

Photoinitiator selection for LED cured coatings

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Background:

LED light sources are rapidly gaining in popularity in the UV cured coatings market as they offer reduced cost, longer life and environmentally friendly alternatives to conventional lamps. Transitioning to LED lighting, however often requires more than just a simple equipment change. Modifications to the chemistry might also be needed in order to effectively compensate for the lower energy levels and narrower wavelength range. This is particularly true in coatings applications, where oxygen inhibition can have a detrimental affect on cure properties¹. In this paper, we will examine how proper photoinitiator selection and concentration can be used to optimize the performance of LED cured coatings.

Oxygen inhibition:

Poor surface cure, due to oxygen inhibition, is one of the most challenging aspects associated with LED cured coatings. Oxygen in its ground state has a "diradical" nature and is highly reactive towards radical species² As a result oxygen can scavenge radicals to form less reactive peroxy compounds, which can terminate the growing chain via radical to radical interaction. The result of oxygen inhibition is observed as a decreased rate of polymerization and ultimately compromised coating performance.³

Formulators have tried to overcome curing issues in a variety of ways¹, each with different degrees of success, but also having their own drawbacks. Some of the frequently discussed remedies include:

- Isolating the coating from oxygen;
- Increasing the amount of energy the surface is exposed to;
- Increasing the concentration of photoinitiator;
- Modifying the coating chemistry/photoinitiator package.

Isolating the coating from the atmosphere is the most straight forward method of mitigating oxygen inhibition, but it is also the most difficult, particularly when curing large areas. Applicators have attempted to reduce the oxygen exposure by blanketing the exposed area with inert gas or covering with waxes and films. This approach works well in laboratory settings, but can be impractical for large, industrial applications.

Increase energy is another way of improving curing of coatings under LED light. Upon inception, LED lamps were limited in the amount of energy they could produce, but as the technology evolved, higher energy lamps capable of producing more free radicals and faster cure speeds were developed. While this significantly improves surface cure, the higher rate of polymerization can have a detrimental effect on depth of cure, depending on the photoinitiator

package the formulator has chosen. This is particularly true with thicker coatings, where the poor depth of cure can lead to poor coating performance in the field.

Similarly, increasing the concentration of photoinitiator in the coating allows for more free radical formation which in turn provides for better through cure. Depending on the type of photoinitiator chosen, this approach can have a detrimental affect on depth of cure as well as obvious economic implications. Care should also be taken that the concentration of free radicals produced does not exceed the amount of available sites, as this could result in a reduction of cure speed.

One variable that has yet to be completely explored is the effect of the type of photoinitiator used in the formulation. Formulators will frequently use combinations they've had success with in the past, but find that photoinitiator performance under conventional UV lamps is not necessarily indicative of how it will do under LED light. In some cases, particularly thick coating applications, entirely new combinations that work using a completely different mechanism can produce significantly better results. In this paper, we will evaluate not only how the concentration of photoinitiators can affect coating performance but more importantly why the choice of material is also critical.

Photoinitiator technology:

In order to determine how photoinitiator selection and concentration effects cure performance, it is important to understand first how photopolymerization works. The process begins with a molecule being exposed to radiation creating a reactive species resulting in photo polymerization of monomers. The two most common types used in coatings are free radical photoinitiators, used to polymerize acrylate based monomers and cationic photoinitiators used in epoxy based formulations. In this paper we will focus only on acrylate based systems.

Upon light absorption, a photoinitiator transitions from the neutral ground state to an electronically excited singlet state. Once in the singlet state a rapid intersystem crossing occurs to form the excited triplet state, which is where radical production most often results³ (Figure 3.1).



Figure 3.1 Photoinitiator radical production process

The exact mechanism of radical formation can vary, depending on the molecules chemical configuration. A (substituted) alkyl group at the R1 (as is the case with acyl-phosphine oxide) undergoes a Type I scission producing two radical species with different reactivity and oxygen sensitivity characteristics² (Figure 3.2).

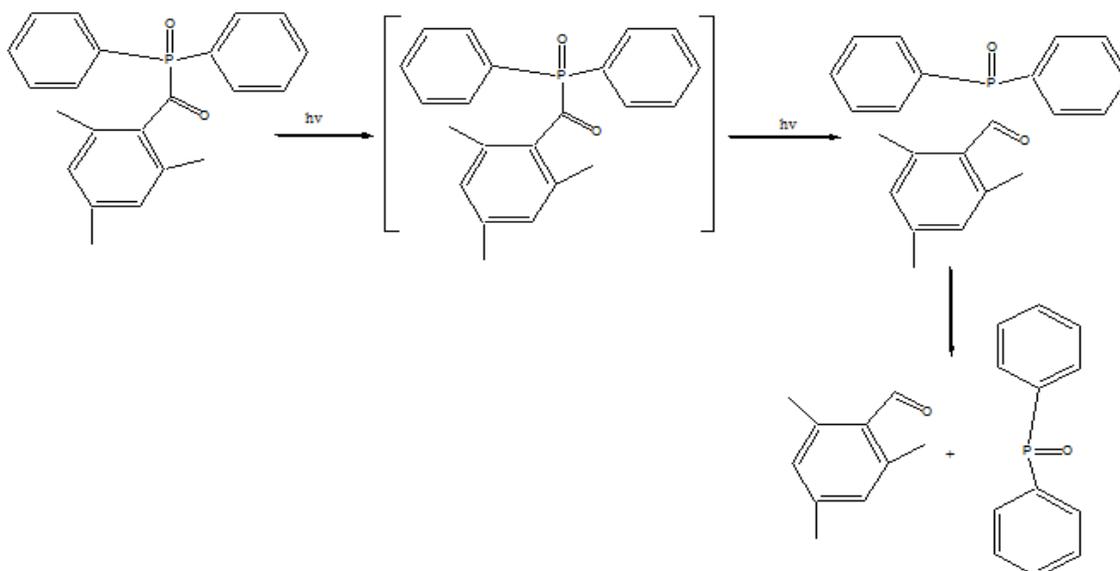


Figure 3.2: α -scission mechanism of acyl-phosphine oxides.

Hexaarylbimidazole, or HABI as it is more commonly known, utilizes a different mechanism to produce free radicals and initiate polymerization. Upon exposure to UV radiation, the HABI molecule is activated to form an excited intermediate compound. Radicals are then produced by hydrogen abstraction or electron extraction from a second compound in the formulation. The secondary compound then becomes the initiating radical resulting in polymerization (Figure 3.3).

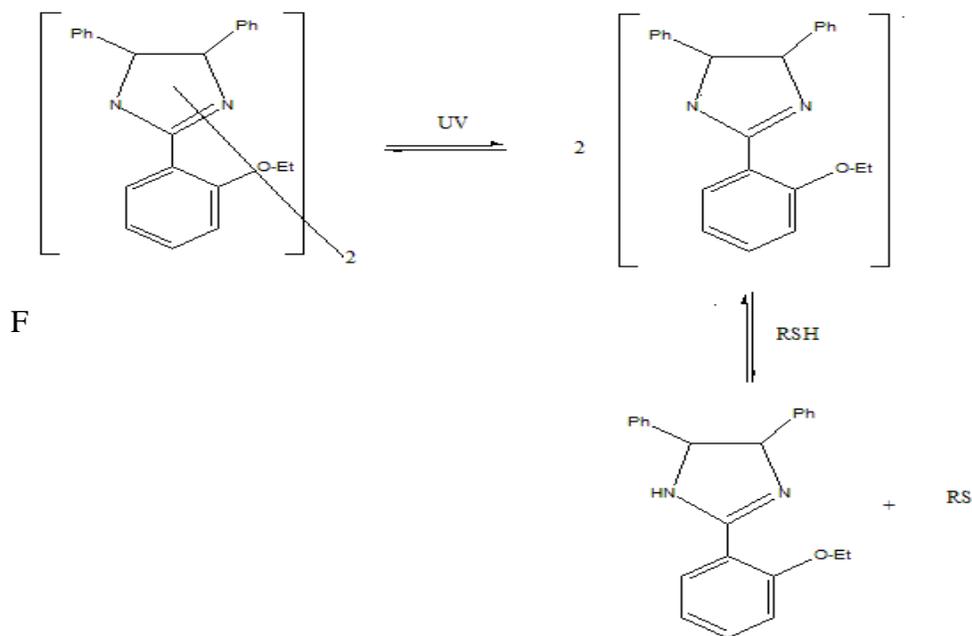


Figure 3.3: HABI radical formation

Numerous HABIs are possible by modifying the substituent groups “R” attached to the aryl groups of the molecule. For example, the structure is called a lophine dimer when “R” is hydrogen. However when chlorine replaces hydrogen, the compound is now called o-Cl-HABI.

The addition of the Cl changes the physical properties and performance of the molecule. There are hundreds of HABIs that can be synthesized by the addition of functional groups to various and /or multiple positions on the aryl groups. Each may exhibit different physical properties and performance. The performance of each material, however, is system and application dependent (Figure 3.4).

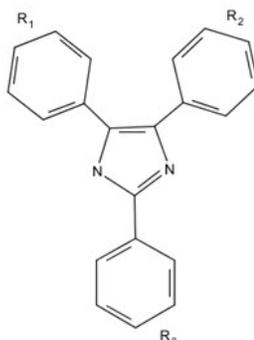


Figure 3.4: HABI molecule

Reaction mechanism is only one consideration when choosing a photoinitiator. Solubility, color, photo speed and cost all play an important role. Researchers will also rely on a compounds UV spectra to determine the suitability of material for their specific application (figure 3.5).

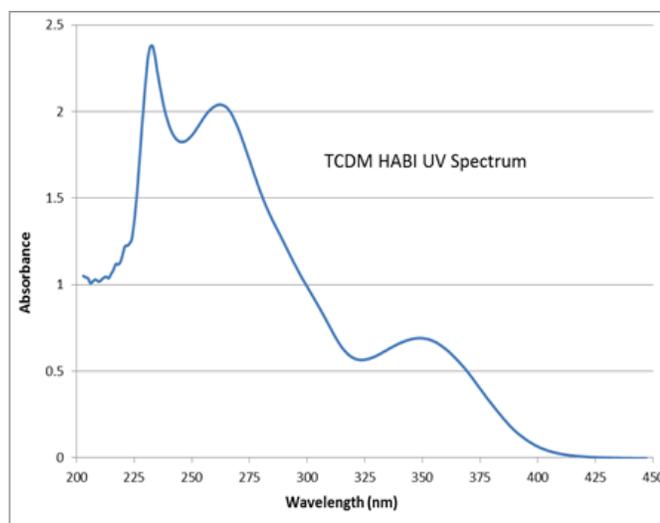


Figure 3.5: Typical UV spectra

Recently, there has been much attention given to optimizing photoinitiator packages for LED applications. In this next section we will explore how photoinitiator selection impacts the curing properties of both thick and thin coatings under LED light.

Photoinitiator effect on surface cure:

In order to evaluate the effect of photoinitiator substitution on surface cure, a series of standard formulations was created. Each formula was comprised of a main acrylate monomer, a diluting monomer and a photoinitiator package, at the following percentages:

Main acrylate monomer-----87% by weight
Diluting monomer-----5% by weight
Photoinitiator package-----8% by weight

The main acrylate monomer was chosen from the following three materials commonly used in UV curable coating applications:

- EO-TMPTA Ethoxylated TMPTA (Allnex)
- CN 131B Aromatic monoacrylate oligomer(Sartomer)
- IBOA Isobornyl acrylate (various)
- HDODA 1,6-hexanediol diacrylate. (various)

The diluting monomer was added to improve the solubility of the photoinitiator package, as well as to facilitate coating draw down. In all cases the diluting monomer used was n,n-dimethyl acrylamide (DMA), a nonionic acrylic monomer. DMA was also chosen as the nitrogen atom, positioned on the backbone can facilitate curing in the presence of oxygen.

The photoinitiator package used for this series experiments made up of three components:

Free radical photoinitiator ----- 12.5 parts
Substituted thioxanthone sensitizer-----25 parts
Electron donor-----62.5 parts

The photoinitiators chosen for this study were selected from the either the imidazole family (Hampford Research) or phosphine oxides (BASF). In all cases, the substituted thioxanthone co-initiator chosen was 2,4-Diethylthioxanthone (DETX) and the electron donor used was 2-Mercaptobenzoxazole (2 MBO).

Testing was performed using a series of 0.8-mil wet film drawdowns on a 0.010 inch aluminum plates. The coated aluminum plates were irradiated using a Phoseon "Starfire Max" LED lamp at 395 nm wavelength. The line speed was maintained at twelve feet per minute throughout the experiment. After each pass, the panels were removed and the degree of surface cure evaluated per the following scale (figure 4.1).

Rating	Description
0	no evidence of cure
1	Dry but smears easily
2	Does not smear, but scratches with fingernail
3	Resistant to finger scratch

Figure 4.1: Rating surface cure

The first formulation tested used EO-TMPTA (Ethoxylated TMPTA*) as the main monomer. This material is commonly used in acrylic coating formulations due to its low toxicity and fast cure speed. Both the imidazole based and phosphine oxide photoinitiator packages dissolved readily into the diluting monomer and the resulting solution added to the TMPTA. The coating material was applied to an aluminum plate and cured under UV light (as detailed above).

Both the imidazole based as well as the acyl-phosphine oxide system showed little surface cure after the first pass and comparable results through four passes. After the fifth and final pass, the imidazole initiated coating was completely cured while the PO coating could still be scratched (Figure 4.2).

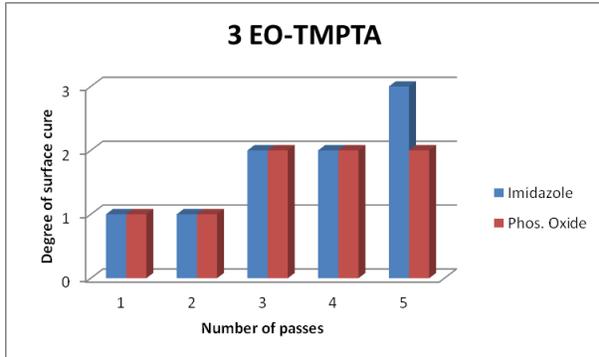


Figure 4.2: Surface cure comparisons #1

The same series of tests were performed, this time substituting Isobornyl acrylate for the main monomer. IBOA is commonly used for coatings due to its hardness and flexibility characteristics. It is somewhat less reactive than the TMPTA, which was demonstrated as neither formulation achieved full cure even after five passes. The phosphine oxide initiated system did show a slight advantages in surface cure after the second and fourth pass (Figure 4.3).

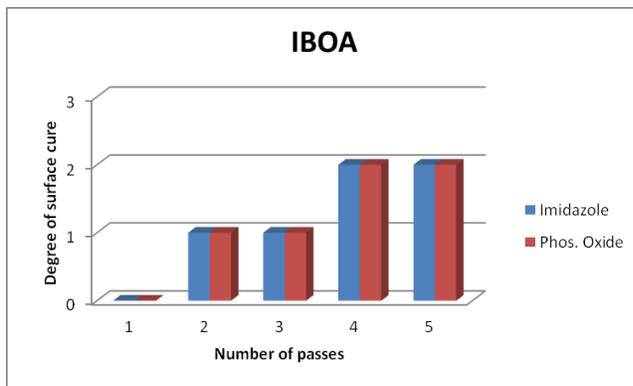


Figure 4.3: Surface cure comparisons #2

Sartomers CN-131B was the primary acrylate for the third and final series of surface cure tests. This particular aromatic monoacrylate oligomer was also chosen due to its high reactivity and fast cure speed. As expected both photoinitiator technologies exhibited full surface cure after only one pass (Figure 4.4). While there were some slight differences in surface cure characteristics (the imidazole based being slightly more cured), the two photoinitiator systems gave very similar performance.

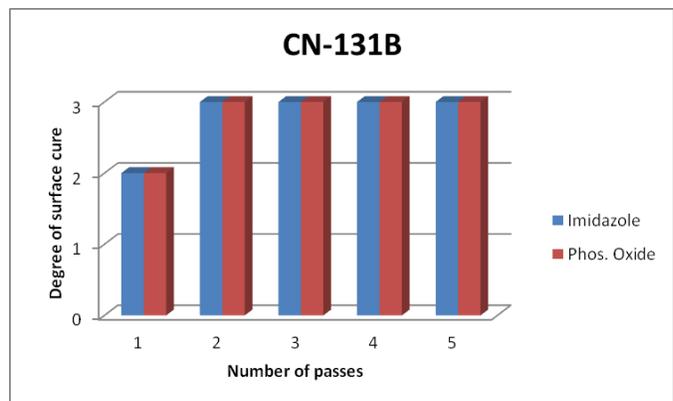


Figure 4.4: Surface cure comparisons #3

Repeating this same series of tests substituting a traditional mercury lamp, all of the formulations tested demonstrated full cure by the second pass. This clearly illustrates the challenges associated with oxygen inhibition under LED lamps normally not seen with mercury lamps.

Photoinitiator effect on depth of cure:

The relationship between surface cure and depth of cure is complex and not always completely understood. Normally, one would expect good surface cure to be an indication of complete through cure as well. While this is the case with conventional lamps, the opposite can occur with LED systems. Additionally, modifications that intuitively would help (i.e. higher photoinitiator concentration) can actually reduce the depth of cure. In this next series of tests, we evaluated how photoinitiators affect the depth of cure in both LED and conventionally cured coatings.

In order to evaluate how photoinitiator selection and concentration effects through cure, we started with a standard coating formulation comprised of equal parts CN-964, IBOA & CN-131B. Two photoinitiators were chosen from the acyl phosphine oxide class as well as two from the imidazole family. For this series of tests, the photoinitiator concentration ranged from 0.5% to 2% by weight. As before, 2-Mercaptobenzoxazole was added to all test solutions as an electron donor.

The four photoinitiators chosen for this study were:

- Mono ethoxy substituted imidazole (Test solution #1)
- Poly methoxy substituted imidazole (Test solution #2)
- Monoacylphosphine oxide (Test solution #3)
- Biacylphosphine oxide (Test solution #4)

Exactly 0.5 grams of each formulation was weighed out into a ceramic Coors evaporating dish and irradiated under LED light (395 nm) for a single pass at 72 feet per minute. The cured coating was removed (Figure 5.1) and the thickness to the nearest 0.001” using a micrometer (Figure5.2).



Figure 5.1: Cured coating



Figure 5.2: Thickness measurement

The chart below (Figure 5.3) details the results obtained from this second series of tests. As was the case with the first series of tests, complete cure was achieved in all cases. When exposed to LED light, there was a anywhere from a 2% reduction in through cure (solution #1) to as much as an 86% reduction (solution #4).

Photoinitiator	Concentration	Fusion D	LED (395 nm)	Percent change
		Depth of cure	Depth of cure	D vs LED
Solution #1 (o-ethoxy HABI)	0.5% bw	145	142	-2%
	1.0% bw	150	142	-5%
	2.0% bw	150	135	-10%
Solution #2 (TCDM HABI)	0.5% bw	145	115	-21%
	1.0% bw	150	78	-48%
	2.0% bw	150	50	-67%
Solution #3 (TPO)	0.5% bw	145	130	-10%
	1.0% bw	150	70	-53%
	2.0% bw	150	40	-73%
Solution #4 (BAPO)	0.5% bw	148	90	-39%
	1.0% bw	150	42	-72%
	2.0% bw	150	21	-86%

Figure 5.3: Effect of photoinitiator on surface and through cure

* Thicknesses between 145-150 mils were considered complete through cure.

Although the mechanism is not completely understood, it has been proposed that achieving a high rate of surface cure is actually detrimental to depth of cure, as it prevents radiation to reach deep into the coating. It also appears that smaller, more mobile photoinitiators as found in solutions one and three, performed better than their larger, bulkier counterparts. Overall, solution #1 should the best overall performance under LED light.

Conclusions:

The transition from broad spectra mercury lamps to lower cost, more environmentally friendly LED's represents one of the most important changes in recent UV/EB technology. There are however, significant challenges formulators face maintaining coating performance within the limited wavelengths these lamps produce.

Poor surface cure due to oxygen inhibition is one of the more common challenges applicators face when converting to LED light. This can be mitigated a number of different ways, either by isolating the coating from the environment, or through modification of the chemistry itself (both monomers as well as photoinitiators).

Incomplete through cure is another problem related to LED lights. It generally occurs when there is not enough energy produced to pass through the cured surface, and seems to worsen as their concentration is increased.

As LED lamps become more and more popular in mainstream coating applications formulators will continue to find ways to optimize overall coating performance.

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