Formulation Developments in UV/EB curable inks and coatings

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Abstract:

• The basics of raw materials and formulations will be discussed. This includes monomers, oligomers, photoinitiators, pigments and additives that are commonly used by formulators. The challenges of converting on wide web flexible packaging films using UV/EB chemistries will be addressed as well as new limitations on materials for food packaging and industrial processes.
Definition of Energy Curable

The use of ultraviolet (UV) light or electron beam (EB) energy to cause polymerization.
## Electromagnetic spectrum

<table>
<thead>
<tr>
<th>Energy</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiowaves</td>
<td>100,000 nm+</td>
</tr>
<tr>
<td>Microwaves</td>
<td>10,000-100,000</td>
</tr>
<tr>
<td>Infrared</td>
<td>800-10,000</td>
</tr>
<tr>
<td>Visible Light</td>
<td>400-800</td>
</tr>
<tr>
<td>UV Light</td>
<td>200-400</td>
</tr>
<tr>
<td>Deep UV</td>
<td>100-200</td>
</tr>
<tr>
<td>Gamma Ray</td>
<td>&lt;100</td>
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</table>
The Ultraviolet Spectrum Definitions

UV-A 315-400 nm
accounts for ~95% of UV radiation reaching Earth's surface. It can penetrate into the deeper layers of the skin and is responsible for the immediate tanning effect.

UV-B 280-315 nm
primarily responsible for sunburn, aging of the skin, and the development of skin cancer.

UV-C 200-280 nm
the most damaging type of UV radiation. Completely filtered by the atmosphere and does not reach the earth's surface.
Advantages

• No Solvents
• No Emissions, No VOCs
• Rapid Cure (< 1 ms)
• Less Energy
• Less Floor Space
• Reduced Cleanup
• Improved Properties (crosslinked, chemical resistance)
• No Spray Powder
• Cool Curing (more discussion later)
• Lower Capital cost vs.. Oven/Incinerator
Disadvantages

• Higher Ink / Coating cost vs solvent or water

• Technical Issues
  o Adhesion
  o Flexibility
  o Application

• Perceptions
  o Odor
  o Toxicology
  o Recycling
Chemistry of UV / EB formulations
Two basic type of chemistry are used

Extend of commercial use

• Free Radical 85-90%
  ▪ Acrylate (*Today’s focus*)
  ▪ Methacrylate
  ▪ Thiol-ene

• Cationic 10-15%
  ▪ Cycloaliphatic Epoxy
  ▪ Vinyl Ether
Typical UV ink formulation

- Pigment  5-25%
- Oligomers  20-40%
- Monomers  5-25%
- Prepolymers / resins  5-20%
- Photoinitiators  5-15%
- Additives  1-10%
Absorption of Pigments

![Graph showing the absorption of pigments across different wavelengths. The graph has a y-axis labeled "extinc. coef." and an x-axis labeled "wave length (nm)". The graph includes curves for black, cyan, yellow, and magenta pigments.]

- Black pigment has a constant absorption across all wavelength range.
- Cyan pigment absorbs in the blue spectrum and has a peak absorption around 400 nm.
- Yellow pigment has a peak absorption around 300 nm.
- Magenta pigment has a peak absorption around 250 nm.

The graph illustrates how different pigments absorb specific wavelengths of light, affecting color perception and printing processes.
Oligomers

- Oligomers are prepolymer with a molecular weight on 400-(3000-5000) grams/mole.
- Functionality >/2
- Imparts
  - Rheology control
  - Pigment wetting
  - Ink Transfer
  - Gloss
  - Chemical resistance
  - Film properties
Oligomers

- Chemical composition
  - Epoxy acrylate
  - Polyester acrylate
  - Polyurethane acrylate
  - Acrylated acrylics
- Functionality
  - Mono, Di, Tri, Tetra, Penta, Hexa, Deca
- Viscosity
  - Vegetable oil to peanut butter.
## Epoxy Acrylates

![Epoxy Acrylates structure](image)

<table>
<thead>
<tr>
<th>Uses and comments</th>
<th>Increases</th>
<th>Decreases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used in coatings</td>
<td>Reactivity</td>
<td>Adhesion</td>
</tr>
<tr>
<td>Used in inks</td>
<td>Hardness</td>
<td>Flexibility</td>
</tr>
<tr>
<td>Used in adhesives</td>
<td>Chemical Resistance</td>
<td>Cost</td>
</tr>
<tr>
<td></td>
<td>Reactivity</td>
<td>Pigment wetting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Misting</td>
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</tbody>
</table>
## Polyester Acrylates

![Chemical structure of Polyester Acrylates](image)

### Uses and comments

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<td>Used in adhesives</td>
<td>Pigment wetting</td>
<td>Cost</td>
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<tr>
<td></td>
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<td>Lithography</td>
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Polyurethane Acrylates

<table>
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<tr>
<td>Used in coatings</td>
<td>Adhesion</td>
<td>Yellowing</td>
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<tr>
<td>Used in inks</td>
<td>Hardness</td>
<td></td>
</tr>
<tr>
<td>Used in adhesives</td>
<td>Chemical Resistance</td>
<td></td>
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<tr>
<td>Aliphatic vs Aromatic</td>
<td>Weatherability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Flexibility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cost</td>
<td></td>
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Acrylated Acrylics

![Acrylated Acrylics](image)

<table>
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<tr>
<th>Uses and comments</th>
<th>Increases</th>
<th>Decreases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used in coatings</td>
<td>Adhesion</td>
<td>Scratch</td>
</tr>
<tr>
<td>Used in inks</td>
<td>Pigment wetting</td>
<td>Abrasion</td>
</tr>
<tr>
<td></td>
<td>Flexibility</td>
<td>Chemical resistance</td>
</tr>
<tr>
<td></td>
<td>Cost</td>
<td>Misting</td>
</tr>
</tbody>
</table>

R = H or CH₃  
R' = C₁ - C₄ ALKYL GROUP  
R'' = C₁ - C₁₈ ALKYL GROUP
Acrylated acrylic structure (general)
# General Properties of Acrylate Oligomers

<table>
<thead>
<tr>
<th>Properties</th>
<th>Epoxy</th>
<th>Polyester</th>
<th>Urethane</th>
<th>Acrylic</th>
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</thead>
<tbody>
<tr>
<td>Viscosity, cP</td>
<td>5K &gt; 1M</td>
<td>500 - 50K</td>
<td>15K &gt; 1M</td>
<td>50K &gt; 1M</td>
</tr>
<tr>
<td>Reactivity, mJ/cm²</td>
<td>100 - 500</td>
<td>100 - 500</td>
<td>200 - 1,000</td>
<td>500 - 2,000</td>
</tr>
<tr>
<td>Adhesion – metal</td>
<td>Fair – good</td>
<td>Fair</td>
<td>Fair – good</td>
<td>Good</td>
</tr>
<tr>
<td>Adhesion – plastic</td>
<td>Poor – fair</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Adhesion – wood</td>
<td>Good – excellent</td>
<td>Fair – good</td>
<td>Good</td>
<td>Good – excellent</td>
</tr>
<tr>
<td>Weatherability</td>
<td>Poor</td>
<td>Poor – good</td>
<td>Good – excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Excellent</td>
<td>Fair – good</td>
<td>Fair – good</td>
<td>Poor – fair</td>
</tr>
<tr>
<td>Scratch Resistance</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Poor</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>Fair</td>
<td>Poor – fair</td>
<td>Excellent</td>
<td>Poor – fair</td>
</tr>
<tr>
<td>Impact Resistance</td>
<td>Poor – fair</td>
<td>Poor</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Stain Resistance</td>
<td>Excellent</td>
<td>Fair – good</td>
<td>Poor – excellent</td>
<td>Poor – fair</td>
</tr>
<tr>
<td>Cost</td>
<td>$</td>
<td>$$</td>
<td>$$-$-$$$</td>
<td>$$$</td>
</tr>
</tbody>
</table>
Monomers

- Reactive diluent to control
  - Viscosity
  - Rheology
  - Cure speed
  - Crosslink density
  - Transfer
  - Tack
- Chemical compositions similar to oligomers but much lower molecular weight.
- Functionality
  - Mono, Di, Tri, Tetra, Penta, Hexa, Deca
- Viscosity
  - Water thin to engine oil.
Monomers

2-PHENOXYETHYL ACRYLATE

NEOPENTYL GLYCOL DIACRYLATE

PROPOXYLATED (3) GLYCERYL TRIACRYLATE
Monomers

ETHOXYLATED (4) PENTAERYTHRITOL TETRAACRYLATE

DI PENTAERYTHRITOL PENTAACRYLATE
Energy curing Process
Free Radical energy curing process

• Initiation
  ▪ Using UV or EB energy to form radicals which react rapidly with monomers and oligomers

• Propagation
  ▪ Reactive monomers and oligomers rapidly form a growing crosslinked network that has physical integrity.

• Termination
  ▪ Along the way, radical species may quench, run into oxygen (inhibits cure), or combine to end the reaction.
UV and EB curing process

• **UV Curing affected by:**
  - Color density
  - Film thickness
  - Light reflectivity

• **EB Curing energy is:**
  - Relatively color “blind”
  - Penetrates thick films
  - A ‘shower’ of electrons
Photoinitiators for Free Radical Curing

• Type I initiators
  ▪ Unimolecular reaction
  ▪ Intramolecular photocleavage
  ▪ Benzoin and derivative / polymers
  ▪ Acyl phosphine oxide and derivative / polymers
  ▪ α-amino alkylphenone derivatives / polymers

• Type II initiators & Synergists
  ▪ Bimolecular reaction
  ▪ Intermolecular H abstraction
  ▪ Benzophenones and derivatives / polymers
  ▪ ITX and derivatives / polymers
  ▪ Amines and amino derivatives / polymers
Additives used in UV / EB free radical curing

- Pigment dispersants
- Talc
- Waxes
- Flow / Rheology modifiers (silica, clays)
- Fillers
- Non reactive polymers
- Slip
- Stabilizer / Inhibitor
Energy Curables in Wide Web Flexible Packaging

Strong interest and practical solutions
Flexible Packaging Requirements

• High quality graphics

• Adhesion to substrates (*met. PET, OPP, PA*)

• Control of friction

• Acceptance to lamination

• Product performance in comparison to existing technology

• Regulatory compliance
Characteristics of EB Curing

- Fast curing, up to 400m/min
- Relatively “cold” process ($\Delta T \sim 5-10^\circ C$)
- Curing less affected by color or print density
- Electrons can penetrate deep
- Cure inhibited by oxygen
- Wet-on-wet printing with a curing unit at end of press
Advantages

• Electronically controlled dose rates – GMP
• Cured product exits the process ‘sterile’.
• No photoinitiators
• Lower energy consumption
• Low heat (IR) radiation on substrate
• Low maintenance means less down time
Disadvantages

• Discoloration of some PA, PVC, OPP

• For PE, the heat seal temperature of the thermoplastic can be increased.

• For OPP, the hot tack window could be altered.

• Some substrates may be subject to chemical breakdown under EB

• Odor
Adhesion to plastics and metallized films

• Surface energy is the sum of dispersive and polar interactions.

\[ \gamma = \gamma^d + 2(\gamma^a \gamma^b)^{1/2} \]

• Should a surface with $>42$ dynes/cm\(^2\) and a good chunk of polar components ($>6$ dynes/cm\(^2\)) on the surface.

• Recommend corona or chemically treated films.

• Polar component chemistries -COOH, -COH, -CO, -OH.

• Mechanical interlocking via anchoring, surface micro-roughness

*Dyne pens show wetting, not adhesion*
EB Offset Lithography

- Roll Offset
- Substrate Tension Control
- Repeat Length Variation
- Line Presses
  - Goss, DG Press, Omet, Drent Goebel
- Central Impression (CI) Offset Press,
  - Comexi, Uteco
Presses

Presses

Courtesy:
http://www.gossinternational.com/products/sunday-vpak-500/?back=products
EB Flexo

- Conventional Flexo

- EB Flexo Technologies

Overhead Oven

Interstation Dryer

Electron Beam
Applications of EB print

• Folding carton: Predominantly in the USA on boxes for dry foods, cereals, pasta, etc.

• Liquid and ice cream packaging: Coated board with EB inks in conjunction with extrusion lamination or UV or EB coatings.

• Shrink sleeve labels: films (PP, PE, PET, PVC, OPS) with reverse printed EB inks with a gravure applied. solvent last down white ink

• Wrap round labels: A range of films (PP, PE, PET, PVC, OPS) with surface printed EB inks
The complete package

Folding Carton Box

Collation Shrink Wrap

Transit packaging

Inner contents wrapper
# Migration mechanisms

## TYPES OF MIGRATION

<table>
<thead>
<tr>
<th></th>
<th>Migration Mechanism</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Penetration Migration&lt;br&gt;Migration from the printed side through the substrate onto the unprinted side.</td>
<td><img src="image" alt="Penetration Migration Diagram" /></td>
</tr>
<tr>
<td>2.</td>
<td>Contact Migration&lt;br&gt;Migration from the printed side to the unprinted side of another sheet in a stack or roll.</td>
<td><img src="image" alt="Contact Migration Diagram" /></td>
</tr>
<tr>
<td>3.</td>
<td>Evaporation Migration&lt;br&gt;Migration due to the evaporation of volatile materials by heating (e.g., cooking, baking, or boiling frozen products in their original packaging).</td>
<td><img src="image" alt="Evaporation Migration Diagram" /></td>
</tr>
<tr>
<td>4.</td>
<td>Distillation Migration&lt;br&gt;Migration through steam distillation during cooking, baking or sterilisation.</td>
<td><img src="image" alt="Distillation Migration Diagram" /></td>
</tr>
</tbody>
</table>
## Packaging categories

<table>
<thead>
<tr>
<th>Non sensitive</th>
<th>Non food packaging or functional barrier between food and packaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitive “indirect”</td>
<td>Food is <strong>not</strong> in contact with the packaging, but there is no safe barrier between both</td>
</tr>
<tr>
<td>Sensitive “direct”</td>
<td>Food is in physical contact with the inner (unprinted) side of the packaging</td>
</tr>
</tbody>
</table>
Food Packaging Applications

• High definition graphics

• Competes with gravure

• Good product resistance

• Low odor

• <10ppb migration performance
Trends & Technology

- More emphasis on high quality graphics
- Fast printing on a wide web
- Multiple substrates and thin films
- Adhesion, product performance
- Low odor, low migration, No emissions
- Cost versus value
- Regulatory compliance
Thank you

Electron Beam

Formulation

Ultraviolet Curing

Regulatory

Food Packaging

SunChemical®

a member of the DIC group
dic

working for you.