UV as the Energy Source for Industrial Processing of Coatings, Inks, and Adhesives

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Summary

UV curing, the process of photoinitiated conversion of polymeric materials from a liquid to a solid, is a popular alternative to conventional drying. UV Curing is highly adaptable to a wide variety of coating applications, owing to some of its key attributes; it is (1) solventless, (2) low-temperature, (3) high speed, and (4) energy-efficient. 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. Key exposure factors are (1) UV irradiance, (2) spectral distribution and (3) time.

Introduction

Ultraviolet Curing, the process of transforming a liquid into a solid by the action of light, is an energy-efficient and relatively low-temperature technology with many applications in coating, printing, adhesives, electronics, and communication products. UV Curing provides improved overall physical or chemical properties of polymeric materials and produce superior results in bonding, surface finish, and durability. It is used on virtually all substrates, plastics, paper, film and foil, wood, metal, glass, fibers and composites. Speed and controllability in a huge variety of applications are driving increasing worldwide markets for this proven technology. UV-cured materials have become widely used in an astounding variety of product applications.

A number of variables of a UV lamp system can be designed or selected to improve the efficiency of a UV curing process. While the desired properties of a cured material are essentially designed into the formulation, the development of the target properties of UV curable materials themselves depends on how well these lamp factors are designed and managed. Variables that can be controlled are: total UV power, UV spectral distribution (wavelength), irradiance and irradiance *profile*, and infra-red energy. The ability to match all of these lamp characteristics to the optical

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and physical properties of a UV curable material widens the range of tools available to the process designer, and yields more efficient and stable UV curing processes in production.

Benefits

UV Curing is highly desirable for processing, owing to benefits of productivity as well as advantages of being a "clean" technology. This process has a number of key attributes:

- no solvents -- cure is by polymerization rather than by evaporation, so VOC and HAP emissions are eliminated;
- low temperature -- heat is not required;
- **high speed** -- cure is nearly instantaneous;
- **energy-efficient** -- energy is invested only in the curing reaction, not in heating;
- **easily controlled** -- inks and coatings do not "dry," so do not set up in printing/coating equipment, or change viscosity;
- quality finishes -- superior resistance to scratch and chemicals.

Applications

UV processing offers major advantages over other finishing methods. Typical product lines involve coatings (on wood, metal, paper, and plastic), inks (for letterpress, lithographic, gravure, and screen printing), and adhesives (for film, foil, or paper substrates). The industries using these technologies are diverse and varied; they include automotive components, medical products, electronics, CD's and DVD's, 2-piece and 3-piece can printing, pipe and tube coating, furniture, fiber optics, flooring, packaging and containers. There is growing interest in UV coatings for automotive applications, and a number of interior parts (and a few exterior parts) are coated with UV coatings. UV coatings for composite and SMC materials are becoming a reality.

Background: Solvent-based versus UV

Solvent-based, thermally cured (or dried) inks or coatings are composed of a resinous binder, pigments and fillers, and diluent solvents. After application to the substrate, heat is applied, driving off the solvents and drying the coating film. The evaporated solvents are generally flammable and toxic, and are of special concern as airborne pollutants. These solvent emissions can require the use of even more energy or capital investment to be incinerated or "scrubbed" and recovered by distillation.

A UV curable system achieves the transition from liquid to solid by means of either chain addition polymerization or an epoxy reaction, triggered by a photochemical interaction. A *photoinitiator* is the active component of the material formulation. It is the energy-absorber which starts the reaction when exposed to ultraviolet light. In UV curable material, the resin binder is replaced by a formulation of liquid

monomers and oligomers, into which a pigment can be dispersed. The coating is completely reactive and the amount, or thickness, that is laid down wet is essentially the same as the thickness after curing. These systems are often referred to as "100% solids."

The principal ingredients of a UV-curable ink or coating are:

Oligomers

Larger molecules; primarily determine the ultimate physical properties.

Monomers

Smaller molecules; affect the (liquid) viscosity and rate of the crosslinking reaction.

Photoinitiators

Respond to UV light and initiate the reaction; low concentration (1% - 2%).

Additives

Pigments, surfactants, de-foamers, etc. - these do not enter into the crosslinking reaction -- they become locked in the crosslinked matrix.

In addition to the chemistry of the UV-curable ink or coating, an important part of the UV system is the lamp system used to expose the materials to UV. UV curing begins with a photon-molecule collision. The effectiveness of the curing process is dependent on the ease or difficulty of projecting photons into a curable material to activate photoinitiator molecules.

The optical properties of the ink, such as optical density (opacity) and the optical characteristics of the curing lamp must be "matched" to produce an effective UV curing system.



A variety of photoinitiators is available to the formulators of inks and coatings. Each type of photoinitiator responds to a different but very specific wavelength range of UV.

A UV Curing system should be thought of as consisting of *three* component parts, all integrally related:

• The application, particularly the end product it produces, will determine the requirements of the physical properties of the cured photochemistry. *Target properties*, such as opacity or hiding, film thickness, hardness or flexibility, resistance to abrasion or scratching, and adhesion are only a few that are determined by the end product and the coating, decorating or bonding process used. Identification of the substrate is not only important to properties such as adhesion and flexibility, but will have a significant effect on the response to infra-red radiation.

• **The photochemistry** is designed to achieve the *target properties* upon exposure to the appropriate energy of radiation. Formulation variables include a seemingly infinite combinations of monomers, oligomers, photoinitators and functional additives.

• The UV lamp system will have a number of variables which will also have a significant effect on the target properties. These are often overlooked when designing the total cure system, and the result is often a marginal or inefficient process.



There are a number of optical and physical characteristics of the curing system (outside of the formulation itself) which affect the curing and the consequent performance of the UV curable material. Some of the recent developments in UV lamps for industrial processing are: (1) the selection and control of the lamp emission spectra to match the optical properties of the film and its photoinitiator, (2) improved lifetime of lamps at sustained high power operation, and (3) the use of

absorptive dichroic reflectors to manage the relative components of UV and infrared energy in the highly focused radiation delivered to surfaces being processed.

Categories of UV Curing

With a variety of materials and product handling methods involved in UV curing, the size of the part, the area of the surface, and the speed of the process will require different curing systems to accommodate them. UV curing might be divided into several categories, distinguished by size of work surface and type of motion of the work piece.

Linear

Linear processing is most common arrangement for curing, and is characteristic of curing flat surfaces. The surface, which has been coated or decorated, is passed under or by UV lamps to expose the surface. Sheet printing presses, roll-to-roll coaters, and conveyors are all variations on linear processing. Typically, a tubular lamp with a focusing reflector, or rows of tubular lamps extend across the surface, providing uniformity of UV exposure in that dimension, while the motion of the work surface provides uniformity of exposure along the direction of travel. Because the lamps can be arranged closely to the surface, very high intensity (irradiance) of UV can be achieved.

The greatest advantage to linear curing is in the fact that in the developmental laboratory, the process is the same process that is transferred to production – the laboratory sample is exposed to a *section* of the larger production system optics, not a scaled-down or reduced-energy adaptation.

Flood (Area)

Static Exposure The simplest method of UV exposure is to place an object or surface under a UV lamp and control the time during which it is exposed. This is often referred to as "static" curing. It is frequently used for laboratory exposure or for low-volume production curing. Flood exposure is regularly used in film transfer and printing plate making.

Dynamic Exposure When the surface is complex, or curved, or even "3D," it becomes more difficult to cover the surface in a linear fashion with focused high intensity light. The illumination may be lower in irradiance (intensity), as the energy is distributed over a larger area. By combining additional degrees of motion of the part, such as rotating *while* passing through the curing lamp region, a complex surface may be adequately cured. Further, lamps of various configurations are be used, depending on type and degree of motion, size and complexity of the surface contours.

Spot

Spot curing is characterized by a small, high intensity "spot" of UV light directed precisely at a work point. It is typically used for UV bonding of adhesives for medical product assembly and electronic assembly. The light is transmitted to the work area by means of a liquid light guide, with a projection lens at the tip. This enables the spot cure system to work in spaces and with small assemblies where a large lamp would be impractical.

Optical Character of Material To Be Cured

The effectiveness of a UV lamp is dependent on the ease or difficulty of projecting photons into a curable material to activate photoinitiator molecules. UV curing is dependent on photon-molecule collision. Photoinitiator molecules are dispersed uniformly throughout the material – but photons are not. In addition to the character of the UV source, there are several optical and thermodynamic characteristics of the film to be cured. These interact with the radiant energy and have significant impact on the process.

Spectral Absorbance

Spectral Absorbance is the relative energy as a function of wavelength absorbed in the material at increasing depth. More energy absorbed near the surface means less energy available at deeper levels, but this varies with wavelength. Total spectral absorbance includes <u>all</u> contributions from photoinitiators, monomers, oligomers, and additives, including pigments.

Inks and pigmented coatings pose special problems, owing to the fact that opacity or color strength are desirable properties. Adhesives, also, are often applied as relatively thick films. Distinct from the *physical* thickness of a film, its *optical* thickness is important.



"Optical Thickness"

The ability to penetrate a film with light may be thought of in terms of "optical thickness" of the film - a combination of the physical thickness of the film and its

absorptivity. It may also be expressed as a ratio of the light flux through the top of the film to the light flux through the bottom. This will aid an analyzing the cure condition as well as explaining depth of cure and adhesion behavior.

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.

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

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 I_0 is the incident energy at wavelength λ , I_a is the energy absorbed, A_{λ} is absorbance at wavelength λ , and d is the depth from the surface or film thickness.

Significance of Absorbance

To examine the significance of this equation, a film is divided into 100 "layers" (each 1% of the physical thickness) to reveal the relative energy absorbed in the top surface (1% layer) and the extreme bottom (1% layer) of the film, as a function of absorbance. There is a great difference in the light energy in these two zones.



Calculations show that the "optimum" 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. This also illustrates that <u>even at the best conditions</u>, energy absorbed at the top surface is **2 to 3 times** the energy absorbed at the bottom! For a film, such as a paint or an ink, with an absorbance of 3.0, this ratio is approximately **one thousand** !

Significance of Spectral Absorbance

To further the difficulty, absorption for any material **varies with wavelength**. The charts below show typical spectral absorption for a photoinitiator, a pigment, and prepolymer. It is readily apparent that short UV wavelengths (200-280 nm) will be absorbed at the surface and not be available at all to lower depths. Typically, film

thickness is limited, and adhesion to a substrate is often the first property to suffer. Even the photoinitiator absorbs energy in the wavelengths it is sensitive to, and blocks that same wavelength from deeper photoinitiator molecules. The graph also illustrates that a photoinitiator that may be appropriate for a clear coating of for a thin film, may not be an appropriate selection for an ink. For ink, a photoinitiator with a longer wavelength response would be a better choice.



Significance of Wavelength

Most UV curing involves *two* UV wavelength ranges at work simultaneously (*three*, if we include IR). Short wavelengths work on the surface; longer waves work more deeply in the ink or coating. This is principally the result of the fact that short-wavelength energy is absorbed at the surface and is not available to deeper layers. Insufficient short-wave exposure may result in a tacky surface; insufficient long-wavelength energy may result in adhesion failure. Each formulation and film thickness benefits from an appropriate *ratio* of short and long-wavelength energy.

The basic mercury bulb emits energy in *both* ranges, but its strong emission in the short wavelengths make it particularly useful for 'clear' coatings and thin ink layers. Higher absorptivity materials, such as adhesives and screen inks are often

formulated for longer wave cure, using long wave photoinitiators. These materials are cured with bulbs containing additives, along with mercury, that emit UV much richer in the long-wave UV. These longer-wave bulbs also emit some short-wavelength energy, which is often sufficient to assist with surface cure.

In more extreme applications, which may require cure of materials with heavy loading of difficult pigments like titanium dioxide, or applications which require curing *through* plastic or glass, long wave curing is *essential* because these materials block short wavelength UV almost entirely.

Lamp Systems

In addition to the chemistry of the ink, coating or adhesive used, a most important part of the UV system is the lamp system itself. There are two major types.

The Mercury Vapor Arc Lamp

A well-known and widely used type of lamp is the mercury vapor arc lamp. In this type of lamp, clear fused quartz tubing is used to enclose the plasma that produces the ultraviolet energy. The fused quartz tubing has a wall thickness of about one millimeter and an outer diameter of 20 to 25 millimeters. The ends of the quartz tubing are sealed around the electrode ribbons to provide a vacuum-tight enclosure. When power is applied to the electrodes, the voltage between them rises until ionization of the starting gas occurs. As the lamp warms and the mercury vaporizes, the plasma changes from that of the starting gas to a constricted mercury arc.

UV (30%), visible light (25%) and infrared energy (45%) are emitted from the mercury arc lamp. The bulb will typically last from 1000 to 2000 hours before degradation at the electrodes and deposits on the interior wall of the bulb reduce its output to the point where it is replaced.

In printing applications and other continuous-feed processes it is desirable or necessary to turn the lamp on and off. It is usual for an arc lamp to have a mechanical shutter incorporated in it, as the bulb requires a few minutes to stabilize at power each time it is started.

The Microwave-Powered Lamp

The microwave-powered lamp can be included in the general category of "medium pressure mercury vapor" lamps, but with a key distinction: microwave energy is transmitted directly into the UV-emitting plasma within the bulb volume rather than being driven by an arc between two metallic electrodes. This permits relatively simple construction of the bulb, owing to the fact that electrodes are not required. In turn, the electrodeless tubular bulb can be made much smaller in diameter. Typical outside diameters range from 10 to 15 mm.

The electrodeless bulb used in the microwave-powered lamp is simply a closed

quartz tube that contains a small amount of mercury, an easily ionized "starter" gas, and other materials to modify the spectral output. A high frequency and high intensity electric field, created by microwaves, excites the gas inside the bulb to extremely high energy and high temperature levels, vaporizing the mercury. The resulting high energy collisions of electrons, ions and gas molecules cause molecules to emit characteristic wavelengths of light, in the ratio of UV (35%), visible (30%) and infrared (35%). The wavelengths of UV emitted and their relative energies are a function of the particular molecules and their concentration in the vaporized fill additive. There is nothing to cause changes in the spectral energy output during the normal operating lifetime of the bulb, typically in excess of 6,000 hours. The electrodeless bulb can be started, stopped, and restarted very rapidly, so does not require the use of shutters.

Lamps: Power

UV lamps usually consist of a tubular shaped bulb, and it is common to describe their operating power in "watts per inch." This is derived simply from the electrical power input divided by the effective length of the bulb. It does not have a direct meaning to the output efficiency of a lamp system, to the spectral conversion efficiency, to the curing performance, nor to the UV irradiance delivered to a work surface.

For arc lamps, input "watts per inch" is the product of the electrode tip-to-tip *rms* voltage and phase-corrected current, divided by the tip-to-tip distance. For microwave powered lamps, input "watts per inch" is the total microwave power in the bulb cavity divided by the end-to-end reflector inside distance. So, while not an indicator of performance, input "watts per inch" is typically used to describe the general class of UV lamp system.

Lamps: Reflector Design

Typically, UV lamps have an elliptical reflector to focus the bulb energy on a line in front of the lamp face. The printed, coated, or decorated surface is typically passed through the high intensity focal zone of the reflector. This will maximize



cure speed. For some specialized purposes, other reflector configurations can be provided. Reflectors made with special, multilayer dielectric coatings (clled "cold mirrors" or dichroic reflectors) can be incorporated in the lamp to absorb much of the infrared energy radiated by the bulb. This can significantly reduce the heating of the surface being processed.

Lamps: Focus

The optical efficiency of the lamp reflector/system is the amount of light collected and reflected versus the total light emitted in any spectral range. The larger the total angle that the reflector subtends around the bulb, and the higher the reflectivity, the higher the optical efficiency. The typical reflector "wraps" about the bulb, including an angle of about 270°, so collects approximately 75% of the light emitted by the bulb.

The radiant energy from the bulb focused by the reflector is affected substantially by the optical efficiency over the range of wavelengths of interest and can be described by:

$$W = \sum_{\lambda_{\min}}^{\lambda_{\max}} W_{\lambda} \cdot R_{\lambda} \cdot (\boldsymbol{\theta} - \boldsymbol{\alpha}) \cdot \Delta \lambda$$

where w_{λ} is the spectral radiance of the bulb per unit length, R is the spectral reflectance, θ is the angle subtended by the reflector, α is the sector of reflector that is obscured by the bulb itself.

Peak Irradiance

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



All three lamps illustrated deliver the same total energy to a surface passing under them, but with 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 inch") but are of different diameters, the smallest yielding the highest peak.

Spectral Output: Special Fills

Additive materials such as metal halides can be included in the fill gas in small, precisely measured quantities. Short wavelength photons emitted by the mercury have sufficiently high energy so that when a photon-molecule collision occurs, an additive material will re-emit at its characteristic wavelengths. This "fluorescence" shows as an enrichment of the spectral output in longer UV wavelengths and is the basic principle of formulation of "special fill" bulbs.

The distribution of the spectral power output of three different high power bulbs is shown. By summarizing the spectral output power distribution in bands of 10 nm wavelength and plotting using the center wavelength of each band, a very reproducible and easy to analyze spectral output chart can be made.

The "H" spectrum at 600 watts per inch is displayed in the first chart. The second chart shows the "D" spectrum at 600 watts per inch. By inspection, the significant enhancement of the "D" spectrum in the 350 to 400 nm range is apparent, as is the enhancement in the 400-450 nm range of the "V" bulb.



These different spectral output bulbs can produce varying curing results in different inks and coatings. Specifically, the "H" spectrum is effective in producing hard surface cures and high gloss finishes. The "D" spectrum, because of the greater penetration of the longer wavelength light, is preferred for curing pigmented materials (inks) and thick sections of clear materials. The "V" spectrum, in the third chart) is especially suited to curing white inks and basecoats which typically containing high loading of TiO_2 .

In the case of the microwave-powered lamp, owing to the fact that no chemical interactions with electrodes occur, the relative concentrations of fill additives do not change. Consequently, its spectral output remains unchanged with continued use.



Irradiance

The "intensity" pattern to which a point on a surface will be exposed as it passes under a lamp rises to a peak directly under the lamp. *Irradiance*, in watts (or milliwatts)/cm², is the measure of the light "intensity" at the surface. (Irradiance is the proper term for radiant energy arriving at a point on a surface per unit area). It has been found that many UV curable inks and coatings respond better to higher <u>peak</u> irradiance, rather to longer exposure to a lower level of energy. Higher bulb power and smaller bulb diameter yield higher peak irradiance.

Energy ("Dose")

Effective Energy Density is the radiant energy, *within a wavelength range*, arriving at a surface per unit area, usually expressed in joules or millijoules per square centimeter (J/cm² or mJ/cm²). Sometimes loosely – but incorrectly – referred to as "dose," it is the total accumulated photon quantity arriving at a surface. ("Dose" is the energy absorbed per unit *volume* or per unit *mass* -- UV radiometers measure energy per unit *area*.) Because energy density is the product of irradiance and time, it is inversely proportional to speed under any given light source, and proportional to the number of exposures (for example, rows of lamps). For an exposure in which irradiance is not constant, such as rising then falling (see Figure 1), it is the time-

integral of irradiance during the time of exposure (t_0 to t_1). This is the UV energy to which a surface is exposed as it travels past a lamp or a sequence of lamps. Effective energy density incorporates irradiance profile, the wavelength range of interest (λ_1 to λ_2) and time:

$$E_{(\lambda_l \to \lambda_2)} =_{t_0} \int^{t_l} I_{(\lambda_l \to \lambda_2)} dt$$

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 expressed as "energy."

When UV exposure is measured or reported as energy (mJ/cm²) only, it may be misleading, as the peak of irradiance can be a far more significant factor in the efficiency of cure of many inks, pigmented coatings, and adhesives. Energy *and* peak should be specified for a UV curable material, as well as spectral response. All of these factors can be significant to the cure performance of the material.

Infrared Energy

Heat can benefit UV curing when it is used to enhance flow-out (for gloss) or mobility (for cure rate and adhesion). It becomes a problem primarily when, for example, the substrate cannot tolerate it or volatilization of the coating occurs.

Infrared (IR) energy is produced by all UV lamps. It is, in fact, emitted by the quartz bulb envelope. Larger bulbs emit more IR than smaller diameter bulbs. This suggests that for heat-sensitive applications, a smaller diameter bulb may be a preferred choice.

The amount of IR energy radiated to the work surface can be controlled somewhat independently from the UV energy. This requires either absorbing the IR or preventing it from being focused onto the surface.

Effect of Infrared on Materials

In a focused system, the infrared energy is concentrated, along with visible and UV light, on the work surface. The principal effect of the IR is to heat the material and substrate instantaneously at the point of focus. This temperature rise caused by the impulse of IR will be a function of not only the radiant flux of infrared, but also the absorptivity (a) of the surface, the specific heat (c_p) of the film and the substrate, its thermal conductivity (k), and density (ρ):

$$\Delta T^{\circ} \approx W \cdot a \cdot f(\frac{\rho_{c_p}}{k})$$

These factors illustrate the response to an IR impulse (a complete expression for a transient response is quite complex). The term $k/\rho c_p$ is the property of a material

called thermal diffusivity.

The temperature rise at the surface is very dependent on how quickly the transient is dissipated into the substrate. A material with a high absorptivity and low conductivity, such as a printed pattern on plastic, will be unable to dissipate the impulse and therefore will experience a higher instantaneous surface temperature than one which absorbs less energy or conducts it more quickly into the substrate, as will metal or glass.

Dichroic Reflectors

There have been elaborate and costly methods applied to reducing IR from UV lamps, but by far the simplest and most direct is the use of a *dichroic* reflector. Dichroic reflectors are designed to be non-reflective to IR emitted from the lamp. Whether the transmission-type or absorbing-type, they reduce the focused IR, and consequently the temperature to which the surface rises.

Dichroic reflectors can effectively reduce the IR projected from UV lamps and thereby reduce surface temperature.

Conclusion

Most UV curable films are "optically thick," and much more radiant energy is absorbed near the surface of the material, and absorbance varies wildly with wavelength. Spectral absorbance is a characteristic critical to the success of a UV design. UV absorbance affects the depth of cure, and IR absorbance affects the observed temperature.

The effectiveness of a UV curing system is the practical result of a process design that combines (1) the method of application of ink or coating, (2) the photochemistry of UV-curable ink or coating, and (3) the UV lamp design into an integrated system. Careful attention to the optical factors and the interaction of inks and lamps can provide a successful UV system with wide operating limits.

High peak irradiance and long wavelengths contribute significantly to depth and speed of cure, especially for "optically thick" films.

Optical characteristics of lamp systems and their interaction with the optical properties of curable materials are an integral part of performance. Lamp characteristics, such as spectral distribution, peak irradiance, and controlled infrared energy can be effectively used, along wit formulation strategies, to design UV systems with acceptable wide "process windows."

Equipment variable affecting the process include the choices of arc type or electrodeless bulbs, spectral distribution, output power (watts/cm), peak irradiance, and reflector type. These various factors can directly affect cure speed and the

properties of the cured printed image or coating; they must be carefully selected for a specific application.

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