Non-Reciprocity of Exposure of UV-Curable Materials and the Implications for System Design

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Abstract

Using exposure data of various (mostly commercial) coatings, inks and paints, this study demonstrates that differences in irradiance profile will result in different material behavior (properties) and consequently, exposure requirements. Using various quantifiable performance characteristics, this study demonstrates the reciprocity failure of UV exposure. This paper introduces the "E-Ip" chart for UV curable materials and simple methods for creating it. To differing degrees, curable materials will exhibit different E-I thresholds of physical property development. Evaluation of the non-reciprocity of any subject material is important to 3-D and multi-lamp system design. It also leads to more precise and more useful exposure requirement specifications for commercial materials, and provides a means of communicating material responsivity essential for production design.

Introduction

It is a fairly common practice for a supplier of commercial formulations to indicate the "cure" requirement of a UV-curable coating, ink, adhesive, or paint in "joules per square centimeter" (J/cm^2) or in "millijoules per square centimeter" (mJ/cm^2). Typically, this does not include much more additional information than the identification of the general UV wavelength band of interest, or the general type of lamp to be used.

A simple "specification" of exposure may not be sufficient because it does not provide enough information for the selection or design of the most effective UV exposure or process configuration. However, it is a practical necessity, owing to the fact that there is no way to know, at the supply level, what film thickness, substrate, or production speed will be required in a user's application. For this reason, the process development step of production design must include a series of test exposures to determine the optimum exposure, and verification of the achievement of all specific physical and chemical properties of the final cured material. Accordingly, the supplier's "specification" of exposure can be, at least, useful to provide some guidance and approximation of optimum exposure.

In the process development step, the four key exposure variables[(1)] are in play.

- Irradiance profile
- Wavelength distribution
- Time and
- Temperature

It should be noted here that exposure, in J/cm^2 or mJ/cm^2 is not a <u>primary</u> variable. It is the time-integral of irradiance -- a composite or secondary variable -- and is important to evaluating the required amount of radiant energy delivered to a surface to achieve a desired "cure."[(2)]

Reciprocity and Non-Reciprocity

Reciprocity is a term often used in a photographic context: ***Reciprocity refers to the inverse relationship between the intensity and duration of light that determines the reaction of light-sensitive material.*** This "inverse relationship" suggests that a result will be the same if the *intensity* is increased (or decreased) in the same proportion that *duration* is decreased (or increased). When this principle is explored in UV curing, we quickly find that most UV-curable materials do not behave this way, hence the "non-reciprocity of UV-curable materials."

An assumption of reciprocity in UV curing would lead to a conclusion that a similar result is achieved at the same exposure level (J/cm^2 or mJ/cm^2) independently from the values of irradiance or time. There are several factors that "interfere" with the simple reciprocity assumption:

1. The complex character of the irradiance profile;
2. The spectral opacity and absorbance of the curable film; and
3. The effect of time of exposure on temperature.

Some Tools: The E-Ip Chart

A very simple variation can be applied in the development lab to yield important design information. This involves only a simple "cure ladder" performed at two or more different distances of the lamp from the test surface, differentiated by the peak of irradiance, and the exposure required to achieve the same cure. For example, if the end process is 3-dimensional, not all surfaces will receive the same exposure. The least-exposed surface may set the pace for the entire process. It would be important to characterize the exposure required for "far" surfaces compared to "near" surfaces. Similarly, it will allow the prediction of behavior under lamps ranging from low power to high power.

Using the "Marginal Failure" Points

The most effective way to use the cure ladder as an analytical tool is to use any of the measurable end properties of the target process. Using a measurable property, the "marginal failure point" can be determined. Simply plotting the marginal failure point against the exposure conditions provides a revealing and useful characterization of the material behavior.

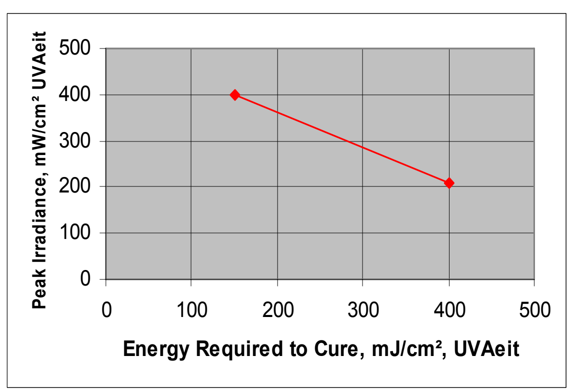

Figure 1. Exposure required to achieve the same chemical resistance (MEK Rubs) at different peak irradiance levels

Figure 1 shows an example of a clear coating for wood products. The peak irradiance of the exposure is plotted on the vertical axis. The horizontal axis shows the energy, or exposure, required to achieve the same result. In this example, "cure" was compared by equal chemical resistance (MEK rubs). In this example, only two data points provide an understanding of the behavior of this material under different exposure conditions. Note that the data was generated with the SAME lamp (bulb, power, etc.) but simply at different distances from the surface, altering the irradiance profile. The design implication of this is that there will be a difference in performance depending on lamp power, or that there will be a difference in "cure" in the *near-field* versus the *far field* of the lamp.

A "classic" example of this interaction is a screen print ink. Using adhesion to a simple polycarbonate substrate as the measure of success, we can evaluate the total energy required to accomplish "cure," illustrated in Figure 2. This is an example of how opacity (passive absorbance) can seriously affect non-reciprocity. Again, these data were taken with the same lamp (bulb, power, etc.). The design implications are large: while actually requiring less total energy, the higher irradiance cured at twice the surface speed as the lowest.

Figure 3 illustrates a slightly different way to present the E-Ip chart data. For this black inkjet ink, chemical resistance was the important physical property. Here, the ink was cured at an exposure of 90 mJ/cm^2. The difference in irradiance (and corresponding speed), although at the same exposure, resulted in a difference in measured chemical resistance.

Some applications and materials can show less extreme results. Figure 4 is a clear hardcoat for paper substrates applied at 0.2 mil (5 µm). Cross-hatch adhesion was measured with #810 Scotch Tape and the marginal failure points recorded. The difference in the energy required corresponds to the difference between the lamp in focus and approximately 1.2" out of focus, and correrspording marginal failure speed of 80 fpm and 40 fpm. This is more typical of a thin, clear, fast hardcoat. Note that reciprocity is still not achieved. (A vertical line would represent pure reciprocity.)

Irradiance Profile

In all of the above examples, the peak irradiance and the irradiance profile were increased or decreased together by varying the distance of a lamp from the work surface. Another example of non-proportional behavior can be demonstrated by altering the irradiance *profile* itself without lowering the peak irradiance. The exposure of Figure 5 was modified by "clipping" the "tails" of the typical irradiance profile, by placing a slit aperture near the focal plane of the lamp, illustrated in Figure 6.

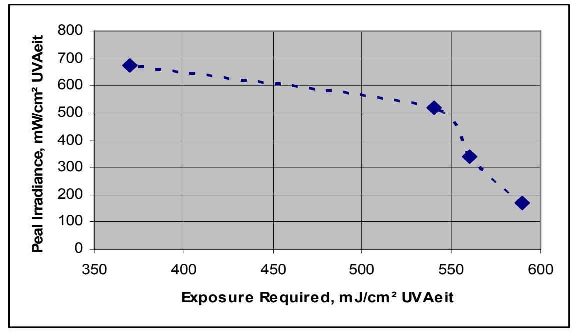

Figure 2 Exposure required to achieve cure as determined by adhesion of a 0.7 mil black screen ink to polycarbonate

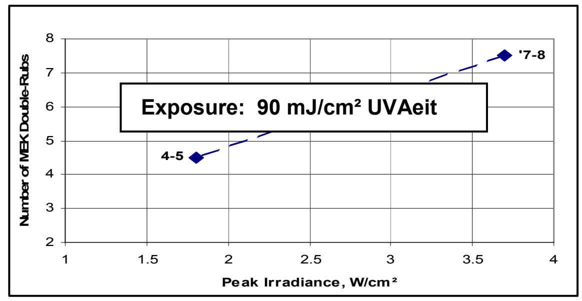

Figure 3 Equivalent exposure of a black ink-jet ink does not yield the same chemical resistance, measured by MEK double-rubs

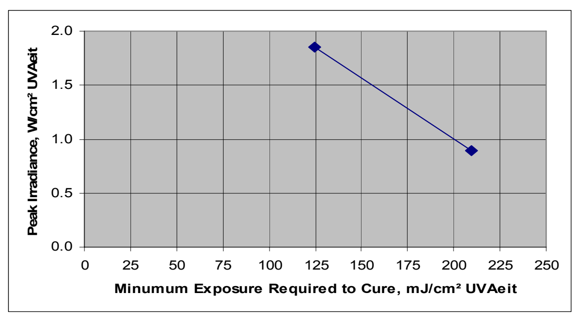

Figure 4 Exposure required to achieve cross-hatch adhesion of a clear hardcoat

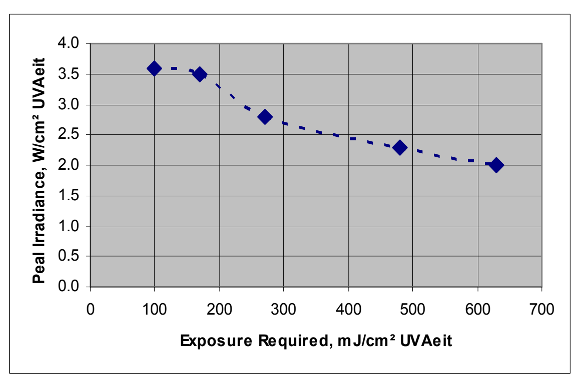

Figure 5 Exposure required to achieve adhesion of a black screen ink on polycarbonate, with the low-irradiance "tails" of the irradiance profile removed.

The ink in Figure 5 is a comparatively heavy, opaque film. It has been well-demonstrated that depth of cure is enhanced by a high peak irradiance.[3] The added implication is that the lower irradiance portion of exposure does not appreciably assist in depth of cure. This is energy delivered that does not contribute to the property of interest. The observation is that without knowing the irradiance profile, it would be difficult to specify the energy actually required to "cure." However, it is repeatedly demonstrated that for these "optically thick" films, a higher irradiance profile can be accompanied by a lower energy requirement.

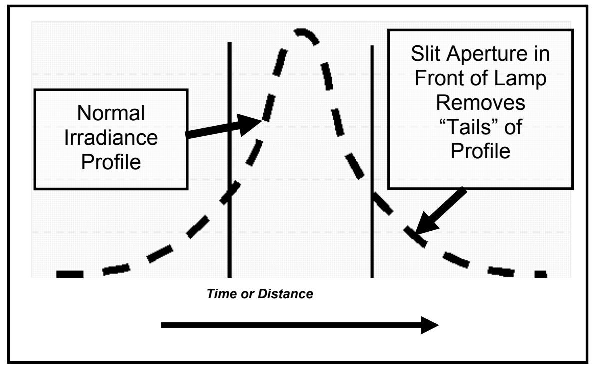

Figure 6 Experimental use of a "slit aperture" to study the peak-to- energy response of a coating

Implications of Molecular Dynamics

Photopolymer chemists understand well the Rates of Polymerization, Rates of Termination, and the implications of forming short chains versus forming long chains on the physical properties of a material. The dynamic behavior of an ink, coating, adhesive, or paint determines the exposure required. For example, "fast" coatings (clear varnishes, thin films, including offset inks) are designed to form properties with high peak irradiance and short-duration exposure. This, of course can be associated with short chain formation and and a higher degree of cross-linking, where the *rate* of exposure (photon flux rate) can be very high. For these films, "cure" speed can be increased by increasing UV power (irradiance) *within the range of general reciprocity*.

A traditional approach to increasing speed for "fast" or "optically thin" films is to add rows of lamps of similar type, size and power. Examining this approach to increased speed, we observe that this maintains the general irradiance peak and profile, while generally restoring the exposure *time*, and a limited kind of reciprocity is assumed. This is not the same as "multiple passes," which may not yield the same result at all. If the time between exposures is large with respect to the 'molecular dynamic' additional "hits" may have little or no benefit.

Slow Films

Some materials, such as some soft adhesives, PSA's, and elastomeric products and flexible gaskets, may require a controlled, slow exposure. A common design mistake is to assume that increasing power will increase production speed. A higher speed means a shorter exposure time. The result may be a product that does not have the desired flexibility, owing to the undesirable formation of more short chains and possibly of more trapped radicals, failing to form longer chains.

Figure 7 shows an elastomeric material, requiring substantial flexilbility and resilience similar to gaskets or contact adhesives. Higher irradiance or shorter exposure resulted in a film with poorer elastic properties. Contrary to what might be intuitive, the

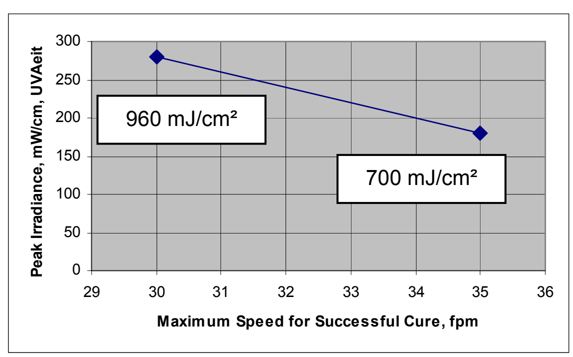

Figure 7 A Thick, Elastomeric Film Can Benefit from Longer, Lower Irradiance Exposure

lower irradiance (and exposure) yielded the desired properties at a higher speed!

Generally, a lower irradiance and a longer time of exposure will yield longer chain formation associated with softness or flexibility, and high irradiance and shorter exposure will produce more short chain formation associated with hard or durable surfaces.

Conclusions

The principal physical properties of a cured film are a result of the oligomers and monomers selected, as well as additives. Development of the target properties in the finished product also relies on the optimum UV exposure. Differences in film weight, substrate, additives, and physical properties can make each application unique. An effective laboratory tool in determining the optimum exposure is a cure ladder, using "marginal failure points" to identify the range of the four key exposure variables in which al of the desired properties are achieved. A relatively simple chart of the material behavior can be generated from a few data points.

Exposure (mJ/cm² or J/cm²) without information on the other of the key variables is a poor way to specify "cure" of a material. Using exposure alone as a specification for design or selection of UV lamps, power, speed, etc., can lead to unanticipated problems in production.

We can never assume that simply increasing power will result in proportionally increased speed. This would be an assumption of *reciprocity*, which most likely, does not apply.

The UV-curable material and the physical properties to be developed dictate what the optimun exposure should be. From that point, the "window"[4] of tolerable variation of the exposure parameters can be determined. This will be important to the design and configuration of the equipment and the determination of the "operating safety factors" to be designed into it.

Author's Note:
This paper has intentionally avoided the identification of any commercial product or any specific applications or products studied. The intention is to demonstrate the concepts and principles presented, based on actual test data.

References

1. Stowe, R. W., "Effects of UV Exposure Conditions on Speed, Depth of Cure and Adhesion;" Proceedings, RadTech North America, 2002
2. Stowe, R. W.; "Optimizing and Controlling UV Systems;" Proceedings, RadTech Asia, 2001
3. Stowe, R. W., "Practical Aspects of Irradiance and Energy Density in UV Curing;" Proceedings, RadTech North America; 2000.
4. Stowe, R. W.; "Practical Relationships Between UV Lamps and the UV Curing Process *Window*;" Proceedings, RadTech North America; 1994