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Resin-based Solutions for Improved Surface Cure in LED Applications

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Outline

- I. Background and Theory
- II. Effect of Molecular Structure on Reactivity
- III. Flexo Ink Evaluations:
 - I. Cure Response
 - II. Resin Effects vs Photoinitiator Concentration
- IV. Conclusion
- V. Acknowledgements

Light absorption in solution: Lambert-Beer Law

$$I = I_0 10^{-\varepsilon c l}$$

$$A = \varepsilon c l = \log I_0/I = -\log I/I_0$$

I/I_0 : transmission = T

$$A = -\log T$$

Absorbed light = $I_a = I_0 - I$

$$I_a = I_0 \cdot (1 - 10^{-\varepsilon c l})$$

ε depends on the wavelength: $\varepsilon = \varepsilon(\lambda)$
 $\varepsilon(\lambda)$ is characteristic of the electronic
and optical properties of the chromophore

**Assumptions: no reflection, no scattering,
diluted solution**

I_0 : incident light intensity

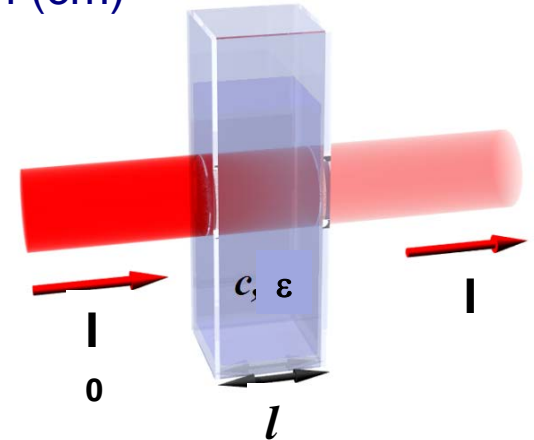
I : transmitted light intensity

A: absorbance of the solution

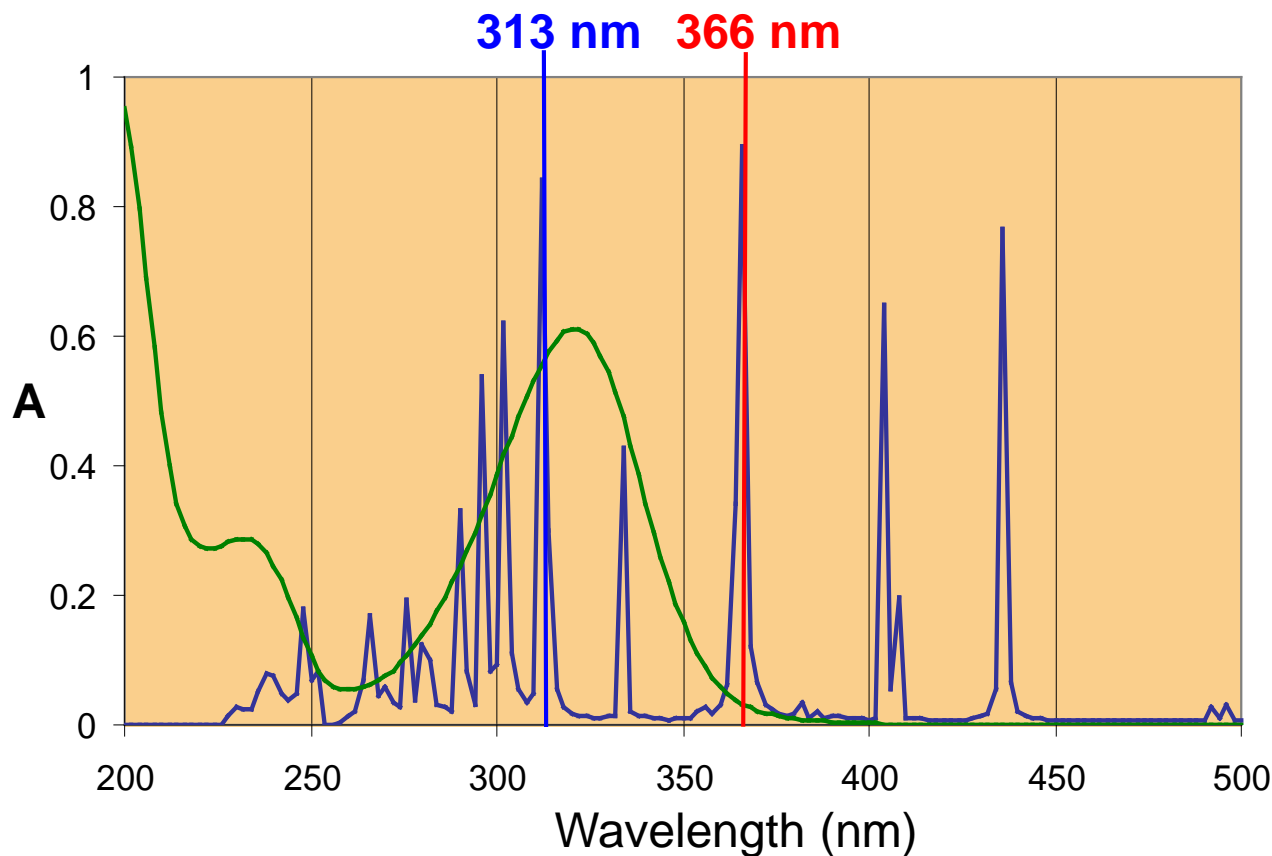
ε : extinction coefficient of the solved
substance ($L \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$)

c : concentration of the solution (mol / L)

l : path length (cm)



Absorption spectrum of red-shifted PI* and overlap with emission of mercury lamp



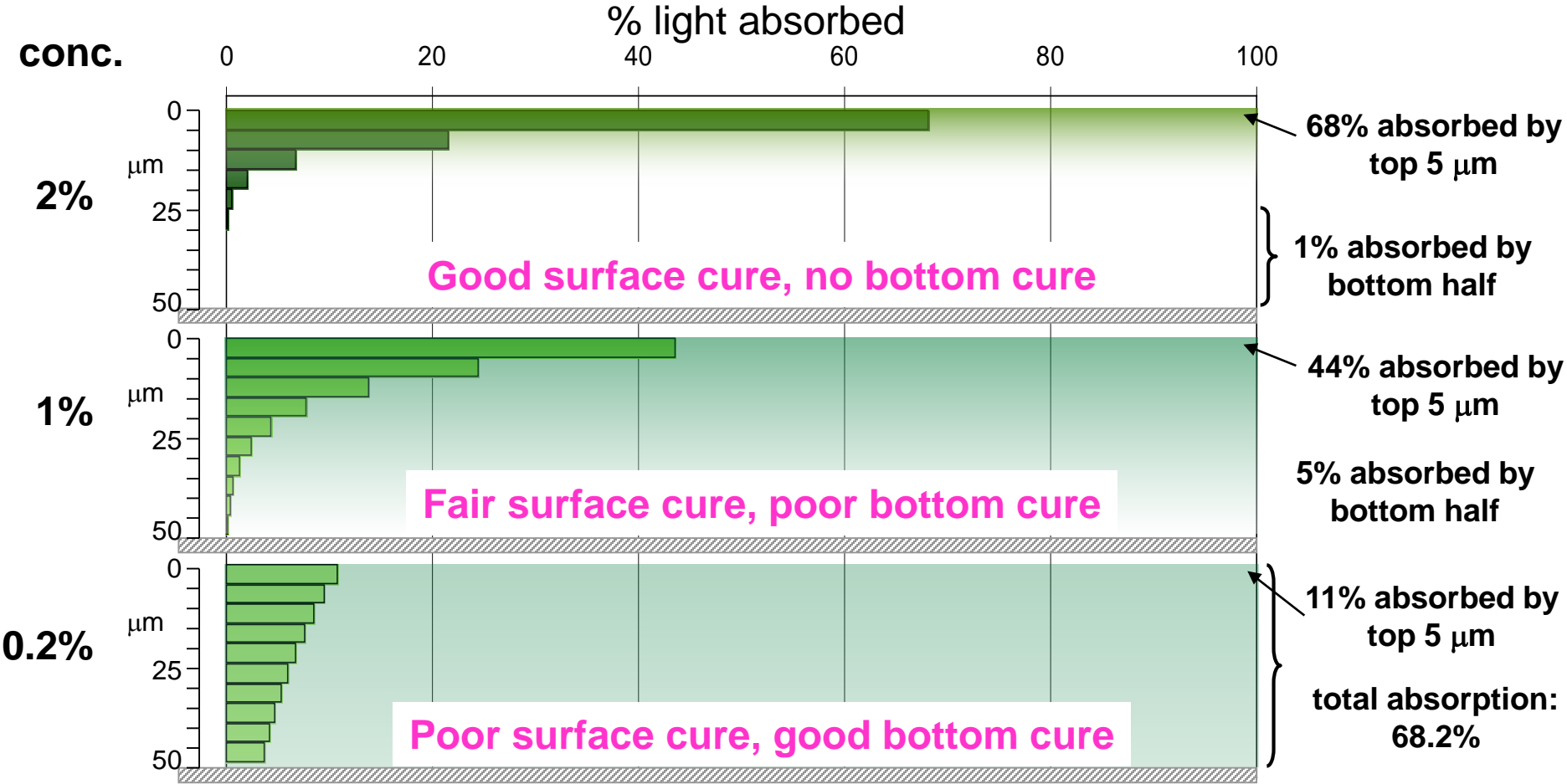
$c = 0.001\% = 2.73 \times 10^{-5} \text{ mol/L}$
 $l = 1 \text{ cm}$

$\epsilon (313\text{nm}) = 19900$

$\epsilon (366\text{nm}) = 1100$

— Emission spectrum of medium pressure Hg lamp (arbitrary units)
* 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1

Effect of concentration on light penetration at single wavelength



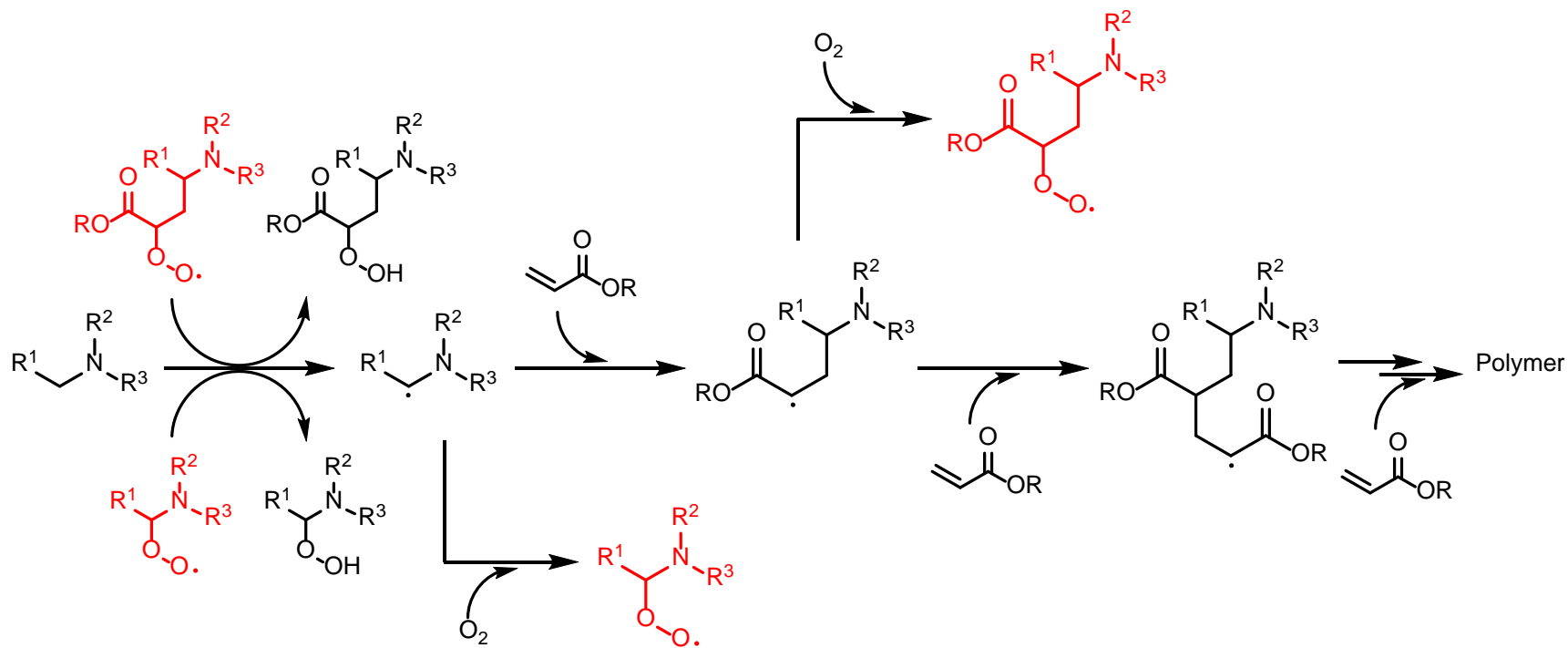
Example: **313 nm** in a 50 μm clear coat

Common issues arising from poor absorption characteristics at longer wavelengths

- Poor surface cure
- Yellowing at high photoinitiator concentrations
- Significant increases in formulation costs with increasing photoinitiator levels
- Reduced formulation latitude

Oxygen Inhibition – Amine-modified Acrylates

Oxygen Depletion by α -Aminoalkyl Radicals



Photocalorimetry Results using Broadband Mercury Source

Expected conversion based on structural factors

$$\% \text{ Conversion} = \Delta H_{\text{exptl}} / \Delta H_{\text{theoretical}}$$

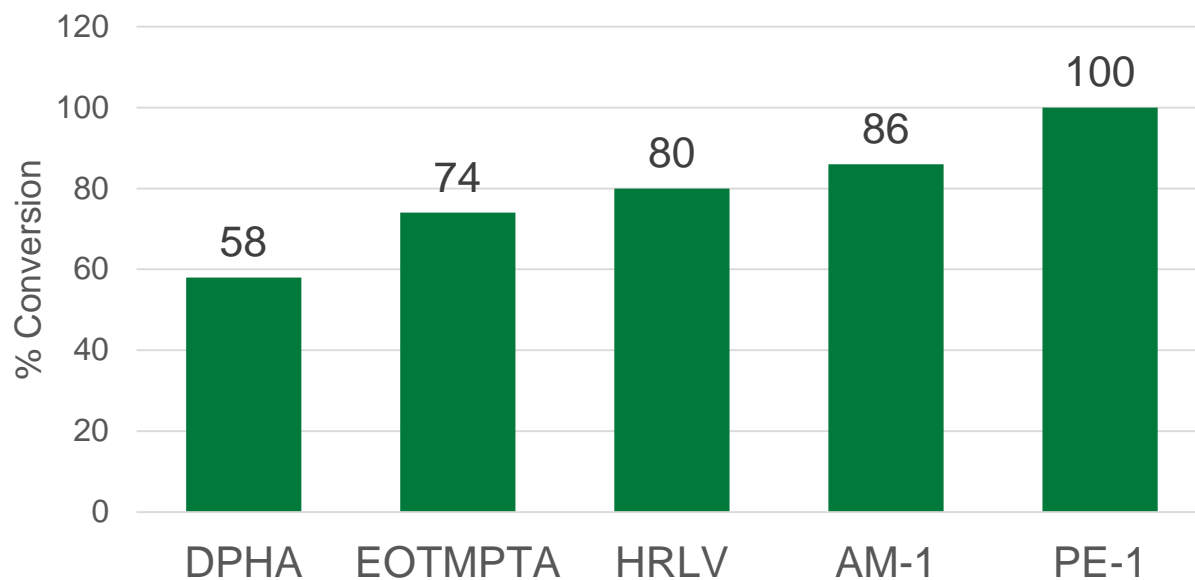
Percent Conversion

least

- DPHA
- EOTMPTA
- HRLV
- AM-1
- PE-1

most

Maximum Percent Double Bond Conversion



Photocalorimetry Results using Broadband Mercury Source

Negative ΔH for amine-functional AM-1 suggests a change in reaction mechanism

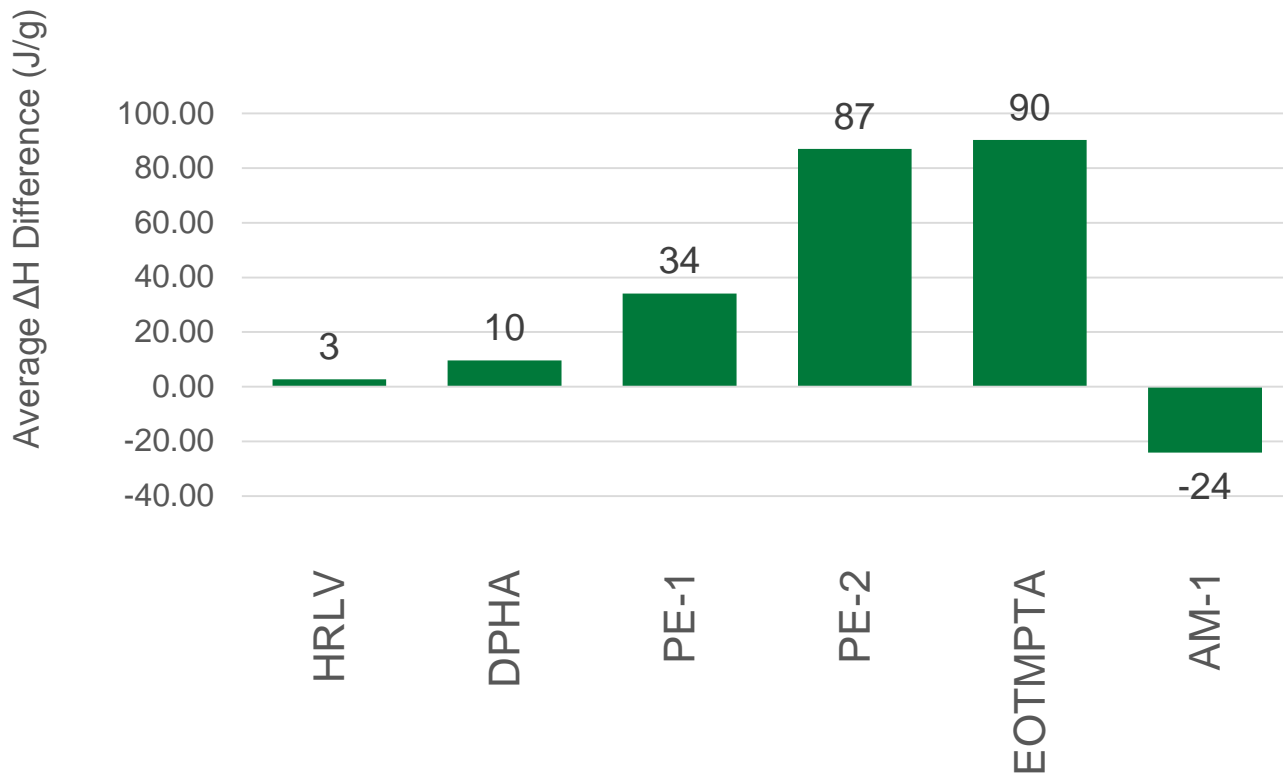
Oxygen Sensitivity

least

- HRLV
- DPHA
- PE-1
- PE-2
- EOTMPTA
- AM-1

most

Average Difference in ΔH between Nitrogen and Air



Flexo Ink Study

390 nm @ 12 W in Air

Pigment Dispersion

Component	%
PE Acrylate	45.1
EOTMPTA	22.3
HMWD	3
Pigment	30

Dispersion Letdown

Component	%
Dispersion	50
Epoxy Acrylate	9-15
Test Resin	9-40
EOTMPTA	16-22
PI	7.5-10.0

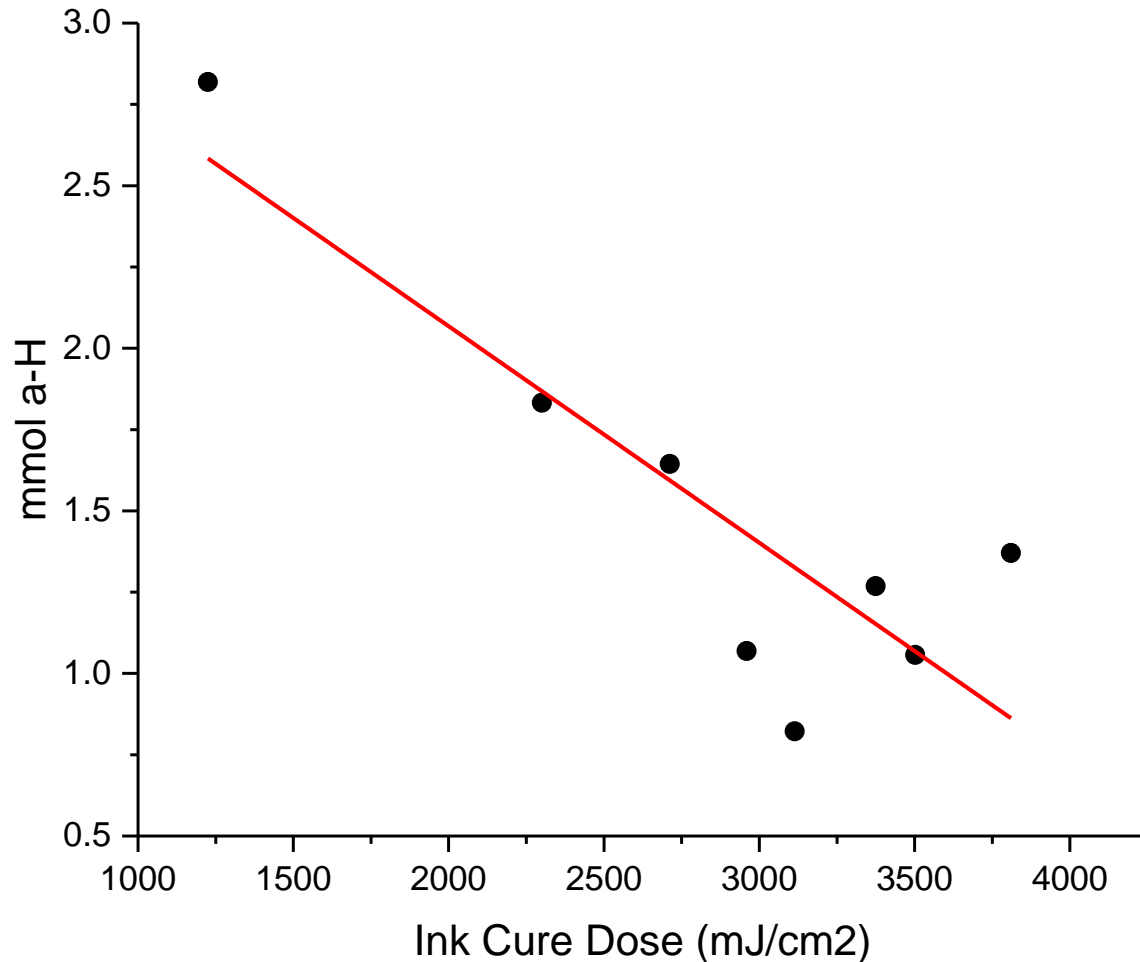
PI - Ethyl (2,4,6 – trimethylbenzoyl) phenyl phosphine



All inks formulated to 750-1000 mPas and applied at 1.8µm

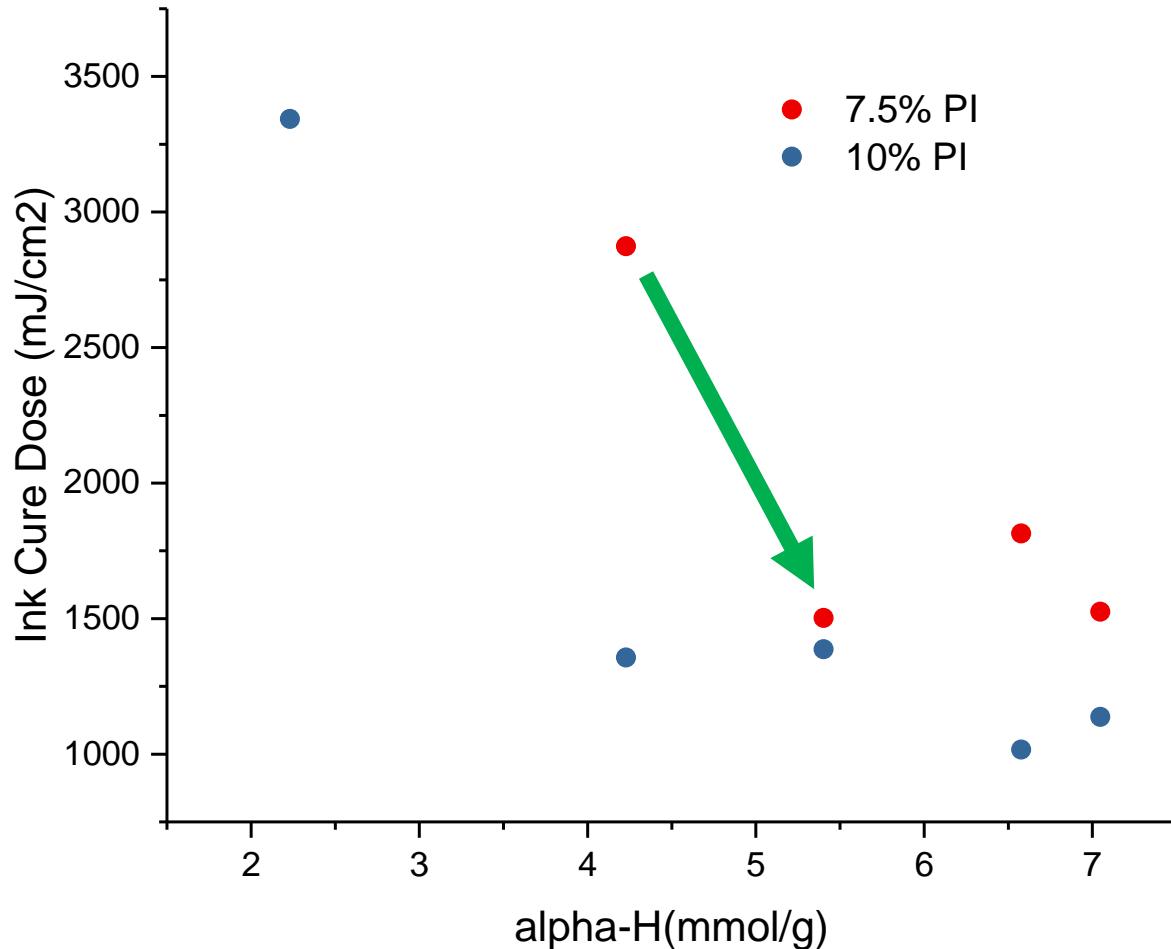
Effect of Resin Modification on Cure Response of Flexo Inks

Clear Correlation Between Level of Abstractable Hydrogens and Cure Response



Use of LED Resin to Enable Lower PI Use in Flexo Formulation

5 mmol/g α -H in ink equivalent to 25% reduction in photoinitiator concentration



Conclusions

- Resin-based approaches can be highly successful in addressing the issues resulting from poor overlap between LED sources and photoinitiator absorption
- Cure performance of UV LED Flexo ink formulations can be significantly improved
- Through appropriate resin structure design and application, Flexo ink photoinitiator concentrations can be significantly reduced

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