UV-LED Curing In Lithographic Inks

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Abstract

Ultraviolet (UV) curing with light emitting diodes (LED) has gained significant popularity in the past 8-10 years. In comparison to UV curing with medium pressure lamps, the UV-LEDs show advantages and disadvantages when curing lithographic inks. The spectral distribution of the UV sources coupled with the absorption spectra of the photoinitiators used provides insight into the film properties of the cured inks. Both technologies allow for commercial, publication and packaging applications which are gaining some market share versus conventional lithographic printing inks. Curing parameters and print quality will be discussed with respect to lithographic printing inks in both web offset and sheetfed applications.

Introduction

Ultraviolet curing with light emitting diodes (UV-LED) is becoming a more popular way of ultraviolet (UV) curing within the last decade. When compared to regular UV-curing with medium pressure mercury lamps, also known as conventional UV curing, UV-LED displays advantages and disadvantages. This report will compare and contrast both technologies and then relate them to the photoinitiators and curing properties of formulations when curing under conventional UV and UV-LED. Finally, research in ultraviolet curing has expanded to include different classes of products which are beneficial to the curing process. These shall be briefly discussed.

What is UV-LED in comparison to conventional UV

UV-LED uses light emitting diodes based on Gallium Nitride (GaN) and Aluminum (Al) -doped GaN diodes which are stimulated using low voltages (<100 V) and low currents (mA) versus a conventional mercury lamp which requires >200 V and several Amperes of current. The energy saving comparison is greater than 75% which translates into saved power.

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Conventional UV curing uses a quartz filled with inert gas a elemental mercury which is electrically energized to emit the multiline spectrum of mercury with many emission bands from 200-450nm. These are well known and have been characterized for decades. All the current photoinitiators used for UV-curing absorb where the mercury spectrum emits. That means that the commercially available photoinitiators were designed and produced with medium pressure mercury lamps in mind. A UV-LED emission spectrum is a narrow distribution (15-20nm) of wavelengths primarily around 385, 395 and 405 nm. They are some 365nm units available, but their lifetime is only 20% of the longer wavelength variety and their power output is much lower. The lower wavelengths will require more development time before wide scale commercial availability is a reality.

UV curing, disinfecting, sterilization, bonding and other UV processes have been dominated by the medium pressure mercury bulb since the 1970's. There are over greater than 3 million installations globally using UV curing. It is only in the past decade where advances in visible light LEDs and now UV-LED have become more accepted and beginning to replace and supplement conventional UV curing. There are close to 1 million facilities globally using UV-LED. A large commercial use is in the UV gel nail polish realm. UV-LED curing for printing is the second largest market.

UV-LED curing systems require less energy and have a more compact footprint as compared to regular medium pressure mercury systems. Energy and space saving top the list of favorable attributes to users. A conventional mercury curing systems emits UV energy as well as a lot of heat, visible light and ozone. The latter must be exhausted since it is a human health hazard. The heat must be managed and is detrimental to thermally sensitive substrates such as plastic films, labels and some papers. Heat can be beneficial since the thermal bump accelerates curing.

UV lamps should be replaced every 1500-2000 hours, while UV-LED have useless lifetimes of 20,000 hours. UV-LED lamps can be turned on and off instantaneously while conventional UV systems need a warm and cool-down period before and after use. This is an advantage for UV-LED systems in a production environment where you do not have to wait 20-30 minutes to be at full power.

Conventional UV curing systems for inks and coatings rely on the emission spectrum of mercury which has dominant lines at 254, 309, 313, 365 and 405nm to name a few. This allows for photoinitiators to be chosen for surface , mid-level and through cure (UVc, UVb and UV-A). A UV-LED emission spectrum is in a narrow distribution (15-20nm) of wavelengths primarily around 385, 395 and 405 nm. Hence, it is centered more on the UVa part of spectrum focusing on depth of cure in the ink or coating film. So there are several advantages and disadvantages to both conventional and UV-LED curing systems.

Photoinitiators

Photoinitiators are chemicals which absorb energy (UV or visible) and generate excited species capable of initiating photopolymerization of UV curable monomers and oligomers such acrylates and methacrylates. Other chemistries are available, but not discussed in this paper. There are 2 basic types of photoinitiators, Type I which absorb UV-light and homolytically cleave to product free radicals which then will initiate photopolymerization. Examples include the aminoalkylphoenone and the phosphine oxides shown in the presentation. A type 2 photoinitiator requires a co-initiator, usually an amine, alcohol or thiaxanthone, in which a a functional group can readily have hydrogens abstracted in addition to the photoinitiator. A Type II photoinitiator absorbs UV photons causing an exited electron in the photoinitiator to abstract a hydrogen from the co-initiator, and in process, splitting a pair of electrons (creating a radical) to initiate polymerization. Examples of the absorption spectra of the photoinitiators and emission spectrum of a mercury lamp and a UV-LED lamp are shown in the presentation. It is important the wavelength output of the UV-LED marry up with the absorption spectrum of the photoinitiator package in the ink or coating to provide excellent curing behavior.

Photoinitiation occurs on the nano to microsecond timescale, while the photopolymerization occurs in the millisecond timescale. These are rapid exothermic processes which are controlled by formulation, substrate, light and process.

UV curing process

The UV-curing process is like any polymerization process. There is initiation, propagation and termination. In the UV processes, cure is a factor of the following processes:

Photoinitiation	Reaction	Effect
Primary Absorption	$PI + Light \Rightarrow {}^1PI^*$	+
Intersystem Crossing	${}^1PI^* \Rightarrow {}^3PI^*$	+
Singlet Decay	${}^1PI^* \Rightarrow PI$	-
Triplet Decay	${}^3PI^* \Rightarrow PI$	-
Primary Absorption	$PS + Light \Rightarrow {}^1PS^*$	+
Intersystem Crossing	${}^1PS^* \Rightarrow {}^3PS^*$	+
Energy Transfer	${}^3PS^* + PI \Rightarrow {}^3PI^*$	+
Intramolecular Cleavage	${}^3PI^* \Rightarrow R^\bullet + R^\bullet$	+
Hydrogen Abstraction	${}^3PI^* + HCI \Rightarrow PIH^\bullet + CI^\bullet$	+
Quenching	$3PI^* + Q \Rightarrow PI$	-
Oxygen Inhibition	$R^\bullet + O_2 \Rightarrow RO_2$	-
Recombination	$2R^\bullet \Rightarrow R\text{-}R$	-

CI = Co-Initiator, PI = Photoinitiator, PS = Photosenstizer, Q = Quencher, R = Radical

Diagram 1

The speed of cure will be a factor of controlling the process and chemistry to maximize UV-crosslinking and hence cure. This is the creation of a *photoset polymer* which is herein defined as a photopolymerized crosslinked matrix.

Beer's law (as in the Beer-Lambert law) can be written as shown

$n = I_{\alpha}\Phi_i = I_o(1\text{-}10^{-E(\lambda)cd})\Phi_i$

n = number of radicals
I = intensity (photons/unit time)
Φ = quantum yield of radicals
E = extinction coefficient of photoinitiaor
λ = wavelength of light
c = concentration of photoinitiator
d = optical path in sample (film thickness)

This relationship shows processes described above will result in a cured matrix with either one of these three properties depending on the formulation and cure conditions;

1. Totally reacted, all chemical sites consumed,
2. Totally reacted, not all sited reacted but all molecules connected, or
3. Not all sites reacted, not all molecules connected, but meets product specifications.

UV curing in most commercial applications results in the third situation. It is up to the specialty chemical producer, the formulator, the convertor and the customer to come up with products and processes that make a product suitable and safe for commercial use.

Formulation considerations for UV-LED

When formulating UV lithographic or flexographic inks, it is important to perform many tests including a cure ladder. A cure ladder is a process whereby a printed ink film on a given substrate is cured with many UV energy levels and the resultant cured film is evaluated for degree of cure. This can be done several ways including spectroscopically, by chemical extraction, mechanically, dielectrically or by a simple solvent rub test. A solvent rub test using isopropyl alcohol (IPA) or methyl ethyl ketone (MEK) can help a formulator determine the level of cure of a specific formulation under given cure conditions. If the ink film is undercured, there might be only 1-2 solvent rubs. A well-cured film will display 8, 10, 20, 50 ro more solvent rubs depending on the chemical make-up and cure conditions. The graphs in the presentation show several examples of UV cure ladders with solvent rubs on the Y-axis and applied UV energy on the X-axis.

It is not surprising that the cure ladders show a different in the degree of cure along with different pigments. Red and yellow inks are easier to cure than cyan and black inks. Black inks are the most difficult since carbon black absorbs a lot in the UV spectrum limiting the activity of the photoinitiation process.

UV cured inks are made of monomers, oligomers, resins, photoinitiators, pigments and additives. Each play a significant role in UV-curing. In conventional UV curing, the formulation is assembled such that surface cure and through cure are optimized since a medium pressure mercury lamps emits in the UVa (325-400nm), UVb (290-320nm) and UVc (220-280nm) ranges. A normal UV-LED lamp emits only in the UVa (325-400nm) range. This means that the surface does not cure as well due to oxygen inhibition factors which slow the cure as shown in diagram 1 above.

In UV-LED, the surface cure can be 'formulated' by several methods. One method is to increase the overall reactivity of the oligomers and monomers providing a faster curing acrylate system. Another method is to increase the concentration of amine and amino acrylates which retard the oxygen inhibition at the surface. A third way is to eliminate oxygen either through nitrogen inerting and curing or a lamination process followed by through curing. Additionally, formulators have found additives which can help boost UV-cure when used in small amounts such as 4-8% in a formulation. These additives appear to increase the chemical resistance of the cured ink film. Like all formulation materials, an excess will not have a beneficial effect and it is important to consider all factors when formulating inks for UV-LED ink and coating applications.

Conclusion

UV-LED is becoming the new way to cure lithographic, flexo and ink jet inks replacing the traditional medium pressure mercury lamp. The process has both advantages and disadvantages which are inherent to the emission spectra of both sources. The photoinitiator selection for UV-LED is much more limited than for conventional UV curing. Surface cure and oxygen inhibition at the surface of a cured UV-LED ink can limit the surface characteristics such as gloss, hardness, chemical resistance, slip and feel. There can be overcome with formulation changes, additives and process changes. UV-LED curing will become more prevalent as converters and processors tackle the issues.