Resin-based Solutions for Improved Surface Cure in LED Applications

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2018 RadTech UV+EB, May 2018
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

\[ I = I_0 \cdot 10^{-\varepsilon \cdot c \cdot l} \]

\[ A = \varepsilon \cdot c \cdot l = \log \frac{I_0}{I} = -\log \frac{I}{I_0} \]

\( I/I_0 \): transmission = \( T \)

\( A = -\log T \)

Absorbed light = \( I_a = I_0 - I \)

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

\( \varepsilon \) 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**

\( \varepsilon \): extinction coefficient of the solved substance (L \( \cdot \) mole\(^{-1} \cdot \) 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

\[
\begin{align*}
\epsilon (313\text{nm}) &= 19900 \\
\epsilon (366\text{nm}) &= 1100
\end{align*}
\]

\[c = 0.001\% = 2.73 \times 10^{-5} \text{ mol/L}\]

\[l = 1 \text{ cm}\]

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
Photocalorimetry Results using Broadband Mercury Source

Expected conversion based on structural factors

\% Conversion = \frac{\Delta H_{\text{exptl}}}{\Delta H_{\text{theoretical}}}

Percent Conversion

least

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

most

Maximum Percent Double Bond Conversion

<table>
<thead>
<tr>
<th></th>
<th>DPHA</th>
<th>EOTMPTA</th>
<th>HRLV</th>
<th>AM-1</th>
<th>PE-1</th>
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</thead>
<tbody>
<tr>
<td>% Conversion</td>
<td>58</td>
<td>74</td>
<td>80</td>
<td>86</td>
<td>100</td>
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</table>
Photocalorimetry Results using Broadband Mercury Source

Negative $\Delta H$ 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 $\Delta H$ between Nitrogen and Air

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average $\Delta H$ Difference (J/g)</th>
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<tbody>
<tr>
<td>HRLV</td>
<td>3</td>
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<tr>
<td>DPHA</td>
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<tr>
<td>PE-1</td>
<td>34</td>
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<td>PE-2</td>
<td>87</td>
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<tr>
<td>EOTMPTA</td>
<td>90</td>
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<td>AM-1</td>
<td>-24</td>
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</table>
Flexo Ink Study
390 nm @ 12 W in Air

Pigment Dispersion

<table>
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<tr>
<th>Component</th>
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<tbody>
<tr>
<td>PE Acrylate</td>
<td>45.1</td>
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<tr>
<td>EOTMPTA</td>
<td>22.3</td>
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<tr>
<td>HMWD</td>
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<tr>
<td>Pigment</td>
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Dispersion Letdown

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
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<tbody>
<tr>
<td>Dispersion</td>
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<tr>
<td>Epoxy Acrylate</td>
<td>9-15</td>
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<tr>
<td>Test Resin</td>
<td>9-40</td>
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<tr>
<td>EOTMPTA</td>
<td>16-22</td>
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<tr>
<td>PI</td>
<td>7.5-10.0</td>
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</tbody>
</table>

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

PI - Ethyl (2,4,6 – trimethylbenzoyl) phenyl phosphine
Effect of Resin Modification on Cure Response of Flexo Inks

Clear Correlation Between Level of Abstractable Hydrogens and Cure Response

![Graph showing the correlation between ink cure dose (mJ/cm²) and mmol a-H.](image-url)
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

Graph showing the relationship between Ink Cure Dose (mJ/cm²) and alpha-H (mmol/g) for different PI concentrations.
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.
Acknowledgements

- Dr. Joseph Gianino
- David Chen
- Stephen Godlew
- Suzanne Dettling
- Emma Coury
- Monica Rasmussen
- Andrew Seecharan
- Dr. Jean-Luc Birbaum
- Dr. Devdatt Nagvekar
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