Introduction to Radiation Curing Chemistry And Technology

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• The European Energy Curing Industry
  – Global and European market overview and segmentation
  – Industrial and graphic arts highlights

• The basics of UV & EB Curing Technology
  – Introduction
  – What is radiation curing?
  – Radiation curing chemistry
  – How to prepare UV/EB curable formulations?
  – Photo initiators
  – UV/EB curing equipment
  – Applications
  – Metal surface tests and requirements

• Conclusion
The European Energy Curing Industry

- Global Market and Breakdown into Applications
- European Market Segmentation and Applications
- The European Energy Curing Industry
  - Industrial Coatings
  - Graphic Arts
- Conclusion
Global market and breakdown into applications

Global UV/EB resin market 2008: 296 K MT*

*Not including UV unsaturated polyesters, UV silicones for release applications, UV PSA’s and photoinitiators.

Asia is by far the major market, with 134,000 MT and growing faster than rest of the world. Only Japan accounts for 57,500 MT.

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Global market and breakdown into applications

Wood & paper is the biggest segment in volume worldwide.
Industrial Coatings including optoelectronics are currently largest outlet for Energy curing in Europe. North America is governed by Graphic Arts while Asian region is leading in Plastics & Electronics.
European Market Segmentation and applications

European UV/EB resin market 2008: 94 K MT

“Others” include adhesives, concrete, composites, dental, non-UV...

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European Market Segmentation and applications

European metal coating market 2008: 1230 K MT

Of which is solvent borne coatings: 858 K mT
The European Energy Curing Industry

Formulation 2008: 130 K MT

- UK / Ireland: 15%
- France: 5%
- Spain / Italy: 13%
- Scandinavia: 11%
- Benelux: 11%
- DACH regions: 38%
- Rest of Europe: 7%

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Industrial Coatings Highlights

WOOD & PAPER
- Furniture (household, flatstock, cabinets)
- Wood Flooring (parquet)
- Outdoor Joinery
- Laminates

PLASTICS / OPTO ELECTR 15 k MT/y
- Specialty applications (opto electronics, automotive, cosmetics, etc.)

METAL & OTHERS 5 k MT/y
- Tube and Piping
- Coil / Can
- Auto Refinish
- Adhesives/dental/ non UV...

Wood Coatings Remains largest segment
Plastics is the Fastest Growing Segment
Metal Coating Still Emerging

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Industrial Coatings Trends 2008-2012

Growth

- Geographical expansion to Eastern Europe (Russia, Poland, Slovenia, …) and Turkey.
- Water-based UV systems expected to grow 3X faster than conventional Radcure.

Technology Shifts

- Waterborne UV (WB-UV) gaining market acceptance in emerging applications, plastics niches and pigmented/high gloss wooden furniture (spray application).
- Consumer electronics continues to migrate over to AP. However, Germany continues to play a leading role in the development and promotion of photovoltaics considering UV coating technology to reduce production costs.

Regulatory

- REACH
- VOC regulations

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Industrial Coatings Trends 2008-2012

Emerging Applications

- **Field Applied coatings for Industrial Floors**
  - Value proposition: productivity
  - Enabler: lamp technology

- **LED curing**
  - LED cured clear coat for automotive
  - LED for DVD bonding
  - ...

- **Automotive Coatings:**
  - Complex truck axles
  - Auto refinish
  - Base coat

- **Coil coating**

...
The European Energy Curing Industry
Graphic Arts Highlights

60 k MT formulation

PRINTING INKS 29 k MT/y
- Lithographic Inks
- Flexographic Inks
- Letterpress Inks
- Screen printing Inks
- Digital Inks

OVERPRINT VARNISHES 31 k MT/y
- High gloss OPV’s
- OPV’s for packaging

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Conclusion

• The European region continues to be an active promoter of UV technology in new applications like metal coatings, electrical sleeves, fiberglass impregnation, abrasives, solar cells, and car refinishing.

• Regulatory environment is creating both challenges and opportunities for UV industry players (REACH, 2010 VOC regulations).

• Sustainability / environmentally friendly products gaining greater visibility.

• More than ever, Europe has to focus on innovation and differentiation accelerated by technology substitution and new VOC legislations to compete effectively in an increasingly global environment.
The basics of UV & EB Curing Technology

- Radiation curing, a long history
- What is radiation curing?
- Radiation curing chemistry
- How to prepare UV/EB curable formulations?
- Photo initiators
- UV/EB curing equipment
- Applications
- Metal surface tests and requirements
Radiation Curing, a long history...

- First patent 1946 to Inmont: UV cured ink based on UPE resins
- First commercial application on UV screen ink early 1960’s.
- 1990’s – numerous industrial applications
  - Inks and coatings
  - Wood coatings
  - Metal, plastic coatings
  - Electronics
- Today UV-technology has a widespread use in many applications all around us.
The basics of UV & EB Curing Technology

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What is radiation curing?
Radiation curing versus conventional drying

- Inks and coatings are cured, not dried as usually in solvent or waterborne systems. The binders are polymerized and form an insoluble 3-dimensional network.

- The polymerization is triggered by
  - UV-light (UV) or
  - Accelerated electrons (EB)

- The transformation from liquid to solid is very fast (<1 second).
What is radiation curing?
What is Ultra-Violet light?

UV light is part of the Electromagnetic Spectrum!

- Gamma-rays
- X-rays
- Optical area
- Microwaves
- Radio-waves

- Ultraviolet Radiation
- Visible Light
- Infrared Radiation

- UV-C: 200nm - 280nm
- UV-B: 280nm - 320nm
- UV-A: 320nm - 400nm

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What is radiation curing?

Drying versus Curing

**Physical drying**
- Solvent evaporation
- Physical drying
- No crosslinking

**Chemical curing**
- No solvent evaporation
- Chemical polymerisation
- Crosslinking produces a rigid network

Heat → Chemical curing

UV - light → Physical drying

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What is radiation curing?
Some Advantages

✓ Low energy requirements
✓ Immediate drying
  – in-line finishing
  – immediate handling
✓ Rapid throughput / high productivity
✓ Less space requirements
✓ High and low gloss
✓ Low VOCs content
✓ UV technology can easily fit into an existing production line
✓ Unique performance
✓ Ability to coat heat-sensitive substrates
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Radiation curing chemistry

**Free Radical (UV or EB)**
- UV – light or Electro Beam
- Production of free radicals from photoinitiator or EB gun
- Polymerisation of C=C from acrylates, methacrylates, vinyl ethers

**Cationic (UV)**
- UV – light
- Production of superacids from cationic photoinitiator
- Ring opening of epoxy group, cyclic ethers

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Radiation curing chemistry
UV curing versus EB curing – Mechanism

Initiation Step

**UV curing**

Photo-initiator $\xrightarrow{h\nu}$ In· In·

**EB curing**

Formulation Compound $\xrightarrow{e^-}$ In·

Propagation (Chain transfer not shown)

Termination Step(s)

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Radiation curing chemistry
Radical Curing – Reactive Species

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Radiation curing chemistry
Radical Curing – Acrylic Acid

Crude oil → Destillation → Naphtha
Cracken → Oxidation → Propene

Acrylic acid

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- Metal surface tests and requirements
Formulation
Radiation curable versus conventional paints

- **Acrylated Oligomer(s)**
  basic coating properties

- **Monofunctional Monomer(s)**
  viscosity reduction, flexibility

- **Multifunctional Monomer(s)**
  viscosity reduction, crosslinking

- **Additives**
  performance fine tuning, pigments

- **(Photoinitiator Package)**
  radical generation

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**Oligomers**
**Solvents**
**Additives**

UV or EB (no PI)

Heat

Cured Coating

Dried Coating

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Formulation

• All Components influence final properties of the coating/paint:
  
  Acrylated Oligomer: Type, molecular weight, functionality
  Acrylated Monomer: Reactive diluent, functionality
  Other Components: Additives, pigments
  Photoinitiator: Type, concentration

• Weight per Acrylate Double Bond plays role in final properties.
<table>
<thead>
<tr>
<th>Formulation</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Acrylates</td>
<td>from ± flexible to very hard, solvent resistant, fast cure</td>
</tr>
<tr>
<td>Aliphatic Urethane Acrylates</td>
<td>very flexible to very hard tough, non-yellowing</td>
</tr>
<tr>
<td>Aromatic Urethane Acrylates</td>
<td>relatively flexible to very hard</td>
</tr>
<tr>
<td>Polyester/polyether Acrylates</td>
<td>low viscous to very high viscous, pigment wetting, adhesion</td>
</tr>
<tr>
<td>Acrylated Amines</td>
<td>increase cure speed</td>
</tr>
<tr>
<td>Acrylated Acrylates</td>
<td>improve adhesion</td>
</tr>
</tbody>
</table>
Formulation
Acrylated Oligomers – Epoxy acrylates

• Most important group are aromatic 2-functional epoxy acrylates

Bisphenol A diglycidyl ether diacrylate

\[
\text{Acrylate} + \text{Bisphenol A diacrylate} \rightarrow \text{Product}
\]

• advantage: fast curing, good hardness, excellent chemical resistance, high gloss
• disadvantage: high viscosity, yellowing performance, poor outdoor performance (except aliphatic epoxy acrylates)
Formulation
Acrylated Oligomers – Urethane acrylates - typical structure

Aliphatic Urethane Acrylate

Aromatic Urethane Acrylate

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Formulation
Acrylated Oligomers – Urethane acrylates

• Two major classes
  - aliphatic urethane acrylates
  - aromatic urethane acrylates

• Wide range of performance depending on chemical structure
  
  From: Soft  To: Hard
  Flexible, high elongation  Stiff, low elongation
  Yellowing  Non-yellowing
  Moderate cure speed  High cure speed
  Low viscosity  High viscosity

• Chemistry is very versatile
Formulation
Acrylated Oligomers – Polyester acrylates - typical structure

CH₂=CH-C-O-R-O-C-R'-O-C-CH=CH₂

polyester di-acrylate

4 CH₂=CH-COOH + Polyester (OH) → Polyester (ester) + 4 H₂O

polyester tetra-acrylate
Formulation
Acrylated Oligomers – Polyester acrylates

- Wide range of viscosities, functionalities and backbone structures
- Properties are variable

Key properties:
- Pigment wetting
- Water balance for lithography
- Relatively low viscosity compared to other oligomers
- Low to high shrinkage
- Good adhesion when low shrinkage
- Moderate to very fast cure response
- 2 to 6 acrylic functions
Formulation
Acrylated Oligomers – Acrylated amines

- Co-initiators (amine synergist) for type II photoinitiators
- Free radical regenerators for surface cure
- Increase cure speed, reduce oxygen inhibition
- No blooming or discoloration of sensitive pigments
- Avoid use with acidic materials

Addition reaction of secondary amine
→ Slight viscosity increase of the acrylate

Addition reaction of primary amine
→ Significant viscosity increase of the acrylate
Formulation
Acrylated Oligomers – Acrylated acrylics

- Adhesion on several substrates
- Low shrinkage
- Low reactivity

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<table>
<thead>
<tr>
<th>Resin</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>Pigment wetting, Wide viscosity range</td>
</tr>
<tr>
<td>Epoxy</td>
<td>High cure speed, Hard and resistant</td>
</tr>
<tr>
<td>Urethane</td>
<td>From hard and tough to very flexible, Aliphatic: non yellowing, outdoor</td>
</tr>
<tr>
<td>Amino</td>
<td>High cure speed (O₂-inhibition)</td>
</tr>
</tbody>
</table>

- Mixture of resins is often used
- Selection based on:
  - chemical, mechanical, curing speed and outdoor properties
  - viscosity, thickness, substrate, price, ...
Formulation
Acrylated Oligomers designed for metal coatings

Typical properties of Urethane, Epoxy and Polyester Acrylates for metal coatings

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Formulation
Acrylated Monomer Functionality

Monofunctional

Difunctional

Trifunctional

Tetrafunctional

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### Formulation

**Acrylated Monomer Selection**

<table>
<thead>
<tr>
<th>Funct.</th>
<th>Diluting power</th>
<th>Reactivity</th>
<th>Flexibility</th>
<th>Shrinkage</th>
<th>Solvent Resist.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td><img src="image1.png" alt="Upward Arrow" /></td>
<td><img src="image2.png" alt="Downward Arrow" /></td>
<td><img src="image1.png" alt="Upward Arrow" /></td>
<td><img src="image2.png" alt="Downward Arrow" /></td>
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<td>Di</td>
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<td>Tetra</td>
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Formulation
Additives

- Pigments
- Dispersing agents
- Stabilizer

- Matting agents: Acematt, Syloid, Gasil....
- Fillers: Talc, Calcium carbonate...

- Defoamers
- Rheology modifier
- Wetting agents
- Flow, levelling agents
- Slip agents
- Adhesion promoter
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Formulation
Photoinitiators – Free radical polymerisation

- Absorb UV light
- Generate free radicals
- Initiate radical polymerisation
- Photo-cleavage or photo-abstraction mechanism

Different types, selection based on:
- UV equipment available
- Weatherability
- Surface cure vs. in depth cure
- Liquid vs. solid (handling)
- Film thickness
- Cost
- Pigmentation level

- Oxygen inhibition
Formulation
Photoinitiators – UV spectrum Hg lamp

“Output spectrum UV lamp should match the absorbance spectrum of the PI”

Absorbance of 4 different photo initiators
Formulation
Photoinitiators versus Radical Initiators

\[ \Delta T : \text{from RT to } >100^\circ C, \text{ depending on R-group, for a 10 hours half time} \]

**ΔT**: immediate generation of radicals, which initiate the polymerisation reaction

- **UV/EB curable paint**: "cure on demand"
- **Heat curable paint**: months at RT, in dark

**Chemical Structures**

- Photoinitiator: \( \text{CH}_3\text{N} = \text{N} \text{CH}_3 \)
- Radical Initiator: \( \text{CH}_3\text{N} \)
Formulation
Photoinitiators – oxygen inhibition

Oxygen Quenching Reaction

\[ [PI]^\cdot + O_2 \rightarrow [PI]\ + O_2^\cdot \]

Oxygen Scavenging Reaction

\[ R^\cdot + O_2 \rightarrow R-O-O^\cdot \]

Low reactivity radical
Formulation
Photoinitiators – oxygen inhibition

- Oxygen reduces the efficiency of photoinitiators
- Oxygen reacts much faster with radicals than acrylates
- Remove oxygen by
  - using amino acrylates: consume oxygen
  - working under N₂-atmosphere: higher cure speed and/or lower photoinitiator level
  - curing through a transparent laminate
Formulation Summary
How to prepare UV/EB curable formulations?

- **Acrylated Oligomer(s)**
  basic coating properties

- **Monofunctional Monomer(s)**
  viscosity reduction, flexibility

- **Multifunctional Monomer(s)**
  viscosity reduction, crosslinking

- **(Photoinitiator Package)**
  radical generation

- **Additives**
  performance fine tuning, pigments

Cured Coating

UV or EB (no PI)

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## Formulation Summary
Guide formulation coating direct on metal

<table>
<thead>
<tr>
<th>Components</th>
<th>Examples</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Oligomer</td>
<td>Flexible oligomers</td>
<td>50-60%</td>
</tr>
<tr>
<td>Monomers</td>
<td>Monofunctional or flexible difunctional</td>
<td>10-20%</td>
</tr>
<tr>
<td>Additives</td>
<td>Adhesion promoters, fillers, pigments</td>
<td>10-15%</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>-</td>
<td>3-8%</td>
</tr>
</tbody>
</table>
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UV Equipment
UV lamp types

- **Arc type**
  A plasma (inert gas + Hg + additive) is created by an electric arc between two electrodes and UV-light is emitted.

- **Micro-wave type**
  Micro-waves are sent through a quartz tube and generate a plasma (inert gas + Hg + additive) which emits UV-light.

- **Excimer**

- **UV LED**

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EB Equipment

Electron beam (EB) curing

- EB machines generate very high speed electrons
  - Cathode produce electrons.
  - Voltage differential accelerates electrons.
  - Direct interaction of high energy electrons with resins creates radicals
  - 80 – 300 keV, penetration to 0.4 mm

- Same resins for UV- and EB-curing
  - Inert atmosphere
  - No photoinitiators

- Thicker, pigmented coatings can be cured with EB in comparison to UV
  - High capital investment
  - Lower energy EB guns at lower cost
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Some applications

Graphics - Inks

Plastics

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Metal Surface Requirements and tests

- Crosshatch
- T-Bend Erichsen Test
- Pendulum Hardness

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Metal Surface Requirements and tests

Xenon test

Outdoor resistance

Corrosion Resistance

Pigment compatibility

Salt Spray test

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• Conclusion
• Metal coatings represent only a very small part of current UV/EB market.
• Radiation curing technology has several advantages over conventional coating technologies for metal.
• Radiation curing chemistry allows tailor made solutions for metal.

• Guidance for resin selection and formulation, please contact us or visit the Radtech website at www.radtech-europe.com