A Novel Approach to UV Curing for PVC and Wood Applications

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The case for curing using solid-state UV light sources is hard to refute: unequalled lifetimes, instantaneous operation, low heat, minimal energy consumption, no ozone production or mercury to contend with. It's a bundle of benefits attractive to anybody considering the alternatives.

But despite the obvious benefits of LEDs, traditions in the UV curing industry, and the wood coating market segment in particular are hard to break and UV lamp sales are still dominated by inexpensive medium-pressure mercury arc lamps of various sorts despite their shortcomings.

The well entrenched combination of a mercury arc lamp and off-the-shelf coatings is often seen by users a simpler and lower risk approach, since these existing coatings have been tailored to the mercury spectra and often do not cure as well with the LED sources. While UV-LED sources for curing have been thought of as being low power and of having limited wavelength options the most significant barrier to acceptance is neither.

The most formidable problem for UV-LED sources in coatings applications has been oxygen inhibition at the surface of the coating. The most popular UV chemistries, employ free radical mechanisms to aid in the formation of long polymer chains. In the presence of oxygen however, there is race between the cross-linking of the polymer and the affinity of oxygen to bond with free radicals, prematurely terminating the polymer formation. The result is a thin surface layer of sticky goo and compromises the final properties of the coating.

Underneath this top-most layer coatings irradiated with LEDs can be completely cured, (often even better than with traditional arc lamps). But coating beauty is frequently skin-deep and oxygen inhibition becomes a show-stopper.

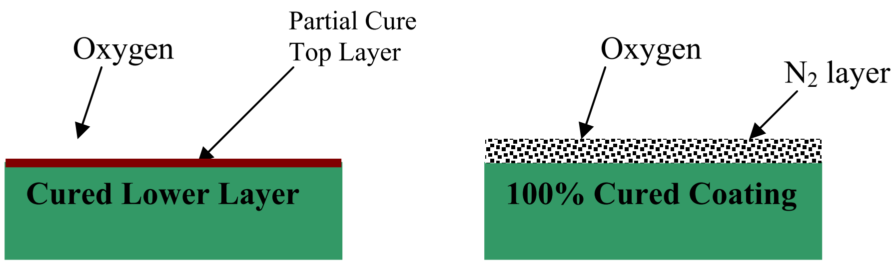
The tide for UV LEDs may be changing however as oil prices soar above $100 a barrel and "carbon footprint" becomes more than just polite conversation. Manufacturers, especially those in the higher wage US manufacturing sector are pressed to find ways to save on capital and operating costs.

Fortunately there have been some significant developments for LEDs that help overcome the problems that have bogged down UV LED development especially for wood and PVC products that are substantially flat.

The Nature of Oxygen Inhibition

The vast majority of UV cure chemistries used for curing in the industrial wood community are classified as free radical mechanisms. In this type of reaction, UV light striking the photoinitiator causes cleavage of some functional group creating a free radical. The free radical combines with the formulations monomers to trigger the polymerization that results in the final hard, durable film. The problem is that the air we breathe in our plant is composed of 21% oxygen and oxygen loves free radicals. (Exactly why people take anti-oxidants to prevent aging).

What happens on the surface of the coating is a race. The free radical may propagate the polymerization or combine with oxygen, prematurely terminating the polymer. It has been demonstrated that shorter wavelength UV sources have a beneficial effect on driving the reaction towards full polymerization with the typical surface cure photoinitiators (like alpha Hydroxyketones) commonly found in formulated wood coatings (often in combination with photoinitators like Phosphene-Oxides that provide a deeper through cure). Shorter wavelength sources (nearer to 230 nm) are used in combination with AHK type systems to provide hard surface cure.



A less than fully polymerized coating can be a sticky matter. The topmost layer of the coating being tacky and lacking surface properties needed in the final product. If the surface is wiped with solvent to remove this top layer (frequently 5% or less of the film thickness, the coating can be fully cured below (where no ambient oxygen was present to cause inhibition.

1. Care-Free Inerting

One way to prevent Oxygen inhibition is to remove the oxygen itself from the curing environment. Actually it is only necessary to remove oxygen from the area near the coatings surfaces, providing an oxygen-free "blanket". This can be done by displacing oxygen with another gas such as inexpensive Nitrogen.

This approach has been successfully used by Finnish-based Tikkurila Coatings, one of the largest coatings manufacturers in Europe and a leading formulator for wood products such as parquet flooring and recently announced at RadTech Europe (November 2007).

Tikkurila felt that the benefits of solid-state curing are so compelling that adding nitrogen inerting to their process made great sense in the long run.

Tikkurila's Luminol and Uvinol UV curing products have been optimized to work well with a new commercial LED curing line at their facility built in co-operation with Phoseon Technology. The Tikkurila pilot line successfully cures parquet flooring at normal production speeds with performance equal to, or better than they experienced with medium pressure mercury lamps in the past.

Several innovative techniques make adding nitrogen inerting to the process inexpensive, easy and trouble-free. Since the amount of nitrogen gas required is relatively small, Phoseon Technology has developed an innovative nitrogen generation and delivery system that integrates directly to their UV Curing systems. This process eliminates the need and cost of using bottled nitrogen gas. This low volume, low flow technique minimizes the amount of nitrogen required and provides uniform distribution of nitrogen in the small space between the LED source and substrate.

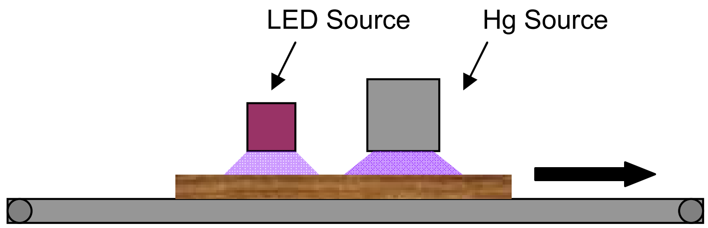
The result is a beautiful, completely cured wood coating with the clarity, gloss and durability demanded for parquet flooring applications.

2. Hybrid Design – An LED Jump Start

Those wishing to begin taking advantage of LEDs benefits without inerting or reformulating can take a clue from the Toyota Prius. An LED/mercury lamp hybrid solution offers off-the-shelf potential.

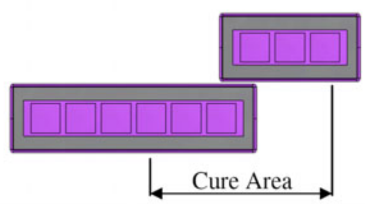
Like the hybrid car, adding an energy-saving LED array to a traditional UV curing lamp can noticeably increase the energy efficiency, performance, and longevity of the overall system.

In recent trials, even adding a UV module prior to a single arc lamp showed significant benefits. The arc lamp, previously operating at 400W/Inch was reduced in power to 125W/Inch. A Phoseon Starfire MAX unit which produces approximately 4W/cm2 was used to provide initial curing. The arc lamp was used to provide cure to the very top surface of the coating where oxygen inhibition would normally have occurred.

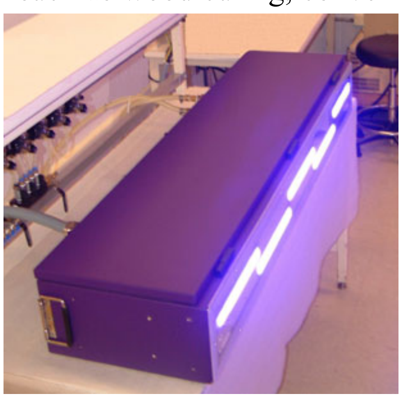


In this configuration, an overall savings in excess of 50% of the energy consumption was realized. Derating the mercury arc lamp also results in increased lifetime of the arc lamp, and better operational stability since arc lamps deteriorate faster as their output power is increased.

In addition, through cure of the coating was actually improved without sacrificing surface properties of the final product.



It's worth noting that another recent advance in UV LED technology has been the steady increase in footprint of the source. Early LED curing units were only a couple of inches long, limiting their applications for wide web applications such as wood curing, converting and other applications where arc lamps of a meter or more are popular.

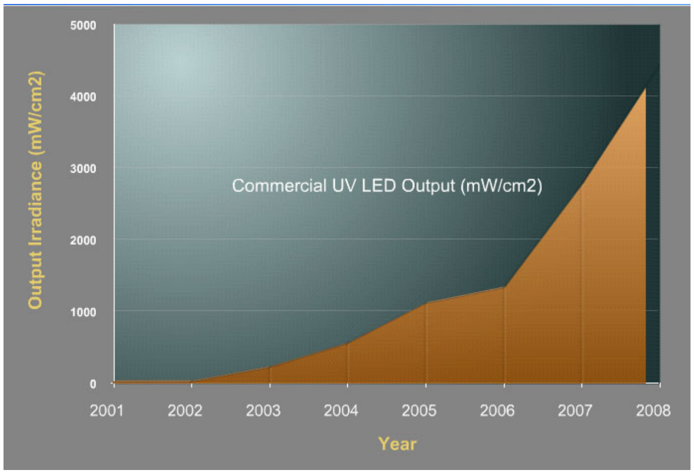


Now UV-LED based UV Curing systems of a meter or more are common. And in fact, UV-LED technology offers advantages since they can be arranged in a staggered fashion with no ill effects on the curing process. It has been proven that these arrangements produce unparalleled uniformity across the substrate and provide consistent properties anywhere the coating is tested. This is not true of arc lamps which experience non-linear degradation as they lamp ages with noticeable variation in intensity across the length of longer arc lamps, especially when these lamps are doped.

The common phenomenon of darkening at the electrodes also results in a measurable drop off of UV output and can result in changes of gloss, color or even loss of properties such as cure or adhesion. Even with new arc lamps, it is difficult to achieve complete uniformity with overlapped lamps since the electrode area near the end of the lamp causes uniformity problems.

Increased Solid-State Power Output

Oxygen inhibition is a race; a competition between free radicals promoting the polymerization of oligomers in the coating, and oxygen scavenging the same free radicals. One way to solve the problem is to use a bigger hammer. It is well established that higher intensity light sources reduce the surfaces susceptibility to inhibition:



"Another major benefit of extreme intensity UV application for free radical initiator chemistries (the most common) is in mitigating surface cure problems due to oxygen inhibition. In short, in addition to "punch through" deep cure mechanisms, extreme intensity effectively seals the surface instantly, preventing unwanted oxygen diffusion into the film afterwards. The effects of this high intensity mitigation were shown dramatically and documented by Jonsson. When very high intensities were used in a comparative study, initial rates of polymerization in air were the virtual equal of those cured in a Nitrogen purged environment. This was not the case, of course, with low intensity irradiance. " *The Case for Extreme Intensity in UV Curing* , Lesco White Paper Number 106.

In the semiconductor world, products get beater, faster and cheaper over time. Like microprocessors or memory sticks, LED capabilities have risen sharply over the last five years. Coatings that could not be cured with the 200 mW/cm2 sources only a few years ago now cure rapidly with sources producing over 4 W/cm2 of output*. A parallel development in the last five years has been that these arrays have gotten larger and less expensive (an unusual but welcome occurrence in the industrial world!).

*The discussion of output raises a point worth mentioning. Traditional mercury lamps are often specified in "watts per inch." It's common for industrial curing systems to use lamps with 200, 400 or 600 watts per inch. Remember that this is not a measure of these lamps output, but rather the power that can be applied to the lamp. So a ten inch, 600 watt per inch lamp uses 6,000 watts of input energy. The output can vary enormously from system to system and so must be measured with a radiometer. Typically UV energy makes up less than one third of the total output of a traditional UV lamp (with heat and visible light making up over two thirds of the output). LED sources by comparison emit only in a narrow bandwidth. The output figures referenced in this paper refer to a radiometric measurement made at the face of the emitter. Be aware however that some LED sources specify output based on some calculated output of the LED's themselves. When comparing UV-LED sources always consider where and how the output is being measured and over what area the peak irradiance is valid as this will determine the dose.

4. The Development of New Photoinitators and Better Formulations.

The slowest, but most promising avenue to the widespread adoption of UV LED technology is the creation of new raw materials and better formulations that exploit the narrow, but highly efficient bandwidth of these devices.

Non free-radical and hybrid cure mechanism are being tested, new photoinitators that are less prone to the effects of oxygen inhibition are also being developed. Cationic cure mechanisms are of somewhat limited use in the wood curing environment where the typical (3%-10%) moisture content along with the frequent alkaline pH of the substrate inhibits the ability to cure cationically.

There is also promising work being done with the existing range of commercially available products. In the digital inkjet world for example, the potential of LEDs to not only “pin” or set inks in advance of full cure by a mercury source is giving way to inks being formulated to fully cure with LED sources.

Chemists have continually prompted LED lamp suppliers to produce devices with shorter wavelength output. The presumption being that this would make curing existing formulations easier. But experiments that have been carried out with commercially available LEDs in the 365nm region have shown this is not the case.

These LEDs are more costly and have lower irradiance than 395nm sources. Trials have demonstrated that any benefit of shifting to a slightly lower wavelength is lost to the lower output power of the emitter. That is, the higher power of 395nm more than compensates for it’s slightly longer wavelength. The 395nm units also provide the advantages of lower cost, and an output which is not categorized as a “UV” source for plant health and safety purposes by regulatory agencies such as NIOSH.

Conclusion

It’s hard to ignore the steady march of LEDs in everyday life. From Rockefeller Center to the National Christmas tree to the ball that falls in Times Square on New Years Eve, LEDs are replacing traditional lamps all around us with their sights set on the everyday light bulb.

The rapid developments in LED production that make lower cost and higher performance of LEDs parallel the same path of most semiconductor devices make LEDs more and more attractive all the time.

In the industrial application of LEDs, and UV curing in particular, improvement in the radiant output of UV LEDs must be combined with the chemistry of UV cure coatings to fully utilize these new long-lasting, energy and environmentally friendly sources.

"When New York City Mayor Michael Bloomberg helped light the Rockefeller Center Christmas tree last month, the 84-foot-tall Norway spruce came alive with 30,000 twinkling lights. For the first time, the famous tree was illuminated with energy-efficient LEDs, or light emitting diodes, rather than traditional light bulbs. Major displays such as the Rockefeller Center tree, the National Christmas Tree in Washington and even the New Year's Eve Ball in New York's Times Square are making the move to LEDs this season.

But when it comes to environmentally friendly holiday lights, many homeowners have already moved ahead with the adoption of LED light sources. Manufacturers and retailers report that consumer sales of the efficient lights have been growing for years. Fans say the lights' versatility, safety and energy efficiency could soon make incandescent bulbs a ghost of Christmas past."

—*USA Today*, December 2007

GE Consumer & Industrial Lighting designer Kathy Presciano observed that traditional 26-light strings burned at 125 watts and lasted for about 1,000 hours. The same size string with LEDs lasts 20,000 hours and burns at 2.3 watts.

The nagging obstacle of oxygen inhibition has been overcome commercially through formulation, higher power sources, clever inerting techniques and even hybrid designs. There is great interest in LED curing from sectors such as automotive refinish and aerospace and military field repair where the portability and safety benefits of the technology are driving innovation. Wood and PVC coatings applications will certainly benefit from the transfer of technology in these arenas aw well.