On Overview of Cationic Curing
Application areas
Advantages of Cationic Curing

• No oxygen inhibition
• Very low shrinkage
• Excellent adhesion
• Dark cure reaction gives high conversion
• Improved coating properties
  • Increased chemical resistance, hardness etc
## Formulation

<table>
<thead>
<tr>
<th>Trade names</th>
<th>Component Function</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>UviCure</td>
<td>Cycloaliphatic Epoxide Main Resin</td>
<td>S105, S128</td>
</tr>
<tr>
<td>UviCure</td>
<td>Oxetane Reactive Diluent, Property Modifier</td>
<td>S130, S140, S150, S160, S170</td>
</tr>
<tr>
<td>SpeedCure</td>
<td>Onium Salt Photoinitiator</td>
<td>992, 976, 938, 937, 939</td>
</tr>
</tbody>
</table>
Resins: Formulation Base

**UviCure S105**
- Principal resin used in industry
- Difunctional cycloaliphatic epoxide
- Low shrinkage (ca. 2-4%)
- Viscosity (ca. 300 mPa.s @25° C)
- Hard polymers
- High crosslink density
- High Tg

**UviCure S128**
- Difunctional adipate based cycloaliphatic epoxide
- Low shrinkage (ca. 2-4%)
- Viscosity (ca. 600 mPa.s @25° C)
- Increased flexibility over UviCure S105
Resins: Reactive Diluents

- Hydroxy functional oxetane
- Low shrinkage
- Low viscosity (ca. 8 mPa.s @25° C)
- Increased flexibility
- Increased adhesion
- High cure speeds

- Aromatic oxetane
- Low shrinkage
- Low viscosity (ca. 8 mPa.s @25° C)
- Increased flexibility over UviCure S130
- Increased adhesion.
Resins: Property Modifiers

**UviCure S150**
- Aromatic difunctional oxetane
- Low shrinkage
- Viscosity [ca. 150-220 mPa.s (25°C)]
- Toughness, flexibility, thermal stability.
- Increased adhesion

![Chemical structure of S150](image)

**UviCure S160**
- Aromatic difunctional oxetane
- Low shrinkage
- Viscosity [ca. 240-300 mPa.s (@50°C)]
- Hardness, chemical resistance, thermal stability
- Increased adhesion

![Chemical structure of S160](image)
Resins Hybrid Crosslinker

- Hybrid Oxetane/methacrylate functionality
- Reduces phase separation in hybrid system
- Adhesion promoter in free radical system
Cationic Photoinitiators

• Generally sulfonium or iodonium salts.
• On exposure to UV light energy produce a strong Brønsted acid.
• The acid initiates the polymerization reactions of epoxy resins, producing a crosslinked film.
• The generated acid remains active and able to initiate polymerisation after UV exposure, known as “dark cure”.

Leading the way

LAMBSON
The Effect of Anion Nucleophilicity

- Reactivity depends on the low nucleophilicity of the anion.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_4^-$</td>
<td>$&lt;$</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>$&lt;$</td>
</tr>
<tr>
<td>AsF$_6^-$</td>
<td>$&lt;$</td>
</tr>
<tr>
<td>SbF$_6^-$</td>
<td>$&lt;$</td>
</tr>
<tr>
<td>$\ldots\ldots$B(C$_6$F$_5$)$_4^-$</td>
<td></td>
</tr>
</tbody>
</table>

- Hexafluoroantimonate is a very reactive anion.
- Arsenic is toxic and so use is not widespread.
- Hexafluorophosphate is the most common anion used.
- Tetrakis pentafluorophenyl borate anion is extremely fast in silicone epoxys, can be effective in non-silicone media but at a high cost.
Sensitizers in Cationics

- Sensitizer is consumed by the sensitization reaction with the onium salt.
- Very efficient with iodonium salts but less effective with sulfonium salts.
- Typical concentrations 3-4% onium salt, 1% acetophenone, 0.5-1% thioxanthone.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Sulfonium Salts</th>
<th>Iodonium Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thioxanthones</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Anthracenes</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Benzophenones</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Acetophenones</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Titanocene</td>
<td>✗</td>
<td>✓</td>
</tr>
</tbody>
</table>
**Sulfonium Cationic Photoinitiators**

- **SpeedCure 992**
  - Sulfonium hexafluorophosphate salt
  - High reactivity
  - Produces long lived acid species
  - Low yellowing
  - Expensive to sensitize.

- **SpeedCure 976**
  - Sulfonium hexafluoroantimonate salt
  - Very high reactivity
  - Produces long lived acid species
  - Low yellowing
  - Expensive to sensitize.
Iodonium Cationic Photoinitiators

- Iodonium hexafluoroantimonate salt
- Benzene free
- Good reactivity
- 50% active in glycidyl ether reactive diluent.
- Low yellowing
- Cost efficient sensitization

- Iodonium hexafluorophosphate salt
- Benzene free
- Good reactivity
- Produces long lived acid species
- Low yellowing
- Cost efficient sensitization
Iodonium Cationic Photoinitiators

- Iodonium tetrakis(pentafluorophenyl) borate salt
- Benzene free
- Very high reactivity in silicone epoxy systems
- Produces long lived acid species
- Low yellowing
Long Wavelength sensitizers

Thioxanthenones

- Able to activate iodonium cationic photoinitiators to LED light (365 – 405nm)
- Charge transfer mechanism
- Will give some yellowing
Free Radical Promoted Cationic Polymerisation

- Radicals give redox decomposition of onium salt to produce acid.
- Norrish Type I photoinitiators SpeedCure 73, 84, 2959, BKL, TPO, TPO-L, BPO etc...

**Mechanism**

Radical Source → UV → $R^*$

$R^*$ + Ph2I⁺ X⁻ → $R^+$ + Ph⁻ + PhI⁻
Lambson Type I Cationic Sensitizers

α Hydroxy Ketones

![α Hydroxy Ketone 1](image1)

![α Hydroxy Ketone 2](image2)

![α Hydroxy Ketone 3](image3)

Phosphine Oxides

![Phosphine Oxide 1](image4)

![Phosphine Oxide 2](image5)

![Phosphine Oxide 3](image6)
• Water acts as a chain transfer agent, reducing coating physical properties by promoting new chain growth and reducing average MW.

• Mostly surface cure phenomenon.

• Cure speed at 50% humidity is half that at 30% humidity.

• Reduce humidity levels at point of cure to maintain physical properties e.g. hot air blowers
After activation of the cationic photoinitiator the polymerisation reactions are thermally driven.

Thermal post curing at will in give very high conversions and resistant coatings.

Rapid curing speeds reached by increasing temperature using hot air blowers or IR lamps.
With offices and facilities in England, Europe, India, China, Japan and America we offer a truly Global Supply Network.

Thank you for your attention
Questions?