METHODS FOR THE DESIGN AND OPTIMIZATION OF UV CURING SYSTEMS

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ABSTRACT

A wide variety of radiometric instruments are now available for measuring the radiant characteristics of industrial and laboratory UV lamps. Relating these characteristics to the performance of a UV-cured product depends on how well the selected parameters match the critical factors of the cure process. Further, the distinction between process *design* and process *monitoring* is significant, especially in the UV exposure characteristics to be measured.

Radiometry can be effectively used to correlate exposure conditions to the physical properties of the cured product. The four key conditions of UV exposure can be quantified, and by relating these to the set of properties required, the range, or "process window" in which the process will operate satisfactorily, can be increased.

INTRODUCTION

The physical properties of UV-cured materials are substantially affected by the lamp systems used to cure them. The development of the intended properties can depend on how well these lamp factors are designed and managed. The four key factors of UV lamps are: UV irradiance (or intensity), spectral distribution (wavelengths) of UV, UV energy (sometimes referred to as "dose"), and infra-red radiation.

The reduction of UV, as it passes into or through any material, is described by the *Beer-Lambert law:*

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

$\boldsymbol{I}_o$ is the incident irradiance (flux rate) at wavelength λ, $\boldsymbol{I}_a$ is the flux rate at depth *d*, $\boldsymbol{A}_\lambda$ is absorbance at wavelength λ, and ***d*** is the depth from the surface or film thickness. UV that is not absorbed in an upper layer of the film and not reflected is transmitted and available to lower layers.

This relationship can be used to characterizes the interaction between the UV exposure and rate of cure at any depth within a film whose spectral absorbance is known. Spectral absorbance includes the *passive* absorbance of oligomers, monomers and additives, and the *active* absorbance of photoinitiators.

Measurement: Process Design versus Process Control

The most important principle of effective radiometry is that the measurements must be relevant to the process or, in other words, must be related to the development of the *physical properties* of the final product. By thoroughly understanding the lamp-chemistry interactions, more precise and useful specifications can be determined for what to measure in the design of a process and for the establishment of meaningful limits that can be applied to process monitoring. In addition, data from radiometry must be communicated in a consistent and uniform way. This facilitates the duplication of the UV exposure conditions that produce the desired curing result, and is also important in the event that problem-solving communication with suppliers is necessary.

The ***process design*** phase determines *exposure* requirements such as peak and focus, irradiance profile, spectral distribution, power level, peak-to-energy ratio, temperature, and time. Radiometric measurements are useful in quantifying the successful exposure parameters, so the process can be reliably duplicated. The function of radiometry is to provide *quantitative* information about the critical requirements of the process and to establish the *limits* within which the process is successful.

Process Design

Objectives:
Optimize the cured properties of the end product.
Quantify the key exposure conditions:
- Effective Irradiance or Profile (W/cm²)
- Spectral Distribution (λ, nm)
- Time or speed (sec. or m/min)
- Infrared or temperature (°F or C)

Transfer the process to production

Process control maintains the process within the "window"[1] of operating limits. The primary purpose of process monitoring is to know when something has changed *before* it threatens the process. If the radiometric data collected doesn't relate to the process "window," it is not significant.

Process Control

Objectives:
Verify that the key optical conditions remain within specified limits ("process window")
Interpret changes in the exposure conditions to maintain control

Irradiance, Spectral Distribution and Energy

There are four key factors (outside of the formulation itself) that affect the curing and the consequent performance of the UV curable material. These are:

irradiance,
spectral distribution,

time, and
infrared (IR) or film temperature.

These factors are the UV *exposure* conditions, which are a consequence of the optical characteristics of the curing system. Simply stated, these are the exposure parameters that are sufficient to define the process.[2]

The time-*profile* of irradiance is characteristic of any lamp design. The peak of the profile is the peak irradiance; the area under the time-irradiance exposure curve is proportional to total energy. The relationship of the peak to total energy is important to cure efficiency. The shape of the irradiance profile is not affected by time or electrical power input -- it is determined by the design and geometry of the UV lamp(s). In use, the profile of a lamp can deteriorate if the bulb sags out of the focused position, or if the reflector has been deformed.

UV Effective Energy Density is the UV energy to which a surface is exposed as it travels past a lamp or a sequence of lamps. It is sometimes loosely (but incorrectly) referred to as "dose." For an exposure in which irradiance is not constant, such as rising then falling, energy is the time-integral of irradiance. Effective energy density incorporates irradiance profile over the wavelength range of interest ($\lambda_1 \div \lambda_2$) and time, t, of exposure:

$$E_{(\lambda_1 \to \lambda_2)} = \int_{t_0}^{t_1} I_{(\lambda_1 \to \lambda_2)}\, dt$$

As with irradiance, when the wavelength range is clearly stated, and it is clear that the meaning is "per unit area," this term can be simply abbreviated as "energy."

Energy is a combination of TWO independent variables – time and irradiance. Because "cure speed" increases with *time* and increases with *irradiance*, the common assumption is that "cure speed is proportional to energy." This conclusion is misleading. This assumption is accepted because most researchers and formulators control only ONE of the two variables, and seldom see the true relationship of both.

A measurement of total UV energy ("dose") is a composite of irradiance profile and velocity, but information about neither irradiance nor time can be extracted from it. Consequently, data on energy alone can be useful in monitoring or control, but is less valuable to design or performance specification.

Infrared (IR) radiation is emitted primarily by the quartz envelope of the UV source. Because commercial UV radiometers do not measure IR irradiance, measurement of surface temperature is the usual method of determining the heating effect of IR. The heat may be a benefit or a nuisance, but is an inseparable factor in the curing process. A non-contacting optical pyrometer[3] is recommended for surface temperature measurement.

Radiometric Instruments and Devices

Radiometers measure *irradiance* (usually watts/cm²) at a point, but over a uniquely defined wavelength band. Because instruments have different *responsivity*, or wavelength sensitivity. and differ in their spatial sensitivity, many users prefer to compare data from instruments only of the same type. More sophisticated instruments will record the entire profile, and report peak and energy data in multiple wavelength bands.[4]

Dosimeters measure accumulated energy at a surface (watt-seconds/cm² or joules/cm²), also over some uniquely defined wavelength band. There are electronic and chemical types. Because this is the only measurement that incorporates *time of exposure*, it tends to be commonly used. Many radiometers will electronically calculate energy

Spectroradiometers are very narrow-band instruments, essentially responding to spectral irradiance, and are highly wavelength-specific -- some with resolution as fine as ½ nanometer. These instruments -- actually miniature monochromators -- can be valuable when there is a need to evaluate irradiance in a selected wavelength band of interest, but they don't measure time-integrated energy. Recent developments in these instruments include the ability to *select* a specific wavelength band for easier evaluation of the spectral distribution of a lamp output or spectral irradiance.[5]

Radiochromic dosimeters are tabs or films that attach to a test surface and respond to total time-integrated energy by changing color or by changing optical density. Depending on the chemistry of the detector, it can change permanently or only temporarily. These photochromic detectors typically respond to a wide range of UV wavelengths.

Some Limitations

Few commercial radiometers accurately respond in the 200-240 nm range. This is primarily due to limitations in filter materials used with photo-detectors, and to internal scattering effects in spectroradiometers. Radiochromic detectors are very responsive to short-wavelength UV, but are rarely calibrated for responsivity in any wavelength band -- they typically require correlation to a radiometer.

Sources of Error, Variations, and Differences[6]

Of the many types of instruments available, all have some characteristic element, which can result in errors in their readings, or variations from reading-to-reading, or differences between instruments. Sources of error, variation, and differences include:

- Responsivity (Wavelength Range, λ_2-λ_1)
- Dynamic Range (Saturation, W/cm²)
- Sampling Rate (Samples per Second)
- Spatial Response (Cosine or other)
- Orientation Preferred (Radial Symmetry)
- Threshhold Response (mW/cm²)
- Instantaneous or Average Peak
- Temperature Tolerance

Avoiding Speed or Sampling Rate Errors
It's not necessary to repeatedly run a laboratory radiometer under a lamp at different speeds to evaluate exposure conditions. First, the irradiance peak and profile *DO NOT CHANGE* with speed of travel of the radiometer. Secondly, energy varies strictly and inversely with speed and can be accurately and quickly calculated, but errors can be introduced at higher speed, depending on the instrument.

The *recommended method* for energy measurement is to select a speed, v_o, at which speed errors are a minimum, record several measurements, $\boldsymbol{E_o}$, and speed -- then *calculate* energy, $\boldsymbol{E_x}$, for any other speed, $\boldsymbol{v_x}$.

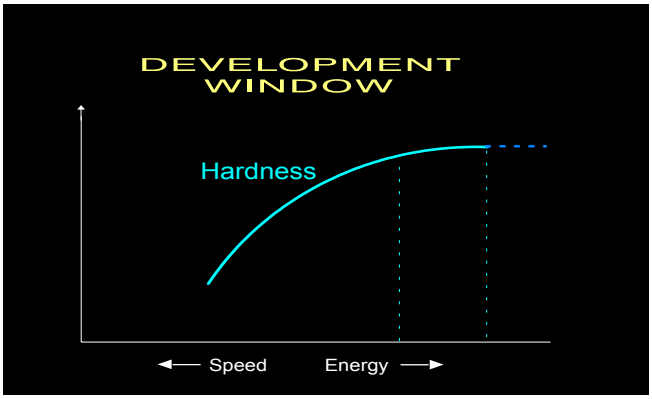
Since $\boldsymbol{E_x v_x = E_o v_o}$, then $\boldsymbol{E_x = E_o \cdot v_o / v_x}$

To calculate energy at any speed, simply multiply an error-free energy measurement by its speed and divide by the desired speed.

Recommended Practice for Reporting Data
A *recommended practice* is to accompany any reported measurement with either an indication of the wavelength range for that measurement or, at least, the identification of the instrument used. All radiometer manufacturers provide information on the wavelength band response of their instruments, and instrument-to-instrument agreement within the same model is generally good. It is essential that this information be included in the descriptive text, if not on the axis labels of charts and graphs. When this information is not reported, the data cannot be duplicated, verified, or transferred to production specifications.

OPTIMIZING THE CURING PROCESS
One of the objects of process development is to yield a process that will operate successfully in a reasonably wide range of conditions. The wider this range, or "window," the more forgiving the process will be in production and less vulnerable to failure. The desired result is a robust process.

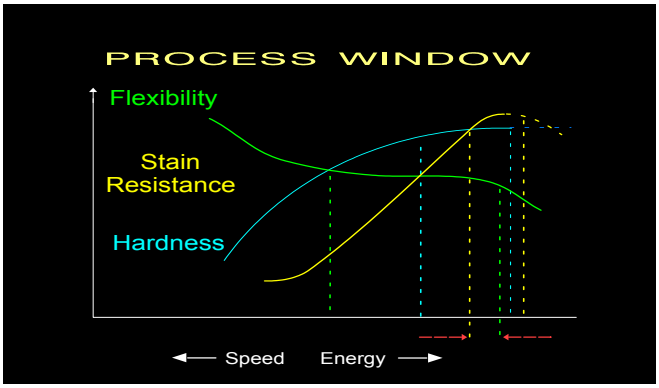
The initial step in the development of a process is the identification of the physical properties that determine success. These properties must be measurable.



1. Applying a "cure ladder," determine the upper *and* lower limits of achievement of target properties. Very often, only one of the limits is evaluated. In the example of hardness, it can be seen that the result of excessive energy is brittleness. The "window" of exposure to achieve the desired result is clearly identified.

2. Find the upper and lower limits of all properties critical to success;

3. Plot these limits on the energy diagram



4. Identify the limiting properties of the aggregate "window" and evaluate how they are affected by changes in: UV wavelength, irradiance, IR, or formulation.

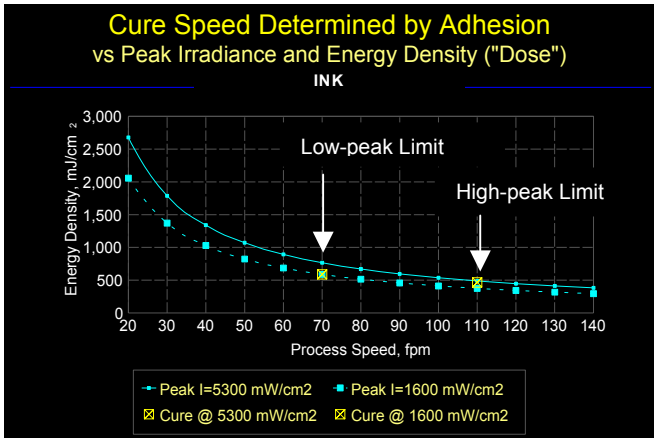
The aggregate "window" will show which properties are limiting the process. Three typical properties are shown in the example. By considering which exposure characteristic has the most effect on surface cure, bulk cure, and deep cure, the choice of which exposure variable to alter becomes clear.

Peak irradiance affects depth of cure and efficiency;
Short wavelengths affect surface properties;
Long wavelengths affect deeper and bulk properties.

This method can be used to improve any UV curing process, but requires a set of versatile UV lab tools

USING THE CURE LADDER TO EVALUATE THE EFFECT OF EXPOSURE CONDITIONS
In the following example, a black ink was exposed to varied conditions of time and irradiance; the measured performance property was adhesion to a substrate.[7] Samples were run at increasing speeds until the desired property, adhesion, failed. The same test set was repeated under higher irradiance. The graph shows the result of two different exposure conditions, 1.6 W/cm² and 5.3 W/cm². The table summarizes a full range from 1 to nearly 7 W/cm².

Irradiance
A simple, but dramatic conclusion can be drawn from this data: the adhesion and cure speed of this ink film benefits significantly from high irradiance. At the same time, the total energy required to produce the desired result is *less*.



Successful "Cure Speed" Determined by Adhesion

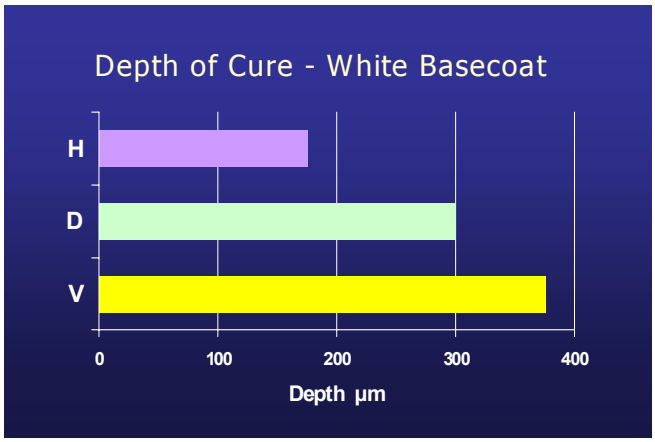
INK

Peak, mW/cm2	Energy, mJ/cm2	Speed, in/sec
6730	365	28
5260	536	22
3430	558	18
1640	587	14
1060	1160	6

0.7 mil NorCote #1019 black screen ink, #355 mesh, on clear polycarbonate
Peak and Energy measured with EIT PowerPuck® at 20 fpm (4 ips), UVA EIT range

Wavelength

Using the cure ladder to evaluate the effects of wavelength on a white basecoat material, for example, we again get a dramatic result. In this example, power and profile were kept constant, while the variable was the seletion of the bulb emission spectra, "H," "D," and "V." Similar results will be observed with inks and other "optically thick" [(1)] coatings.



CONCLUSION

Radiometry is a powerful analytical tool for UV curing process design and invaluable as a QC tool for process monitoring. It is important to identify the key exposure parameters that have the most significant effect on the performance of the end product.

For process *design*, it may be necessary to evaluate a significant number of parameters and variables to optimize a process and assure a wide operating "process window." Process optimization means matching the lamp system and the required exposure variable to the ink, coating, adhesive and its application, and matching the UV curable chemistry to the job to be done. To evaluate the effects on the physical properties of the final cured product, correlation with exposure variables is essential. These variables can be expressed in terms of irradiance profile, spectral distribution, total energy, and infrared energy (or temperature). Multi-band radiometers, mapping radiometers (to evaluate profile), and spectrophotometers can record information on a significant number of these parameters. In addition to facilitating the optimization process, these measurements are used to determine the operating limits for production process control.

Once designed and optimized, monitoring the process in production may be limited to "surveillance" on only a few key parameters -- those which, when out of pre-determined limits, affect the result. From process design, these critical parameters were identified. Relatively inexpensive, simple and rugged tools and methods can be used in production monitoring. These may be on-line monitors, dosimeter tabs, single band radiometers, and the like. Ultimately, these measurements must be related to target properties to be achieved and must be correlated with measurements of the optimized process from the process design parameters.

Selecting a method of measurement or a particular radiometer should be based on the specific process and the identification of the key variables that have the greatest effect on the process.

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References

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