrodeless Lamps
Spectral Output of Lamps (nanometers)	300-500	200-500	200-500	200-500	200-500	200-500
Nominal Intensity (mW/cm²)	20-60	175-225	1000-2000	1800-5000	225-275	1700 - 2000
Typical Adhesive Cure Rate						
(UV/Visible Cure Adhesive)						
Between Surface Cures (Glass)	1-4 sec	1-3 sec	<1-2 sec	1 sec	3-5 feet/min	5-20 feet/min
On Surface Cures*	40-240 sec	10-40 sec	2-10 sec	1-5 sec	1-3 feet/min	3-10 feet/min
(UV Cure Adhesive)						
Between Surface Cures (Glass)	2-6 sec	1-4 sec	1-3 sec	2 sec	2-4 feet/min	5-15 feet/min
On Surface Cures	30-600 sec	20-50 sec	3-5 sec	1-3 sec	1-2 feet/min	1-10 feet/min

Ranges represent the fastest and slowest cure times of Dymax formulations under the stated lamps.

*Some formulations never achieve a dry surface cure, though most do. The time range stated represents the fastest to the slowest curing products.

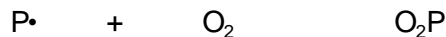
Differences In Curing Chemistry

All light curing formulations include, in addition to the basic resin chemical constituents - oligomers, monomers, thickeners, adhesion promoters, etc. - photoinitiators that react when exposed to light of the correct wavelengths to cause polymerization of the resins. These photoinitiators are organic molecules which can absorb light and become excited molecules which degrade and produce radical species. It is these radicals that initiate the polymerization of the monomers and meth(acrylate) oligomers. This general reaction is applicable for both thin and thick layer curing resins. However, one of the chemical problems associated with the generation of the radicals is their quenching by molecules of oxygen. This is know as oxygen inhibition.

Figure I - Free Radical Formation



Figure II - Opportunities For Atmospheric Oxygen Inhibition



Oxygen inhibition retards the development of cure on the surface of the coating. Inks need to cure in thin layers to surface dryness very fast (at high run rates) upon exposure to high intensity light. The oxygen inhibition problem is, thus, a serious concern for thin film coatings. To overcome this phenomenon in thin film coatings, a series of steps are typically taken: (1) the region under the lamps can be flooded with nitrogen gas (to eliminate the oxygen); (2) amino alcohols, which mitigate the oxygen effect can be incorporated into the formulations; (3) highest intensity lamps are utilized.

The oxygen inhibition issue is frequently less of a concern for thick film structural resins. Many UV cured structural adhesives are placed between clear substrates for cure which eliminates the oxygen altogether, and the thick layer surface cures can be long enough (1 to 30 seconds typically) to eliminate the tacky surface upon exposure to high and even low to moderate intensity UV lights. In other words, by the time a $\frac{1}{8}$ inch cure depth has been effected, the surface usually cures quite dry to the touch.

Some general formulating differences to achieve the different features exhibited by structural adhesives and thick layer coatings versus inks and thin layer coatings, are shown below in Table IV:

**Table IV
Some Formulating Differences Between Inks And Adhesives**

Inks and Decorative Coatings	Adhesives and Protective Coatings
Multifunctional monomers and oligomers	Mono or difunctional more typical
Pigments, dyes and colorants	Rarely used
Co-curing catalysts maximize line strength	Rarely used
Highly cross linked formulations to achieve fastest cures	All degrees of cross linking depending on physical and processing properties desired
Amino alcohols recommended can be used	Not typically used
5-50 Micron thickness typical	Thin layers only recommended between surfaces

III. Thin And Thick Layer Resins - Sharing A Common Technology Base

In his excellent article, "Understanding UV Curing Relationships", Mr. Richard Stowe described the basics of the curing technology underlying the UV resin curing industry. He correctly identified the components of a UV curing system as including ***the application, curable chemistry of the resin and the lamp system***. More importantly, he explained that the parameters that define a successful cure are entirely dependent on the end-product requirements. In other words, the cure is only successful if the desired properties of the end product are achieved. (We would add that the ease, consistency and cost effectiveness of this occurring is also a primary indicator of success to users of the technology.)

Additionally, Mr. Stowe explains how the optical characteristics of resins impact curing, and finally, he explains the basic concepts of UV curing, as well as the terminology used in describing the significant aspects of this phenomenon. (Reference "Wavelength Magazine" Issue 1.1, Pages 14-18).

IV. Thin And Thick Layer Resins - Common Advantages

Reasons photocuring is being adopted in favor of conventionally cured resins are similar for both thin and thick layer resins. Some of the most compelling are listed below:

Reasons To Use
Reduced cost per unit; net economic advantage
Faster production rates
V.O.C. reduction - improved air quality
Lower rejects
Properties not matched by other materials
All in line process (100% Q.C.)
Space savings
Less waste
Easier to use/control
Eliminate costly fixtures and jigs
Low temperature cures
Energy savings

When Photocuring May Not Be The Best Choice

As with any technology, there are times when a photocuring process may not be the best choice. The primary one would be if some aspect of the assembly blocks resin from exposure to light. For most practical purposes, light curing adhesives and sealants require direct exposure to light in order to cure. There are however, exceptions to this rule. The main one is that some UV curing resins also have other, secondary curing mechanisms that will work in some applications. UV curing catalysts have long been combined with activator and heat curing systems in a variety of resins. More recently, two-part systems and systems that are also sensitive to curing upon

exposure to oxygen and moisture have been developed. These systems are practical where UV curing is the primarily curing mechanism and the majority of the resin is light cured. Another exception are the UV epoxies that claim to continue to cure following exposure to light. This is a very compelling claim as it inspires thoughts of a brief initiation starting a chain reaction that can continue until complete regardless of circumstances. As a matter of fact, the circumstances are limited, difficult to predict consistently, and vary widely from application to application.

Summary

Understanding the differences between thin and thick layer resin markets, applications, processing requirements, and chemistry is helpful in deciding whether or not photocuring can or should be used as a successful alternative to some other coating or bonding method. Furthermore, once the distinction is clear, and the range of properties clearly understood, choosing the best resin and equipment for the application becomes a much easier task.