Specialty Photoinitiator and Radiation Curing Material Development

IGM Resins

Susan E Bailey, PhD; Technical Manager- North America

Adhesive and Sealant Council 2017
Atlanta, GA
WHO ARE WE?

- Global manufacturer and supplier of radiation curable raw materials
- Founded in 1999, a dynamic, flexible company experiencing significant growth
- Unique integrated strategy focused solely on supply to the radiation cure industry
- Global manufacturing presence, R&D capabilities and customer technical support.

- R&D labs and Manufacturing for photoinitiators in Italy and China
- R&D labs and Manufacturing for acrylate monomers and oligomers in US and Asia
- Application labs in Italy, France and China.
IGM. WE BRING IT ALL TOGETHER.

**RAW MATERIALS**
- Photoinitiators: Omnopol, Esacure®, Omnirad, Omnicat
- Monomers: Photomer®, Omnimer
- Oligomers: Photomer®, Omnilane
- Additives: Omnistab, Omnivad

**UV RADCUR INKS & COATINGS**

**IGM RAW MATERIALS IN CUSTOMER FORMULATION:**
- PHOTO INITIATORS
- UV MONOMERS
- UV OLIGOMERS
- UV ADDITIVES

**END MARKETS:**
- Graphic Arts
- Wood Coatings
- Metal Coatings
- Plastic Coatings
- Electronics
- Adhesives
- Others
Special thanks to
Elena Bellotti
Marika Morone
Gabriele Norcini
OUTLINE

• Coating Process and Design
  – Materials for radiation curing
  – Equipment wavelength, UV LED

• Photoinitiator Designs
  – Multifunctional photoinitiator
  – Multifunctional co-initiator
  – New development for low yellowing

• Summary
WHAT IS RADIATION CURING?

Absorption of light leads to creation of initiating species

\[
\text{PI} + \text{light} \rightarrow \text{PI}^* \rightarrow R\cdot \text{or} R^+
\]

**Photoinitiator** \(\rightarrow\) **Excited State Processes**

Radiation Curable Formulations:
monomer, oligomer, additives, and photoinitiator (UV cure)

Cured Polymer Network: polymer, incorporated oligomer, additives, and cross-link bonds (some unreacted photoinitiator, monomer)
PHOTO INITIATOR SELECTION VS LAMP TYPE

Omnirad 1173

Compare the Absorption of the PI with the Emitted Energy for the best fit
Omnirad TPO

Compare the Absorption of the PI with the Emitted Energy for the best fit
CONSIDERATIONS FOR PHOTONINITIATORS

- High absorption of incident light
  - wavelength and molar extinction
- Absence of toxicity and odor
- Shelf stability in monomers
- Solubility/Processing
- Color contribution
- Scalable synthesis
Esacure 1001M:
Type I ketosulphone photoinitiator as well as Type II benzophenone sensitizer

![Chemical Structure](image)

**Appearance**: Off white/pink powder

**Purity, %**: ≥94%

**Melting Point, °C**: ≥ 100.0 °C

**Absorption in Methanol**

![Absorption Graph](image)
Alpha and beta cleavage of the ketosulphone generates radicals able to activate a polymerization with acrylic systems. These radicals can also generate more stable products.*

Low odor post exposure


*- J. P. Fouassier, “Photoinitiation, photopolymerization and photocuring”, pg 29.
### PERFORMANCE- Type I

**Through-Cure in m/min**

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Through-Cure in m/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone/ ketosulphone</td>
<td>60</td>
</tr>
<tr>
<td>Morpholino derivative</td>
<td>100</td>
</tr>
<tr>
<td>Difunctional alpha hydroxyketone</td>
<td>61</td>
</tr>
<tr>
<td>Morpholino derivative</td>
<td>57</td>
</tr>
</tbody>
</table>

**THROUGH-CURE**: recorded as the fastest belt speed in which the film resists the thumb-twist test

*Co-initiator Esacure A 198 3%*
Regarding the other photosensitive part of the molecule, a coinitiator is needed to generate reactive radicals to start the polymerization. The mechanism is below:

**CO-INICIATOR - Type II**

**Tertiarty amine synergist- Omnirad EDB**
Ethyl-4-(dimethylamino)benzoate
(off white powder)

**Amine acrylate- Photomer 4250**
Multifunctional acrylate with amine functionality
(pale yellow liquid, 350 cPs at 25 °C)

**Multifunctional amine- Esacure A 198**
Difunctional, high molecular weight amine co-initiator
(off white powder)
EUPIA approved
EFSA guideline – sml 50 ppb
Swiss List – List A – sml 50 ppb
Nestlé exclusion list – Non-listed
## PERFORMANCE – Type II

- Clear (Laboratory Formula) –  
  Fusion equipment Hg lamp 120W/cm 12µm

<table>
<thead>
<tr>
<th>Co-Initiator (3%)</th>
<th>Esacure 1001M (3%)</th>
<th>Omnirad Benzophenone (3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tack-free</td>
<td>Color Stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>YI</td>
</tr>
<tr>
<td>Omnirad EDB</td>
<td>93</td>
<td>3.8</td>
</tr>
<tr>
<td>Esacure A 198</td>
<td>&gt;100</td>
<td>4.0</td>
</tr>
<tr>
<td>Photomer 4250</td>
<td>85</td>
<td>3.1</td>
</tr>
</tbody>
</table>

- **TACK FREE**: fastest belt speed (m/min) in which tack free film were generated
- **YELLOW AND WHITE INDEX**: measured by BYK color Guide 45/0
**PERFORMANCE – UV LED CURE 365nm**

- **UV LED Clear** (Laboratory Formula) – 
  Esacure 1001M (3%)

<table>
<thead>
<tr>
<th>Co-Initiator (3%)</th>
<th>LED 365nm, 12W/cm, 12µm</th>
<th>Tack-free</th>
<th>Color Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>YI</td>
<td>WI</td>
</tr>
<tr>
<td>Omnirad EDB</td>
<td></td>
<td>43</td>
<td>6.25</td>
</tr>
<tr>
<td><strong>Esacure A 198</strong></td>
<td></td>
<td>45</td>
<td>8.54</td>
</tr>
<tr>
<td>Photomer 4250</td>
<td></td>
<td>40</td>
<td>6.06</td>
</tr>
</tbody>
</table>

- **TACK FREE**: fastest belt speed in which tack free film were generated
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Photoinitiator Design for LED and low yellowing
**KETOCOUMARIN**

- **LFC 3644**: Type II photoinitiator based on ketocoumarin moieties
  - Highly efficient with low oxygen sensitivity

![Chemical Structure of KETOCOUMARIN](image)

**Appearance**
- Slightly yellow powder

**Purity, %**
- ≥95%

**Melting point**
- 68 °C

**Solubility, 20 °C**
- >20% HDDA, IBOA, TMPTA, TPGDA
- >10% TMPEOTA
## PERFORMANCE – UV LED CURE 365nm

- UV LED Clear (Laboratory Formula) – Photoinitiator (3%) + Esacure A198 (3%)

<table>
<thead>
<tr>
<th></th>
<th>LED 365nm, 12W/cm, 6µm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tack-free (m/min)</td>
<td>Color Stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>YI</td>
</tr>
<tr>
<td>LFC 3644</td>
<td>70</td>
<td>10.8</td>
</tr>
<tr>
<td>Omnirad ITX *</td>
<td>90</td>
<td>10.8</td>
</tr>
</tbody>
</table>

• **TACK FREE**: fastest belt speed in which tack free film were generated
• **YELLOW AND WHITE INDEX**: measured by BYK color Guide 45/0

*ITX=2-Isopropyl thioxanthone, Type II*
PERFORMANCE – UV LED CURE 365nm

- UV LED Clear (Laboratory Formula) – Photoinitiator (3%) + Photomer 4250 (3%)

<table>
<thead>
<tr>
<th></th>
<th>LED 365nm, 12W/cm , 6μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tack-free (m/min)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>LFC 3644</td>
<td>49</td>
</tr>
<tr>
<td>Omnirad ITX</td>
<td>60</td>
</tr>
</tbody>
</table>

**TACK FREE**: fastest belt speed in which tack free film were generated

**YELLOW AND WHITE INDEX**: measured by BYK color Guide 45/0
**PERFORMANCE – UV LED CURE 395nm**

- UV LED Clear (Laboratory Formula) – Photoinitiator (3%) + Co-Initiator (3%)

<table>
<thead>
<tr>
<th></th>
<th>LED 395nm, 16W/cm , 6µm</th>
<th>Tack-free (m/min)</th>
<th>Color Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>YI</td>
</tr>
<tr>
<td>LFC 3644 + Esacure A 198</td>
<td>85</td>
<td>12.2</td>
<td>49.4</td>
</tr>
<tr>
<td>LFC 3644 + Photomer 4250</td>
<td>42</td>
<td>6.1</td>
<td>63.4</td>
</tr>
<tr>
<td>Omnirad TPO **</td>
<td>45</td>
<td>5.5</td>
<td>65.3</td>
</tr>
</tbody>
</table>

• **TACK FREE**: fastest belt speed in which tack free film were generated
• **YELLOW AND WHITE INDEX**: measured by BYK color Guide 45/0

**TPO= 2,4,6-Trimethylbenzoyl-diphenyl phosphine oxide, Type I, no co-initiator, average of multiple runs**
**YELLOWING**

**b* Value Over time**

![Bar Chart]

- **Conditions:** *UV LED Clear Laboratory Formula*
  - Aliphatic 9-functional urethane acrylate/PETIA 1:1, 6μm thickness
  - 1 pass at 50 m/min, LED at 395 nm (8 W/cm²)
  - PI 3% w/w, Co-initiator 3% w/w, when needed
Conditions:

*UV LED Clear Laboratory Formula*

Aliphatic 9-functional urethane acrylate/PETIA 1:1, 6µm thickness

1 pass at 50 m/min, LED at 395 nm (8 W/cm²)

PI 3% w/w, Co-initiator 3% w/w, when needed
SUMMARY

• Photoinitiator design includes factors of efficiency and structure/property relationships

• Design Strategies for LED
  – Multifunctional PI and Co-Initiator (Esacure 1001M + Esacure A198)
  – Low Yellowing (LFC 3644, experimental ketocoumarin system)

• Outlook
  – Development focus on high efficiency photoinitiator systems with design towards manufacturability and final product requirements
Thank You!

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