Example LED source

Phoseon RX Fireline 395 LED 8W/cm²
Watercooled with AGT 1.7kW chiller

Information from product brochure and Phoseon website
http://www.phoseon.com/technology/led-uv-wavelength.htm
# Common Photoinitiators

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCPK</td>
<td>1-hydroxy-cyclohexylphenyl ketone</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>HMPP</td>
<td>2-hydroxy-2-methyl-1-phenyl-1-propanone</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>TPO</td>
<td>diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>BAPO</td>
<td>phosphine oxide, phenyl bis(2,4,6-trimethylbenzoyl)</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
**Photoinitiator Spectrum**

Molar absorptivity ($\varepsilon$) relates to absorbance by Beer-Lambert law:

$$A = \varepsilon \, b \, [c]$$

where $A$ is absorbance, $b$ is path length, and $[c]$ is concentration.

- LED absorbs 380-420nm
- HCPK and HMPP do not absorb in this region
- TPO and BAPO both have high molar absorptivity ($\varepsilon$) at 395nm

*Perkin Elmer UV-Vis Spectrometer*
*Cuvettes: 1 cm PMMA Solvent: Methanol*
More Absorptivity = Less Concentration

Conversion
2-phenoxyethyl acrylate cured by 395 LED at low 200 mJ/cm\(^2\) (Intensity 1000mW/cm\(^2\)) as measured by FTIR
0.25 wt% BAPO = 56.8%
0.50 wt% TPO = 61.4%

Higher Molar absorptivity means you need less concentration for equal curing
Photostability is important to monitor

LEDs often emit near visible light range meaning photoinitiator will often absorb and react under visible light therefore **Photostability** is important to include in design.

**Photostability of Photoinitiator**

- **BAPO at 0min under Flourescent light**
- **BAPO at 60min under Flourescent light**
- **TPO at 0min under Flourescent light**
- **TPO at 60min under Flourescent light**

**Reacted Photoinitiator**

At 395nm under GE F15T8 bulbs (fluorescent light) for 60 min

- 0.25 wt% BAPO = 42%
- 0.50 wt% TPO = 15%

Perkin Elmer UV-Vis Spectrometer
Cuvette: 1 cm PMMA
Absorbance in Visible Range = Color

LEDs often emit near or in visible light range meaning photoinitiator will often absorb somewhere in this range which will give the coating color.
Absorbance in Visible Range = Color

DataColor iQC color inclusively in CIE $L^*a^*b^*$ color space (ILL D65-10° deg. Observer).

Color strength depends on molar absorptivity in visible range, concentration, and coating sample thickness
Yellow is important consideration

Remember color depend on coating thickness!

DataColor iQC color inclusively in CIE L*a*b* color space (ILL D65-10° deg. Observer).

Photoinitiator breaks apart (Photobleaches) as it reacts removing color from sample
Optimizing the Concentration

Higher photoinitiator concentration will not get you the proper cure if you do not have enough light.

![Graph showing conversion vs. concentration for different photoinitiators.](image)

20 mil thick films of 2-phenoxyethyl acrylate
Cured by 395 LED at low 200 mJ/cm² (Intensity 1000mW/cm²)
as measured by Nicolet 8700 FTIR Spectrometer - 810nm peak

More light will not help if there is not enough photoinitiator.
Higher concentration of photoinitiator will shield the light and create cure gradients.
Optimizing the Concentration - Surface vs Through Cure

Photolysis products can have effect on through cure due to shielding
Conclusions

- Photoinitiator must absorb where LED emits
- More molar absorptivity means less concentration is needed for equal curing
- Absorbance in visible range (where many LED emit) results in your photoinitiator being colored
- Color depends on molar absorptivity, concentration, thickness and photolysis products
- Absorbance in visible range decreases your photostability
- Proper cure depends on the dose/intensity of light emitted as well as photoinitiator concentration
- Higher photoinitiator concentration causes cure gradients in coatings
- Photolysis products can shield depths in coating decreases through cure
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