Effects of UV Exposure Conditions on Speed, Depth of Cure and Adhesion

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[Presented at RadTech North America 2002, Indianapolis, IN; April 9-12, 2002]

ABSTRACT

The physical properties of UV-cured materials are substantially affected by the lamp systems used to cure them. The development of the intended properties, whether a varnish, an ink, or an adhesive, can depend on how well these lamp factors are designed and managed. The four key factors of UV exposure are: UV irradiance (or intensity), spectral distribution (wavelengths) of UV, time-integrated UV energy (or "dose"), and infra-red radiation. Inks and varnishes will exhibit very different response to peak irradiance or energy, as well as to different UV spectra. One of the properties that is the most sensitive to peak irradiance and correct wavelength is depth of cure and resulting adhesion. Depending on the irradiance profile, some of the UV energy is wasted and does not assist in deep cure and adhesion. The ability to match the various lamp characteristics to the optical properties of the curable materials, widens the range in which UV curing is a faster, more efficient production process.

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INTRODUCTION

There are a number of factors (outside of the formulation itself) which affect the curing and the consequent performance of the UV-curable material. These factors are the optical and physical characteristics of the curing *system*[1]. Among them are the key elements of the UV source:

UV Irradiance is the radiant power, within a stated wavelength range, arriving at a surface per unit area, usually expressed in watts or milliwatts per square centimeter. Irradiance varies with lamp output power, efficiency and focus of its reflector system, and distance to the surface. (It is a characteristic of the lamp geometry and power, so does not vary with speed). The intense, peak of focused power directly under a lamp is referred to as "*peak irradiance.*" Irradiance incorporates ***all*** of the individual effects of electrical power, efficiency, radiant output, reflectance, focus, bulb size, and lamp geometry. When Irradiance is measured in any specific range of wavelengths, it is called "*effective irradiance.*"

UV Energy Density is the radiant energy, *within a stated wavelength range*, arriving at a surface per unit area. Sometimes loosely referred to as "dose," it is the total accumulated photon quantity arriving at a surface, per unit area. Energy is inversely proportional to speed under any given light source, and proportional to the number of exposures (for example, rows of lamps). It is the time-integral of irradiance to which a surface is exposed as it travels past a lamp or a sequence of lamps, usually expressed in joules or millijoules per square centimeter. (Unfortunately, no information regarding *irradiance*, irradiance profile, or peak can be derived from a measurement of energy ("dose"), although many researchers and formulators continue to use this measure alone). In this paper, "energy" will be taken to mean "energy per unit area."

Spectral Distribution is the relative radiant energy as a function of wavelength or wavelength range. It is the wavelength distribution of radiant energy emitted by a source or arriving at a surface. It may be expressed in power units or in relative (normalized) terms. Analyzing the radiant energy from a bulb by grouping spectral energy into 10-nanometer bands yields a distribution plot (or table) which is more convenient to apply to spectral power and energy calculations than fine-resolution data. This distribution may be applied to the *radiant* output of a lamp, or to the *irradiance* at a surface.

Infrared Radiance: The amount of infrared energy emitted by the quartz envelope of the UV source. The heating effect it produces may be a benefit or a nuisance. (IR and its control are addressed in other papers[2]). This is difficult to measure, so it is often easier to measure its effect on the temperature of the work surface.

Significance of UV Irradiance

All inks, coatings, or adhesives will absorb the UV arriving at the surface, but the radiant power available deeper within the film will depend on the absorption in the film. ***The higher the radiant power at the surface, the higher the power at any depth within the material.***

The reduction of light energy as it passes into or through any material is described by the Beer-Lambert law. Energy which is not absorbed in an upper layer of the film and not reflected is transmitted and available to lower layers, according to the following expression:

$$I_{a\lambda} = \frac{I_{o\lambda}(1 - 10^{-A\lambda})}{d}$$

$\boldsymbol{I_o}$ is the incident energy at wavelength **λ**, $\boldsymbol{I_a}$ is the energy absorbed, $\boldsymbol{A_\lambda}$ is absorbance at wavelength λ, and ***d*** is the depth from the surface or film thickness.

Examining this law as it relates to radiant power absorbed in the top (surface) and the bottom (contact layer) of a film permits the analysis shown in Figure 1. By dividing the Beer-Lambert expression into 100 "layers," we can display the relative UV flux through the extreme top "layer" and the extreme bottom "layer." The relationship shown in Figure 1 is true for any film of any physical thickness.[3]

Calculation further shows that the "optimum" (theoretical) absorbance of a film of any thickness is 0.4 to 0.43. In other words, the maximal absorption in the bottom layer occurs when there is a "best" combination of film thickness and absorption.[4] As we see, this "ideal condition does not often occur in practical inks and coatings, as it represents a very low absorbance (very transparent) film. Figure 1 also illustrates that <u>even at the best conditions</u>, energy absorbed at the top surface is **2½ to 3 times** the energy absorbed at the bottom! For a film with an absorbance of 3.0, this ratio of top to bottom power is approximately **1 thousand**!

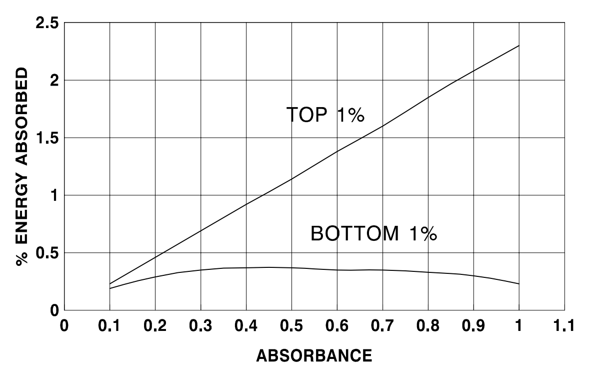

Figure 1
Light Energy Absorbed in Top and Bottom of a Film

For any film with a fixed spectral absorbance, the <u>only</u> way to increase I_a (photon fluence rate) at any depth is to increase irradiance, I_o , at the surface.

Peak Irradiance

Peak irradiance is the highest power level of radiant energy at the work surface. Typical irradiance profiles are illustrated in Figure 2.

All three lamps illustrated in Figure 2 deliver the same total energy to a surface passing under them, but at different irradiance levels (note that the area under each curve is the same but the peak is very different). These bulbs have the same electrical power input ("watts per cm") but are of different diameters, the smallest yielding the highest peak.

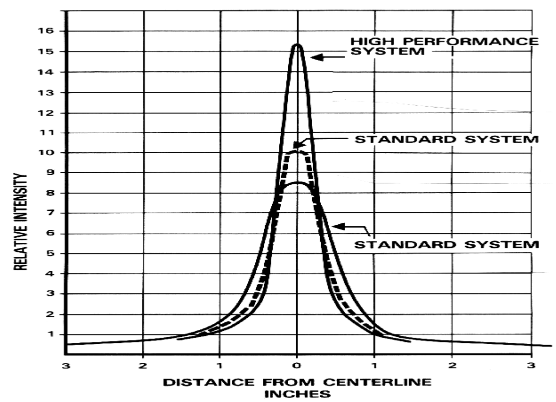

Figure 2
Irradiance Profile at Focus of Typical UV Lamps

The elliptical reflector is generally the highest efficiency of reflector, as it has the greatest "wrap," or included angle of reflected energy about the bulb. Often reflector shapes other than the simple ellipse are considered. Table I shows the relative merits, measured by speed to achieve cure of a black screen ink. This demonstrates the effects of bulb diameter and reflector geometry with lamps of the same power, but different peak irradiance and optical efficiency.[5]

TABLE I

Lamp Diameter, Reflector Type, (120 w/cm)	Cure Speed, (m/min)	Energy, (mJ/cm^2)	"Index of Effectiveness," Speed/Energy
9 mm, elliptical	21.2	140	151
23 mm, elliptical	13.6	200	68
23 mm, parabolic	12.1	190	64

Black screen ink on polycarbonate, 390 mesh

Controlling maximum peak irradiance is principally through the selection of lamp geometry, because it is integrally associated with reflector design and bulb diameter. Reflector shape (e.g., elliptical or parabolic), reflectivity and precision of shape, bulb diameter, radiant efficiency, electrical power input will contribute to peak irradiance at any distance from the lamp.

Which is More Important -- Irradiance or Energy ?

Energy density ("dose") is the most commonly reported measure of UV exposure, but when referenced alone, without other information, is an incomplete specification. Energy is included here as an important measure in process specification because it is the only one that incorporates the factor of *time*.

The *specific wavelength* range must be reported also, as it will very from type-to-type of measuring instrument. Most radiometers measure irradiance but calculate energy electronically. Radiochromic films record cumulative exposure (energy) only.

Irradiance Profile

The measurement of energy density incorporates irradiance *profile*, the wavelength range of interest, and time. The exposure *profile* is characteristic of any lamp design. It is not possible to increase the peak-to-energy ratio of a lamp -- this is determined by its design. Increasing lamp power does not alter the peak-to-energy ratio (at any speed). Typically, once a lamp is selected, the only *controllable* variables in a curing process are speed and lamp power. This gives the (unfortunate) impression that energy ("dose") is the only measurement needed. It also leads to the unfortunate conclusion that increasing electrical power is the only way to increase irradiance.

The cured properties of clear coatings and varnishes (low absorbance) *tend* to correspond to the total energy applied. In other words, their practical cure speed may be increased by increasing the UV power, somewhat independently of irradiance or irradiance profile. Increasing the number of exposures under second or successive lamps will increase cure speed incrementally, but not proportionally.

Materials with a higher optical density will exhibit higher absorption of UV power, resulting in diminished power at depths within the film. These more *optically thick* materials *(see Figure 1)* may exhibit loss of throughcure or adhesion, as energy decreases with increase of speed, for example. More opaque materials will tend to show more dependency on the intensity, or peak irradiance to achieve throughcure.

Method of Determining Sensitivity to Peak Irradiance

An easy laboratory test to determine the extent to which a coating or ink is affected by peak irradiance is to compare the cure achieved with a test lamp at a high peak of focus with the cure achievedwhen the lamp is out of focus (low peak of irradiance). If the results are the same, the material is relatively insensitive to the irradiance profile. If the effect of peak is significant, then increasing the peak will improve the speed performance, most often evidenced by adhesion behavior. (If a high-peak lamp is not available, this appraisal cannot be performed).

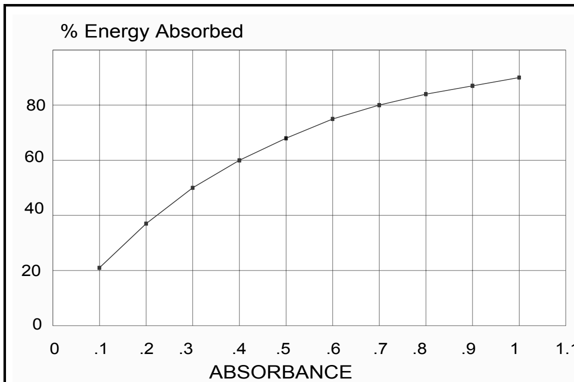

Figure 3
Energy Absorbed in a Film vs. Absorbance

Energy Absorbed in the UV Curable Film

Figure 3 illustrates the absorption of

radiant energy in a UV-curable film. Clearly, varnishes and clear coatings will absorb different energies, even in the same thickness of film.

Spectral Absorption

All inks and coatings each have their own characteristic *spectral* absorbance, ranging from high absorbance of short UV wavelengths, to lower absorbance for longer wavelengths.[5] ***Spectral absorptivity is a key factor in determining the best wavelengths for most effective curing.***

A Simple Method to Determine Spectral Absorption

The absorption of a film can be demonstrated with even the simplest of instruments.

A black screen ink and a clear coating were compared by printing them on a quartz plate, and measuring the effective transmission with a multi-band radiometer (Table II and Table III). This simple measurement demonstrates the fact that the *absorption is different at different wavelength bands*, and is very different for materials of different absorptivity.

A quartz plate is used as the substrate. The ink was screened with a #355 mesh, yielding a film of approximately .7 mil (18 micron). Measurements were made with the quartz plate over the radiometer, before and after printing, thus eliminating (or reducing) the effect of the quartz plate transmission and reflectance. The radiometer was an EIT UV Power Puck® (modified for high irradiance); the lamp was a Fusion UV I600 (240 W/cm) with a 13 mm diameter "D" bulb. These results are shown in Table II.

Table II
Absorption of Energy in UV Screen Ink

	Radiant Power, mW/cm^2	
	UV_A(320-390nm)	UV_B(280-320nm)
Top Surface of Ink	6660	1995
Top of Substrate (bottom of Ink)	138	157
Absorbed in Ink	98 %	92 %
Available for Cure at substrate	2 %	8 %

Table III
Absorption of Energy in UV Press Varnish

	Radiant Power, mW/cm^2		
	UV_A (320-390nm)	UV_B (280-320nm)	UV_C (250-260nm)
Top Surface of Coating	2162	2161	254
Top of Substrate (bottom of Coating)	1400	880	15
Absorbed in Coating	35 %	59 %	94 %
Available for Cure at Substrate	65 %	41%	6 %

The same set of measurements were made on a clear press varnish (GPI Sun Chemical), with a film thickness of 0.5 mil (13 micron), and are shown in Table III. The radiometer was a UV Power Puck® (modified for high irradiance); the lamp was a Fusion UV I600 (240 w/cm) with a 13 mm diameter "H" (mercury) bulb.

"Optical Thickness"

The combined effects of spectral absorptivity and physical thickness result in a distinct ratio of photon flux through the top of the film and the bottom. When this ratio is greater than 10, the film can be described as ***optically thick.*** A film can be optically thick to short wavelengths, while being opticcally thin to longer wavelengths, but the ratio of flux will be fixed for any specific wavelength.

Peak and Energy

As illustrated in Figure 2, different configurations of lamps will have different irradiance profiles. If we are interested in the peak irradiance (intensity) in relation to the shape or width the profile, we can examine this ratio. A highly focused lamp will have a higher ratio than a lamp system that is poorly focused or has been moved out of focus. In fact, the peak of the profile curve is the peak of irradiance, and the area under the curve is proportional to energy. *Peak irradiance is not a function of speed, but is consequence of lamp configuration and power.*

A Dramatic Illustration of the Effect of Peak Irradiance - Screen Ink Adhesion

Table IV is typical "cure" data for a black screen ink. NorCote #1019 black screen ink was printed onto a polycarbonate substrate with a 355 mesh screen, yielding approximately 0.7 mil (18 micron) film thickness. A *cure ladder* (results with increasing speed) was run with a Fusion UV F600 (600 W/cm electrical input) lamp, with a 13 mm diameter "D" bulb. Peak-to-Energy ratio was varied by successively moving the lamp out of focus (an easy technique of varying irradiance). The range of peak irradiance was nearly 7 to 1. Energy and peak irradiance were measured with an EIT PowerPuck®. Energy at higher speeds was calculated by applying the inverse speed relationship. Data point pairs (peak & energy

Table IV
Successful "Cure Speed"
Determined by Adhesion

Peak, mW/cm^2 UVA	Energy, mJ/cm^2 UVA	Speed, in/sec
6730	365	28
5260	536	22
3430	558	18
1640	587	14
1060	1160	6

0.7 mil (18 micron) NorCote #1019 black screen ink, #355 mesh, on polycarbonate, F600, "D" Bulb

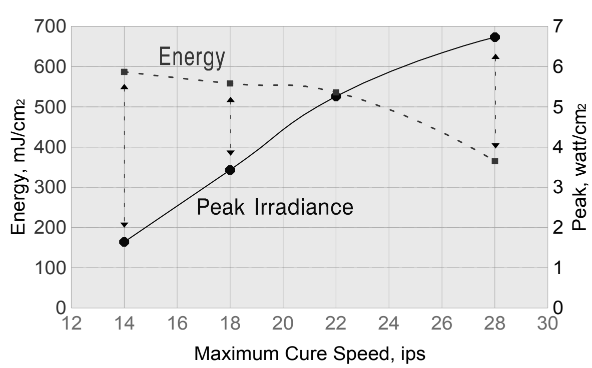

Figure 4
Peak Irradiance and Energy to Achieve Adhesion
Black Screen Ink, 0.7 mil (18 micron), F600, "D" Bulb

required) represent achievement of successful cure, determined by satisfactory adhesion, measured with a traditional cross-hatch tape-peel test.

Successful cure speed of an optically thick film of an absorptive material is clearly affected by peak irradiance In order to examine the relationship further, we can plot peak-to speed, and the correspondidng energy required (Figure 4). Again,each data point pair represents the speed up to which successful 'cure' (adhesion) was achieved.

Experiment With Narrowed Exposure Width -- Altered Irradiance Profile

In an experiment to explore the peak-to-energy ratio further, a slit aperture was placed in front of the lamp so that the peak irradiance is approximately the same as the test above, but the exposure profile is limited to a width of approximately 2 inch (25 mm), thus reducing the total energy, and increasing the peak-to-energy ratio. The slit aperture blocks the lower-irradiance "tails" of the exposure profile. The data is shown in Table V and in Figure 5.

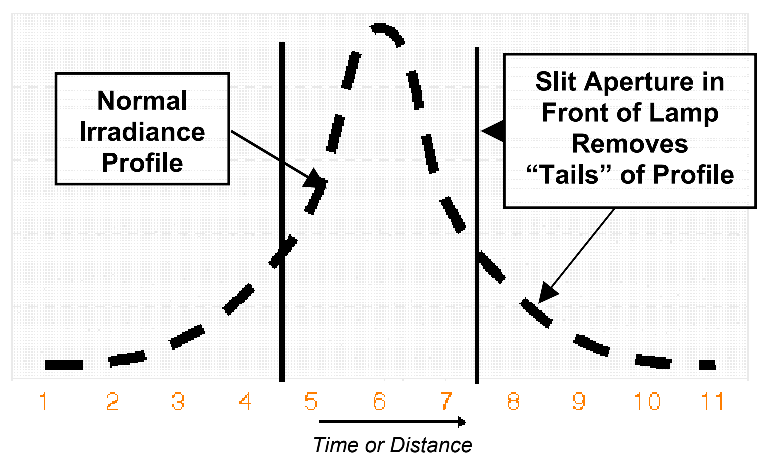

TABLE V
Successful "Cure Speed"
Determined by Adhesion
(Exposure profile narrowed with use of 2" slit aperture)

Peak, mW/cm$^2_{UVA}$	Energy, mJ/cm$^2_{UVA}$	Speed, in/sec
6320	197	16
4810	231	12
2670	277	6
1610	346	3
1007	380	2

0.7 mil (18 micron) NorCote #1019 black screen ink, #355 mesh, on polycarbonate, F600, "D" Bulb

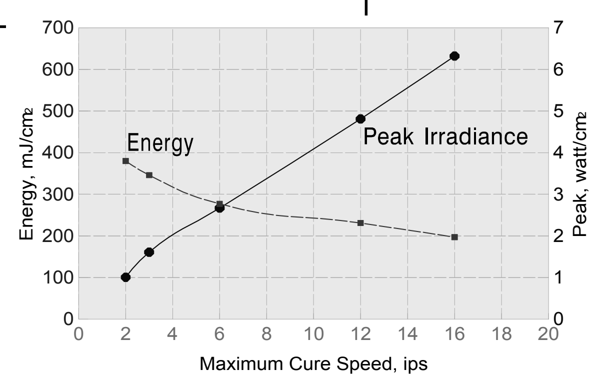

Figure 5
Peak Irradiance and Energy to Achieve Adhesion
(Modified Irradiance Profile)

It is easier to see the significance of this data when plotted on the same graph (Figure 6). The

Figure 6
Effectiveness of Cure Conditions, Screen Ink
(Figures 4 and 5 combined)

experiment not only demonstrates the fact that "cure" can be achieved under a variety of conditions, but that by altering (or selecting) the exposure profile, a significant difference in the cure *efficiency* can be achieved.

Significance of Peak Effectiveness

Examination of Figure 6 suggests that the same cure speed can be achieved with lamps or lamp geometries having different peak-to-energy ratios. However***, the higher the ratio, the less total UV energy is required to accomplish cure***. When UV energy is reduced, so is the radiant energy associated with visible and IR energy to which the surface is exposed. This will reduce the surface temperature of the cured film.

Peak and Energy Effects with Flexo Ink

Flexographic inks are usually laid down at film thickness from 4 to 7 µm (.1 to .25 mil). While they are inks and have a high absorptivity, the physically thinner film will exhibit less overall absorption than heavier screen inks.

Owing to the thin film section, even though of a high absorptivity, there will be less of the total incident energy absorbed in the film, leaving a higher radiant flux at the film-substrate boundary. This should make flexographic inks less peak-sensitive than screen inks.

Table VI
Flexographic Ink
(from Asmann[6])

Peak, mW/cm^2 UVA	Energy, mJ/cm^2 UVA	Speed, in/sec	Tape Peel
2360	449	10	4.8
1470	454	9.2	4.8
1060	454	8.8	4.3
770	441	8.3	4.4
600	449	7.6	4.0

Cavanagh Black Flexo Ink
(Cavflex 60 Black 30-165, E0613)

Asmann[6] explores lamp factors as they affect "cure" of a flexo ink. In this experiment, UV energy is adjusted by varying transport speed, and peak is varied by setting the lamp progressively farther from the surface. The object was to examine cure with varying peak, yet nearly constant energy.

It is evident from the tape peel test data in Table VI that adhesion is significantly affected by the irradiance level. The data clearly indicates that the adhesion is significantly influenced by the peak irradiance, and the relative contribution of peak and energy is consistent with expectation of a *thin film* of an *absorptive material.*

Clear Coats and Varnishes

The "traditional wisdom" is that the cure requirement of clear coatings and varnishes can be expressed in energy terms only. From Table VII, it is understandable that a "clear" material can tolerate a wide range in irradiance before the radiant power level in the material is diminished to the point that cure is affected. Some previous studies have explored peak and its effect on depth of cure and conversion in clear material.[7]

A coating of approximately 0.5 mil (13 micron) of GPI Sun Chemical Suncure was applied to Lenetta paper, and a cure ladder run to determine simple "loss of cure," determined by tack. The lamp was a Fusion UV F300 with an "H" bulb. Energy and Peak in the UVA_{EIT} and UVB_{EIT} ranges were measured.

The surprise here is that the energy required to cure, rather than being constant, is also *reduced* with higher peak irradiance.

Table VII
Successful "Cure" of a Clear Coating

Peak, mW/cm² $\xi_{A,B}$	Energy, mJ/cm² $\xi_{A,B}$	Speed, in/sec
1690	43	60
1290	43	50
770	53	35
480	58	30

0.5 mil GPI Sun Chemical Suncure varnish

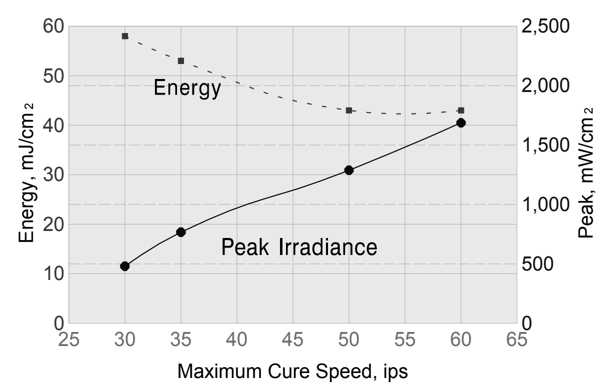

Figure 9
Clear Press Varnish
Peak Irradiance and Energy to Cure

Jönsson and Bao[8] also demonstrate that there are significant differences in the double bond conversion at an upper and a lower layer of a clear coating film when exposed to a low-irradiance source, and that these differences are *reduced* when exposed to a high irradiance source.

CONCLUSION

There are several factors that affect depth of cure -- and consequently adhesion -- in inks or coatings. The most important of these is *spectral absorptivity* of the ink or coating itself. A UV curable material will have a distinct spectral absorptivity curve, depending on its ingredients. Monomers and oligomers will absorb in the short wavelength UV; photoinitiators will, of course, have their own characteristic spectral absorption, and pigments or other additives will extend the absorption into the longer UV.

High absorbance of inks and physically thick films cause a reduction in radiant power in deeper layers, resulting in adhesion failure. While the bulk of the film may be "cured," there is inadequate energy at the boundary with the substrate. A simple method of overcoming this is to increase irradiance.

We can make several general observations:

- Energy alone is not an adequate specification of cure conditions;
- High irradiance is critical to achieving depth of cure for absorptive films;
- High irradiance can improve curing efficiency by reducing the energy required to cure.

The shape of the UV exposure profile -- the rise to a peak of irradiance followed by a corresponding fall -- is another source of some inefficiency. Because the irradiance profile has a somewhat complex shape, there is a portion of this profile that will not contribute to 'throughcure.' Experiments reduced these "tails" of the typical curve in order to explore and demonstrate the benefit of increasing the peak-to-energy ratio of the profile.

"Wasted energy," in the form of exposure to wavelengths or irradiance levels that do not activate photoinitiators, is an inefficiency in UV curing. The UV energy (and other radiant energy) which is absorbed by the film is a function of its spectral absorptivity, irradiance at its surface, and time of exposure. Methods that can reduce the *total energy* delivered to a film, while accomplishing "cure" will increase the efficiency of the process.

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