# Mitigation of Oxygen Inhibition in UV LED, UVA, and Low Intensity UV Cure

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## INTRODUCTION

Oxygen inhibition is an age-old problem for coatings that cure via free-radical polymerization. Molecular oxygen can physically quench the triplet state of the photoinitiator/sensitizer, or it can scavenge the free radicals or active radical centers to produce unreactive peroxide radicals. The end results range from reduced coating properties to uncured, liquid surfaces on the coating. This issue is even more pronounced in low intensity cure processes, such as UV LED or UVA cure, which frequently result in tacky, uncured surfaces. There are known physical and chemical ways to reduce oxygen inhibition or improve surface cure. This paper will discuss these methods, provide starting point formulations that use the chemical solutions, and show the cured coating properties of these formulations.

## OXYGEN INHIBITION OF FREE RADICAL POLYMERIZATION

A schematic of UV initiated free radical polymerization is shown in Figure 1. Photoinitiator is I, double bond containing materials are depicted by R and R´, and AH is a material with easily abstracted hydrogens (chain transfer agent). The photoinitiator absorbs UV energy and generates a carbon based free radical in the radical formation step. This free radical then initiates the polymer chain through reaction with R. The steps of propagation, chain transfer, and termination then occur throughout the process. The molecular weight, molecular weight distribution, and polymer composition are determined by the relative ratios of the steps.

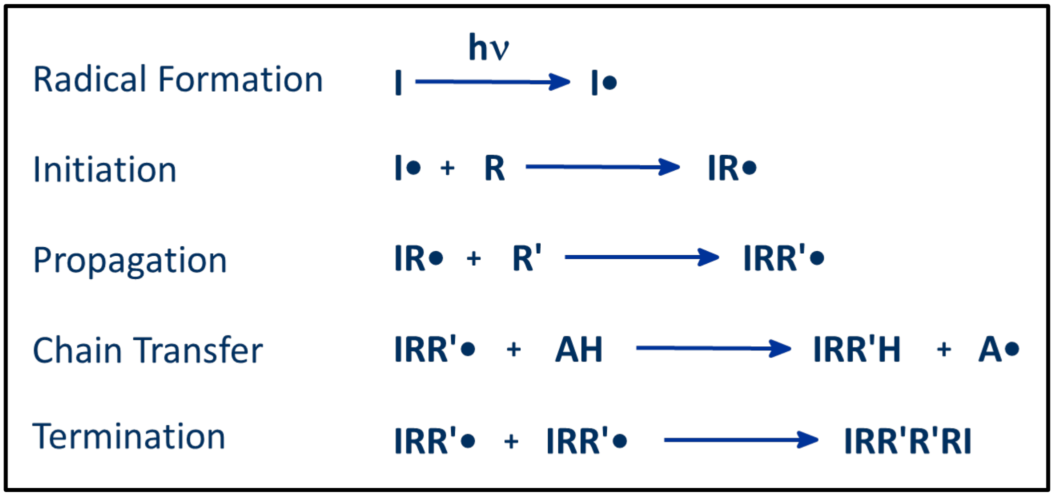


**Figure 1.** UV Initiated Free Radical Polymerization

Figure 2 shows the reactions of oxygen with photoinitiator (PI) and free radicals ($R^{\bullet}$). In the reaction of oxygen with the excited state of the photoinitiator, the photoinitiator is quenched and returns to an unexcited, non-reactive state. The end result is fewer free radicals produced by the photoinitiator, with fewer initiated polymer chains, and less polymer formation in the coating.

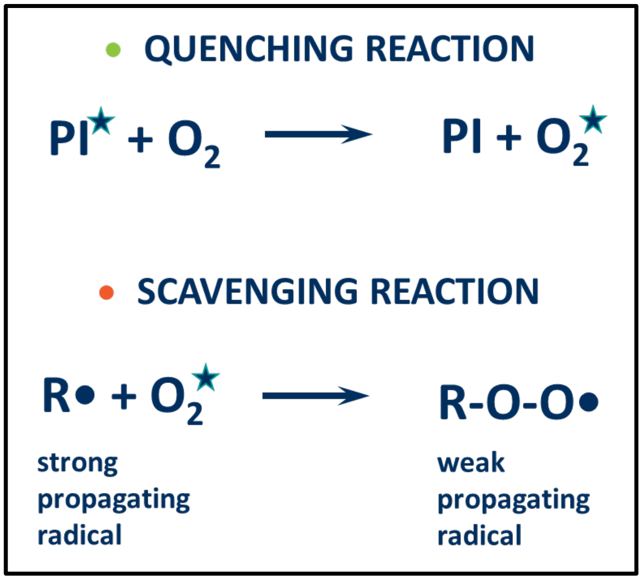


**Figure 2.** Reactions of Oxygen in UV Initiated Free Radical Polymerization

When the triplet state of oxygen reacts with a carbon-based free radical, it converts the growing chain to an oxygen based free radical. This oxygen based radical is less reactive than the carbon based radical, and slows down the free radical polymerization, resulting in lower molecular weight chains. In either case, the reaction with oxygen may give a range of results, from reduced coating properties to uncured, liquid surfaces on the coating.

## MITIGATION OF OXYGEN INHIBITION

Since oxygen is present at about 21% in air, oxygen inhibition of free radical polymerization is a very real problem in the energy cure industry. Oxygen is present in two places: in the bulk material and at the surface of the coating. Oxygen is generally required in the bulk material to provide storage stability. (In this case, the oxygen inhibition is a welcome attribute.) This bulk oxygen is consumed fairly rapidly upon exposure to UV, and has little impact for most coatings. The oxygen at the coating surface is replenished as it is consumed, and causes most of the issues seen in the industry. Since this oxygen is at the surface of the coating, oxygen inhibition is frequently referred to as a surface cure problem.

There are known physical and chemical ways to reduce oxygen inhibition or improve surface cure:

1. Remove oxygen from the UV cure zone by use of inert gas, by use of waxes that migrate to the surface and form a barrier, or by use of films that are in direct contact with the coating.[1] In UV waterbased systems, the water vapor may act as an inert gas.[2]

2. Increase free radical concentration by increasing the photoinitiator concentration or the light intensity (irradiance).[1]
3. Use chemicals that react with the peroxy radicals.[1]

These solutions have been and are currently used in the industry, but they all have advantages and disadvantages.

The removal of oxygen is not an easily implemented or cost-effective solution. Nitrogen inerting is used in some specialty applications, but the typical end use cannot afford the cost. Inerting a web-based application can also be especially difficult. Waxes can be used, but they impact the final properties of the coating, and time is needed for migration of the waxes to the surface of the coating. Laminating adhesives is an example of an application that uses film as an oxygen barrier. In this case, the film becomes part of the product. When water is evaporated from waterbased UV coatings, the water vapor acts as a barrier to oxygen. If UV cure is immediate after water evaporation, very good surface cure is obtained.[2]

The light intensity is determined by the available UV curing equipment, and often cannot be changed. Higher intensity lamps are also generally more expensive. Increased photoinitiator levels may result in increased concentrations of undesired residuals or by-products. It may also result in lower molecular weight polymer chains, and reduced coating properties, due to increases in initiation and termination reactions. (See Figure 1.)

The use of reactive chemicals is the most commonly implemented solution to mitigate oxygen inhibition. The chemicals that react with peroxy radicals contain easily abstractable hydrogen atoms. These abstractable hydrogen atoms are found in compounds containing sulfur (thiols), nitrogen (amines), or oxygen (ethers). The hydrogens on the carbon atoms alpha to the sulfur, nitrogen, or oxygen are those that are easily abstractable, and there are many of these in each molecule. The efficacy of these compounds, for the same equivalency, is thiols > amines > ethers. Improvements in performance are noted when the thiols, amines, and polyethers are acrylated. The acrylate functionality insures that the materials become part of the polymer backbone, and cannot migrate or bloom to the surface. A reduction in odor may also be obtained through acrylation. Figure 3 shows the mechanism for the reaction of an amine with oxygen. Since there are six abstractable hydrogens in this amino compound, it can react six times with oxygen.

One drawback of the use of thiols is odor. However, improvements in purity have reduced the odor of many thiols. Advantages of using thiols may be improved thermal resistance, reduced moisture absorption, and improved adhesion. The use of amines can result in yellowing (either upon cure or after cure), residual odor, and moisture sensitivity. The yellowing can be masked or lessened through use of dyes or optical brighteners. Ethers are the least effective solution to oxygen inhibition, but can be used in large quantities via polyether structures. Many urethane acrylates utilize polyether backbones based on polyethylene oxide, polypropylene oxide, or polybutylene oxide. Since large amounts of these polyethers are required, the performance properties of the coating are affected by polyether choice. Diluting acrylates may also be ethoxylated or propoxylated to give reduced oxygen inhibition. The ether groups can cause reduced temperature resistance of coatings, and depending on the type of polyether, reduced water resistance.

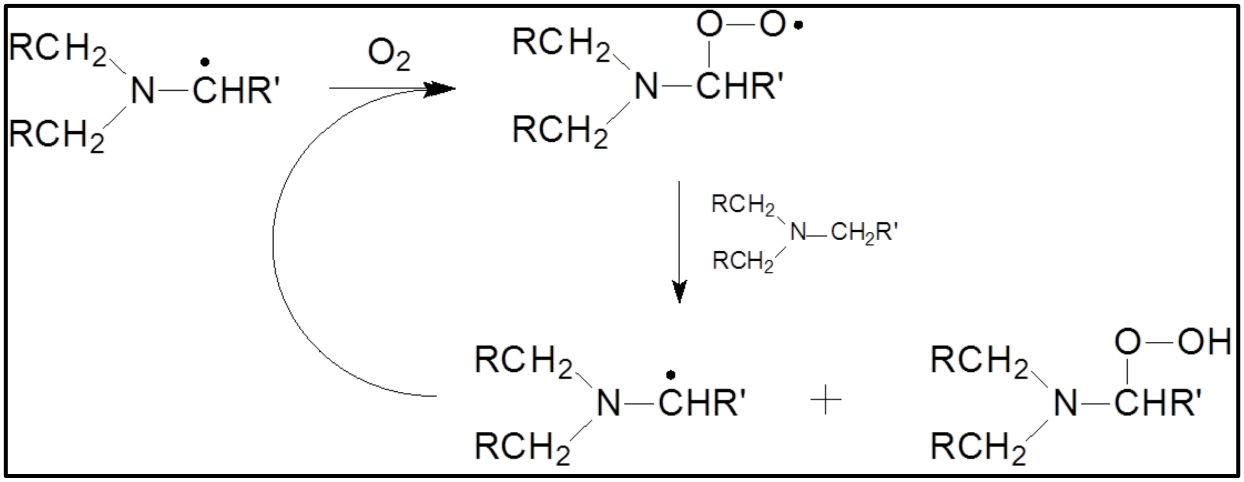


**Figure 3.** Reaction of Amine with Oxygen

The polyethers may be used alone or in combination with the thiols or amines to provide further improvements in cure performance. When polyethers are used alone, the deficiencies of the thiols (odor) and amines (yellowing, odor, moisture sensitivity) are absent. The ultimate cure speed of these products is determined by the molecular weight, the acrylate functionality, the type and amount of modification, and the type of resin (epoxy acrylate, urethane acrylate, polyester acrylate, etc.). See Table 1 for a summary of the methods to mitigate oxygen inhibition, and the advantages and disadvantages of each.

**Table 1.** Methods to Mitigate Oxygen Inhibition, with Advantages and Disadvantages

| Method | Advantages | Disadvantages |
|---|---|---|
| Inert Gas | Does not adversely affect coating properties | Expensive; difficult to implement |
| Waxes | Inexpensive | Affects final coating properties; time needed for migration |
| Films | Good solution when film becomes part of product | Cost/disposal of film when not part of product |
| Increase PI Concentration | Easy to implement | Increased residuals/by-products; reduced coating properties |
| Increase Light Intensity | May not affect coating properties | Part of existing equipment; cost |
| Thiols | Improved thermal resistance; reduced moisture absorption; improved adhesion | Odor |
| Amines | Inexpensive; possible improved adhesion | Yellowing upon or after cure; residual odor; moisture sensitivity |
| Ethers | Can be used in large quantities | Affects coating properties; reduced temperature resistance; possible reduced water resistance |

## LOW ENERGY CURE SYSTEMS

In the past, UV curing systems have typically consisted of one or two medium pressure mercury bulbs, with broad spectral emissions, and with the wattage steadily increasing over the years from 200 to 600 watts per inch. (See Figure 4.) These systems were generally designed to obtain the fastest cure speed possible, with productivity gains the ultimate goal. Today, curing systems are being designed with other goals also in mind. Safety and environmental concerns, cure temperature, energy consumption, and maintenance schedules are all influencing the design of these new curing systems. As a result, some of the newer cure systems deliver less energy to the coating, and eliminate shorter wavelength UV. Both of these factors tend to increase the impact of oxygen inhibition on UV cure.

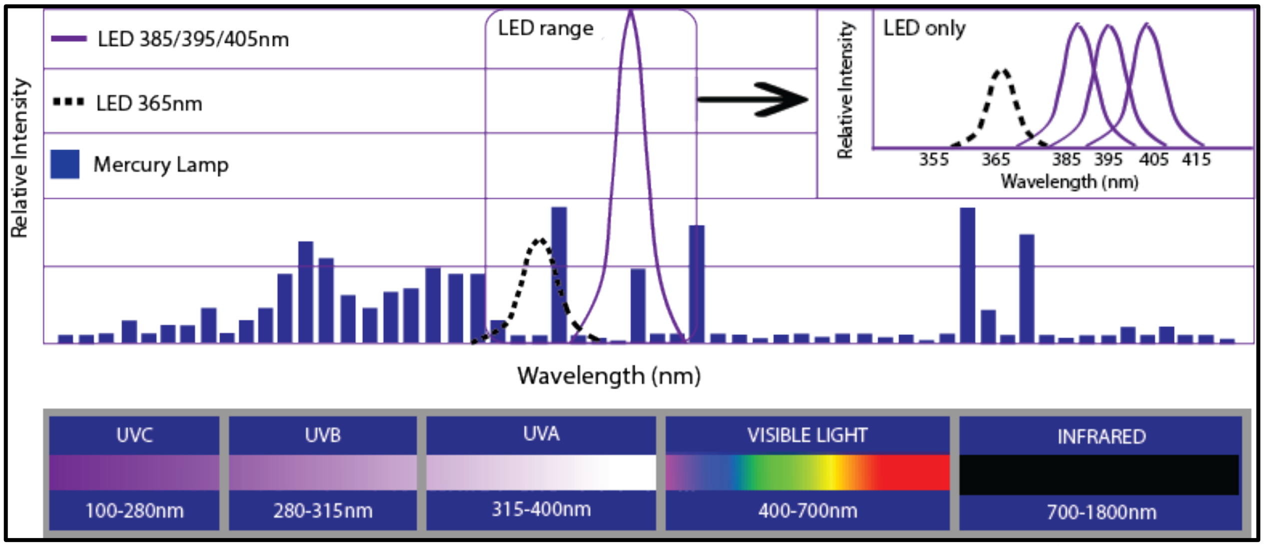
As mentioned earlier, increasing the irradiance increases the concentration of free radicals, and higher concentrations of free radicals consume more oxygen. Conversely, low energy cure systems, with lower irradiance, result in lower concentrations of free radicals and more oxygen inhibition. The irradiance should be measured at the substrate, to determine the delivered energy, because delivered energy decreases with distance from the lamp to the substrate.

There is also a wavelength dependence on absorption of UV. Shorter wavelengths (UVC) tend to be absorbed at the surface of a coating, longer wavelengths (UVA) tend to penetrate the coating to be absorbed near the substrate, and mid-wavelengths (UVB) are absorbed near the middle of the coating. (See Figure 4 for wavelength nomenclature.) Some of the newer energy cure systems do not emit UVC wavelengths, resulting in increased oxygen inhibition at the surface of the coating.

UVA lamps, by definition, primarily emit wavelengths in the UVA range. Most LED lamps emit at 395 nm, also in the UVA range. LED lamps with 385 nm and 405 nm emissions are also used, and lamps with 365 nm emission are available, but at lower intensity. (See Figure 4.) The LED lamps have seen a steady increase in peak irradiance, from 1.1 Watts/cm$^2$ to 16 Watts/cm$^2$. Improvements in the optics of UV LEDs have also led to an increase in the irradiance that is delivered to the substrate surface.

## FORMULATION & CURE BASICS

Better surface cure can also be improved via conventional formulating guidelines and design of cure equipment. Increasing the functionality or double bond concentration of the coating gives a more crosslinked or harder coating. Increasing the viscosity of the coating decreases the oxygen diffusion into the coating, and improves the surface cure.[1] Thicker coatings suffer less from oxygen inhibition due to the bulk polymerization reaction, which increases viscosity and significantly reduces oxygen diffusion.[3] Decreasing the distance from the lamp to the substrate increases the irradiance delivered to the substrate. Increasing the exposure time, via slower cure speeds or multiple lamps, also generally increases the extent of cure. These basics can be combined with the oxygen inhibition mitigation techniques to further improve coating performance.



*courtesy of Phoseon Technology

**Figure 4.** Mercury Lamp and LED Emission Spectra

## EXPERIMENTAL RESULTS & DISCUSSION

Table 2 shows the improvement in surface cure when a thiol (mercapto acrylate) is used at 20% in an LED cure application. (The LED had an emission wavelength of 395 nm, and a peak irradiance of 8 W/cm$^2$.) With the thiol present only one pass is needed to obtain a surface that cannot be marred with a fingernail. In the absence of thiol, surface marring is still present after 4 passes. Better surface cure is also noted when curing the same formulation with standard medium pressure mercury lamps.

**Table 2.** UV LED Surface Cure with and without Thiol (Mercapto Acrylate)

| Component | % | |
|---|---|---|
| 3 functional Urethane acrylate | 85 | 65 |
| Dipropylene glycol diacrylate; diluting monomer | 10 | 10 |
| Mercapto modified polyester acrylate | 0 | 20 |
| Phosphine oxide based photoinitiator | 5 | 5 |
| Reactivity, # of passes at 5 m/min.<br>Determined by surface marring by fingernail.<br>30 µ coating on Leneta Chart.<br>395 nm, 8 W/cm$^2$ UV LED lamp.<br>1 cm distance from lamp to substrate. | >4 | 1 |

Increasing the concentration of the thiol also increases the surface cure. Table 3 shows fast cure speed (greater than 40 m/min), when 40 parts of mercapto modified polyester acrylate is used in a formulation. Using 20 parts of mercapto modified polyester acrylate and 20 parts of unmodified polyester acrylate reduces the cure speed to 5 m/min. Formulations without any mercapto modification do not cure after 4 passes at 5 m/min.

**Table 3.** Effect of Thiol Concentration on UV LED Surface Cure

| Component | Parts | | |
|---|---|---|---|
| 3 functional Urethane acrylate | 65 | 65 | 65 |
| Dipropylene glycol diacrylate; diluting monomer | 10 | 10 | 10 |
| Mercapto modified polyester acrylate | 0 | 20 | 40 |
| Unmodified polyester acrylate | 40 | 20 | 0 |
| Phosphine oxide based photoinitiator | 5 | 5 | 5 |
| Reactivity, # of passes x m/min. Determined by surface marring by fingernail. 30 μ coating on Leneta Chart. 395 nm, 8 W/cm$^2$ UV LED lamp. 1 cm distance from lamp to substrate. | 4 x 5 NOK | 1 x 5 | 1 x >40 |

Table 4 shows the effect of cure distance on surface cure using a formulation that contains 20% thiol. At small distances, 0.5-1.0 cm, only 1 pass at 5 m/min is needed for good surface cure. At 2.0 cm distance, 2 passes at 5 m/min are needed to obtain a non-marring surface. The irradiance is decreased at the further cure distance, resulting in less polymerization at the surface, and reduced surface properties.

**Table 4.** Effect of Distance from UV LED Lamp to Substrate on Surface Cure

| Component | % | Distance (cm) LED to Substrate | | |
|---|---|---|---|---|
| 3 functional Urethane acrylate | 65 | | | |
| Dipropylene glycol diacrylate; diluting monomer | 10 | | | |
| Mercapto modified polyester acrylate | 20 | | | |
| Phosphine oxide based photoinitiator | 5 | | | |
| | | 0.5 | 1.0 | 2.0 |
| Reactivity, # of passes at 5 m/min. Determined by surface marring by fingernail. 30 μ coating on Leneta Chart. 395 nm, 8 W/cm$^2$ UV LED lamp. | | 1 | 1 | 2 |

The effect of coating thickness is shown in Table 5. Thinner coatings (10 μ) are 3-4 times less surface reactive than thicker coatings (30μ). The bulk polymerization in the thick coating increases its viscosity, reducing the diffusion of oxygen into the coating, and allowing surface cure.[3] (In this experiment the LED array was arranged lengthwise in order to provide more UV exposure.)

Table 6 shows the impact of the coating functionality or double bond concentration on surface cure. In this experiment, the concentration of the thiol is held constant, and the functionality of the other acrylate components is varied from 2.76 to 6.0. There is a very large increase in reactivity as the functionality is increased, from 10 m/min to 40 m/min. (The UV LED array is in the lengthwise configuration for this experiment.)

**Table 5.** Effect of Coating Thickness on Surface Cure with UV LED Lamps

| **Component** | **%** | **Distance (cm) LED to Substrate** | | | | | |
|---|---|---|---|---|---|---|---|
| 3 functional Urethane acrylate | 65 | | | | | | |
| Dipropylene glycol diacrylate; diluting monomer | 10 | | | | | | |
| Mercapto modified polyester acrylate | 20 | | | | | | |
| Phosphine oxide based photoinitiator | 5 | | | | | | |
| | | 0.5 | | 1.0 | | 2.0 | |
| **Coating Thickness (μ) on Leneta Chart** | | **10** | **30** | **10** | **30** | **10** | **30** |
| Reactivity, # of passes at x m/min.<br>Determined by surface marring by fingernail.<br>395 nm, 8 W/cm$^2$ UV LED lamp. | | 3 x 5 | 1 x 15 | 3 x 5 | 1 x 15 | 4 x 5 | 1 x 15 |

**Table 6.** Effect of Coating Functionality on Surface Cure with UV LED Lamps

| **Component** | **%** | |
|---|---|---|
| 3 functional Urethane acrylate | 57 | -- |
| Dipropylene glycol diacrylate; diluting monomer | 18 | -- |
| 6 functional Urethane Acrylate | -- | 75 |
| Mercapto modified polyester acrylate | 20 | 20 |
| Phosphine oxide based photoinitiator | 5 | 5 |
| Reactivity, # of passes at x m/min.<br>Determined by surface marring by fingernail.<br>30 μ coating on Leneta Chart.<br>395 nm, 8 W/cm$^2$ UV LED lamp.<br>1 cm distance from lamp to substrate. | 1 x 10 | 1 x 40 |

Table 7 shows the impact of amine modification on the cure speed of polyester acrylates. The coatings were applied to aluminum test panels at ~ 12 μ thickness, and cured with one 300 watt/inch medium pressure mercury lamp. Cure speed is the minimum line speed required to give a mar free surface. Polyester Acrylate 2 is notable for exhibiting the highest reactivity, but all of the amine modified polyester acrylates have higher reactivity than the non-amine modified product. Based on past experience and literature, similar results are expected with the use of low intensity UV cure.[1]

Table 8 compares the surface cures of various polyether and polyester based urethane acrylates. Thick resin castings of 15 mm were exposed for 20 minutes to a 20 watt fluorescent black light (Philips F20T12/BL). They were then assessed for surface cure via mar resistance and tack. Only UA 1, a difunctional polyether based urethane acrylate, exhibited a completely mar free, non-tacky surface. UA 4, another polyether based urethane acrylate with 2.3 functionality, was second best. The other polyether based resin, UA 6, has a very low Tg, and did not perform well in this test. (Mar resistance and surface tack is influenced by the Tg of the polymer.) The polyester based urethane acrylates did not give mar-free surfaces. Figure 5 provides data on cure time versus content of UA 1 when using a low intensity UVA lamp. As the concentration of UA 1 is increased, the cure time decreases.

**Table 7.** Effect of Amine Modification on Polyester Acrylate Cure Speed

| Component | Parts by Weight | | | |
|---|---|---|---|---|
| Polyester Acrylate 1 (no amine modification) | 100 | - | - | - |
| Polyester Acrylate 2 (amine modified) | | 100 | - | - |
| Polyester Acrylate 3 (amine modified) | | - | 100 | - |
| Polyester Acrylate 4 (amine modified) | | - | - | 100 |
| 2-hydroxy-2-methyl-1-phenylpropanone | 3 | 3 | 3 | 3 |
| Benzophenone | 2 | 2 | 2 | 2 |
| Viscosity at 25°C, cP | 504 | 3350 | 139 | 622 |
| UV energy, mJ/cm$^2$ | 640 | <90 | 230 | 110 |
| Cure speed, fpm | 30 | 200 | 110 | 155 |

Table 9 shows the improved cure response of UA 1 as compared to polyester based urethane acrylates when cured with standard medium pressure mercury lamps (600 watts/inch). The formulations in Table 9 were prepared to have equal resin (urethane acrylate) content. The surface cure energy is the UV energy required to achieve a mar free surface, with lower energy indicating greater reactivity. The polyether based resin, UA 1, has the highest reactivity.

Monomers, or acrylated diluents, can also be modified to contain ether groups. It has been previously shown that ethoxylated diluting acrylates have faster cure speed than the corresponding non-ethoxylated products.[4] Several diluting acrylates were evaluated in this reactivity study: 2-phenoxy ethyl acrylate (2-PEA), oxyethylated phenol acrylate ($P(EO)_2A$), tetraethyleneglycol diacrylate (TTEGDA), ethoxylated trimethylolpropane triacrylate (TMPEOTA), and alkoxylated pentaerythritol tri/tetra-acrylate ($PE(OR)_XTA$). Also in this study, the propoxylated monomers showed “no net benefit in reactivity from the propylene oxide groups”.[4]

**Table 8.** Low Intensity Cure of Urethane Acrylates

| Component | % | | | | | |
|---|---|---|---|---|---|---|
| UA 1 polyether based; 2 functional | 96.2 | | | | | |
| UA 2 polyester based; 2 functional | | 96.2 | | | | |
| UA 3 polyester based; 2 functional | | | 96.2 | | | |
| UA 4 polyether based; 2.3 functional | | | | 96.2 | | |
| UA 5 polyester based; 2 functional | | | | | 96.2 | |
| UA 6 polyether based; 2 functional | | | | | | 96.2 |
| 2-hydroxy-2-methyl-1-phenylpropanone | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 |
| Surface cure; 20 min. exposure<br>0 = no surface tack or marring <1 <2 <3<br><4 = wet surface | 0 | 4 | 2 | 1 | 2 | 3 |

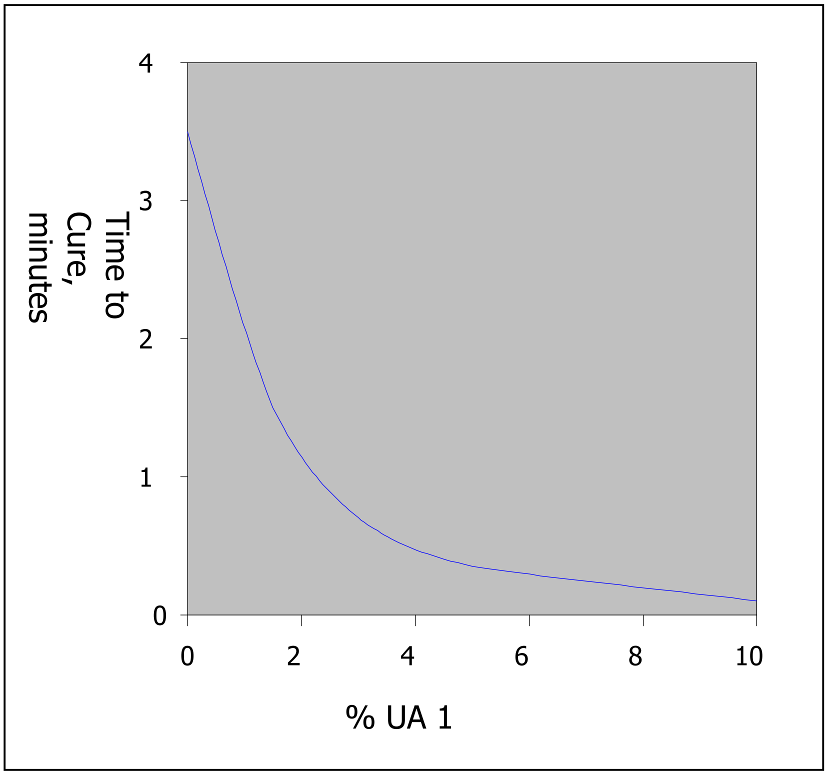


**Figure 5.** Cure Time versus UA 1 Content using Low Intensity UVA Lamp

**Table 9.** Cure Response of Urethane Acrylates with Standard Medium Pressure Mercury Lamps

| Component | Parts by Weight | | |
|---|---|---|---|
| UA 1 polyether based; 2 functional | 35 | | |
| UA 3 polyester based; 2 functional | | 35 | |
| UA 7 polyester based; 3 functional | | | 35 |
| Tripropylene glycol diacrylate (TPGDA) | 40 | 35 | 40 |
| Trimethylolpropane triacrylate (TMPTA) | 25 | 25 | 25 |
| Hexanediol diacrylate (HDDA)* | 0 | 5 | 0 |
| 2-hydroxy-2-methyl-1-phenylpropanone | 4 | 4 | 4 |
| Viscosity at 25°C, cP | 408 | 412 | 1696 |
| Surface cure energy, mJ/cm$^2$ | 495 | 914 | 640 |

*HDDA is present in UA 3, and is shown separate in the Table to demonstrate equal oligomer content

## CONCLUSIONS

In both low and high energy cure applications, acrylates modified with thiols, amines, or ethers can be used to mitigate oxygen inhibition and increase surface reactivity. The surface reactivity increases with the concentration of the modified acrylate. Increasing the functionality or thickness of the coating also improves surface reactivity. Decreasing the distance from the low energy lamp to the substrate aids surface cure.

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