Introduction to the Basics of UV/EB Chemistry and Formulations

SUNY ESF

Institute for Sustainable Materials and Manufacturing

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Esstech, Inc.

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Agenda

- Introduction to UV/EB Curing
- Basic Formulation strategy
- Oligomers
- Monomers
- Photoinitiators
- Cationic Cure
- Electron Beam

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Energy Curable Industrial Coatings

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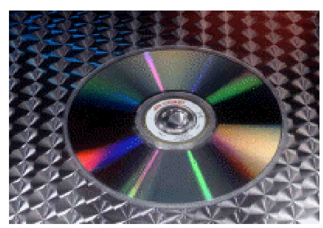
Energy Curable Graphic Arts Applications



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What is Energy Curing?

- Using UV energy, visible light, or high energy electrons as opposed to thermal, evaporative, or oxidative (air-dry) cure to form a coating, film or ink
- Types of energy used for energy curing:
  - Ultra Violet (UV): 200 – 400 nm
  - Visible light: typically 380 - 450 nm
  - Electron beam: low energy electrons

While I will try to use the term "energy curable", please note that the terms "radiation curable or "UV/EB curable" may be used interchangeably.

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Why Use Energy Curing?

- Productivity, Productivity, Productivity
  - Seconds to cure vs. minutes or hours
- Lower Overall Cost (per cured part)
  - 100% solids, cure speed, recycling of coating, etc
- Single component formulas
  - Eliminates mixing errors found in 2 component systems
- Regulatory Concerns (VOC emission)
  - Avoid solvent use in most cases
- Smaller equipment footprint
  - Less floor space needed
- Energy costs (esp. now with high oil prices)
- Did I mention Productivity?

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Areas of Strength for EC

- Scratch Resistant Coatings (plastic, paper up-grade)
- Over Print Varnishes
- Printing Inks (Litho, Flexo, Screen)
- Wood Coatings
- Electronic & Fiber Optic Coatings
- Photopolymer Plates

EC can generate a high crosslink density network that results in a coating with high gloss and hardness, scratch and stain resistance and fast cure. EC also works best with flat substrates, which are found in all of the above markets.

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Areas for Improvement

- Adhesion to some metals, esp. during post-forming
- Adhesion to some plastics
- Tear resistance
- Low gloss in 100 % solid systems
- Low film weight for 100% solids
- Overall cure of 3-D parts

EC coatings can have high shrinkage, which adversely affects adhesion to non-porous substrates. Lack of solvent coupled with a fast cure reduces the formulator's ability to meet low gloss, low film build requirements. Additional lamps are needed to cure 3D parts since EC is a line of sight cure method.

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RADIATION CURING

TYPES OF RADIATION USED

- UV - ultraviolet photons
- EB - low energy electrons

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RADIATION CURING CHEMISTRY

- **Free Radical**
  - Polymerization through double bonds
  - (Meth)Acrylate double bonds most common functionality
- **Cationic**
  - Polymerization through epoxy groups
  - Cycloaliphatic epoxies most commonly used

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RADIATION CURING CHEMISTRY

- **Free Radical Curing - UV**
  - Photoinitiator absorbs UV light and generates free radicals
  - Free radicals react with double bonds causing chain reaction and polymerization
- **Cationic Curing - UV**
  - Photoinitiator absorbs UV light and generates a Lewis acid
  - Acid reacts with epoxy groups resulting in polymerization

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RADIATION CURING CHEMISTRY

- **Free Radical Curing - EB**
  - Electrons open double bonds initiating polymerization - no photoinitiator required
- **Cationic Curing - EB**
  - Electrons decompose photoinitiator to form acid - photoinitiator is required for polymerization

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UV CURING

- Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning
- Photoinitiator Package
  free radical generation

UV Light → CURED PRODUCT

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EB CURING

- Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning

Electrons → CURED PRODUCT

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Formulating for properties

Some desirable properties for coatings:

- Adhesion
- Cure speed
- SARC (scratch & abrasion resistant coatings)
- Weatherability
- Flexibility
- Pigmented systems

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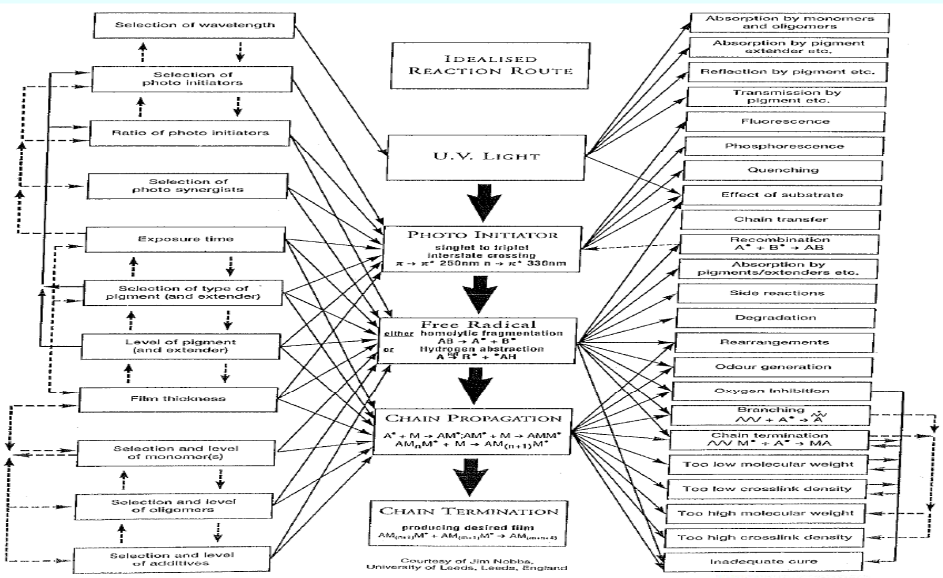
Everything You Always Wanted to Know About UV Formulating



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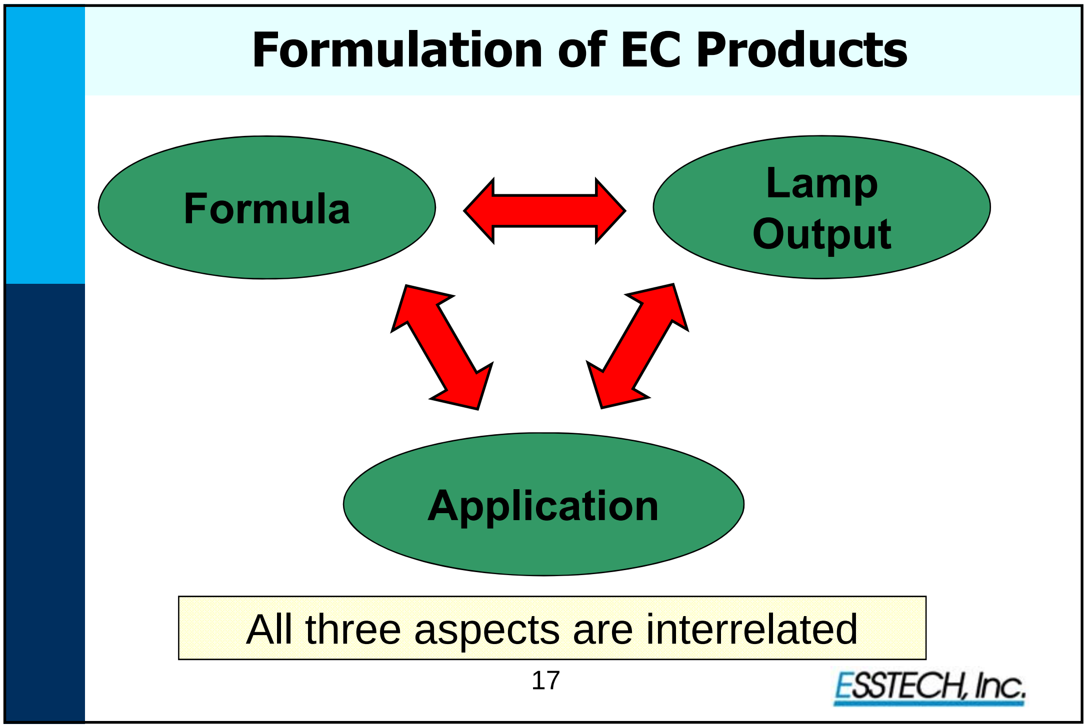
Formulation of EC Products
Formula
Lamp Output
Application
All three aspects are interrelated
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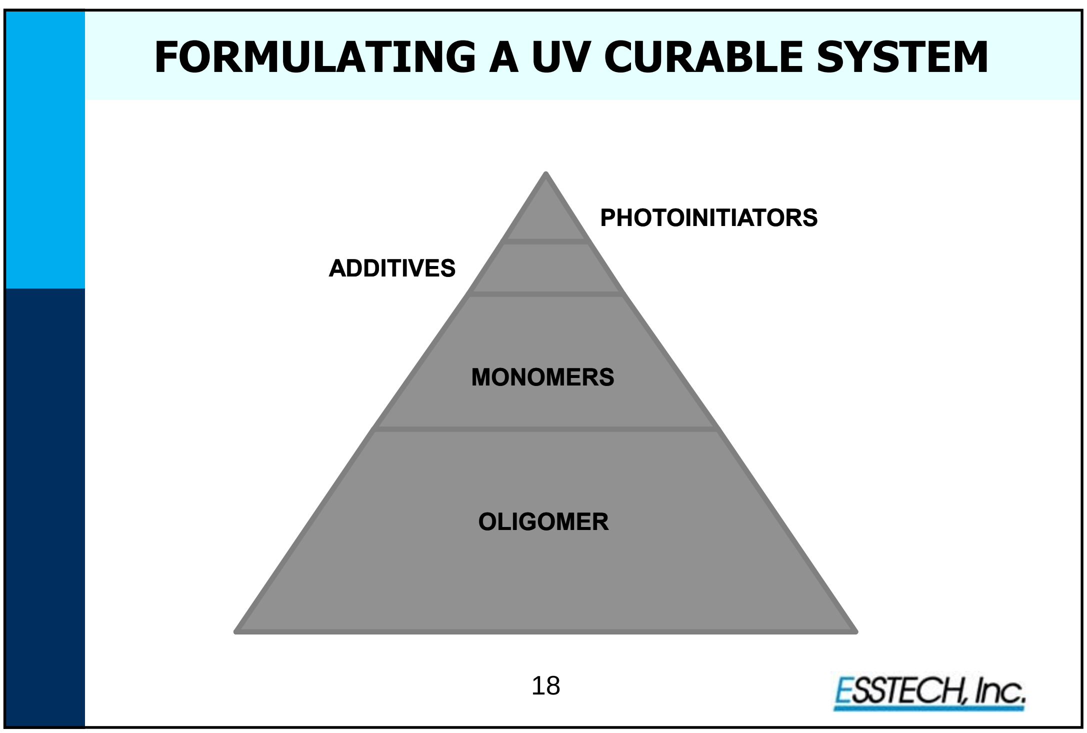
FORMULATING A UV CURABLE SYSTEM
PHOTOINITIATORS
ADDITIVES
MONOMERS
OLIGOMER
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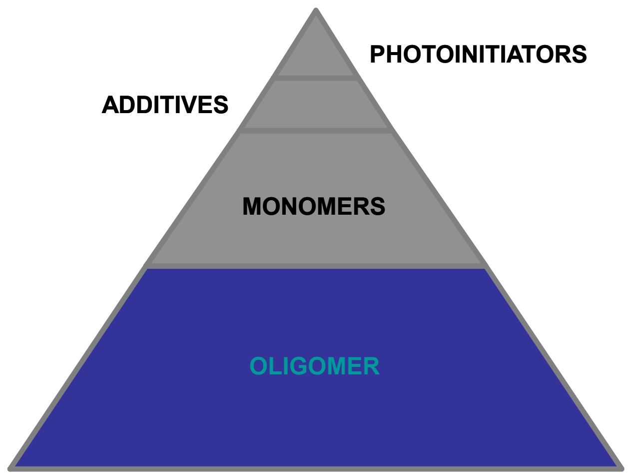
FORMULATING A UV CURABLE SYSTEM



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OLIGOMER TYPES

(Meth)Acrylated	Characteristics
Epoxies	fast curing, hard, solvent resistant, lower cost
Aliphatic Urethanes	flexible, tough, non-yellowing, best weathering properties
Aromatic Urethane	flexible, tough, lower cost than aliphatic urethanes
Polyesters	low viscosity, good wetting properties
Acrylics	good weathering properties, low Tg
Specialty Resins	adhesion, special applications

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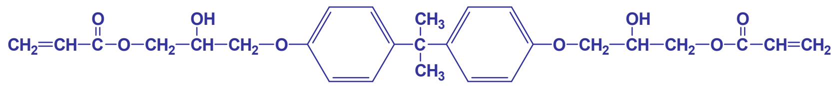
OLIGOMERS

Epoxy Acrylate



bisphenol A diglycidyl ether diacrylate

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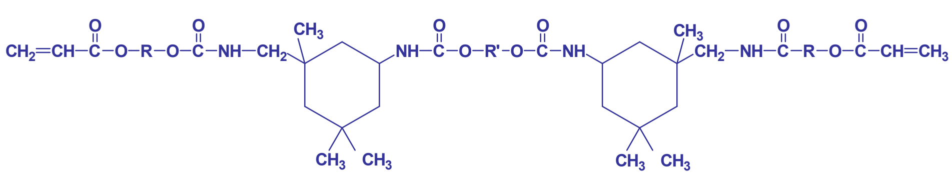
OLIGOMERS

Urethane Acrylate



aliphatic urethane diacrylate

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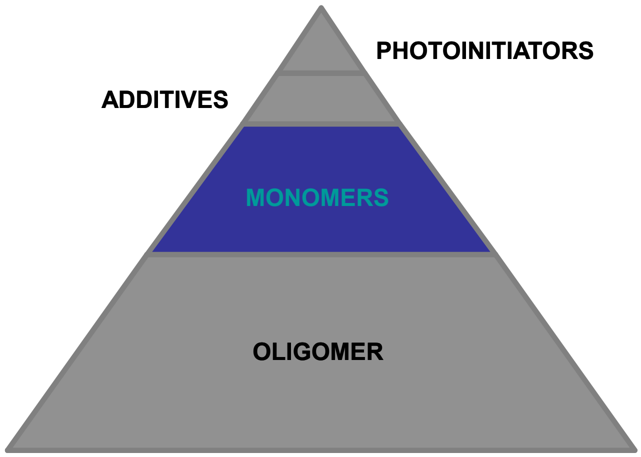

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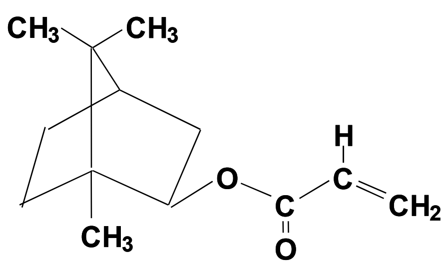
MONOMERS

Monofunctional Monomer



IBOA
isobornyl acrylate

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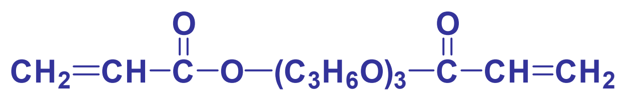
MONOMERS

Difunctional Monomer



TRPGDA
tripropylene glycol diacrylate

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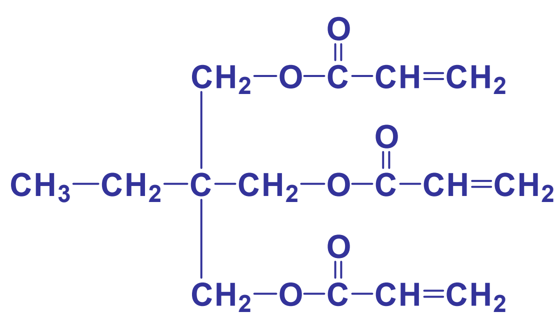
Trifunctional Monomer



TMPTA
trimethylol propane triacrylate

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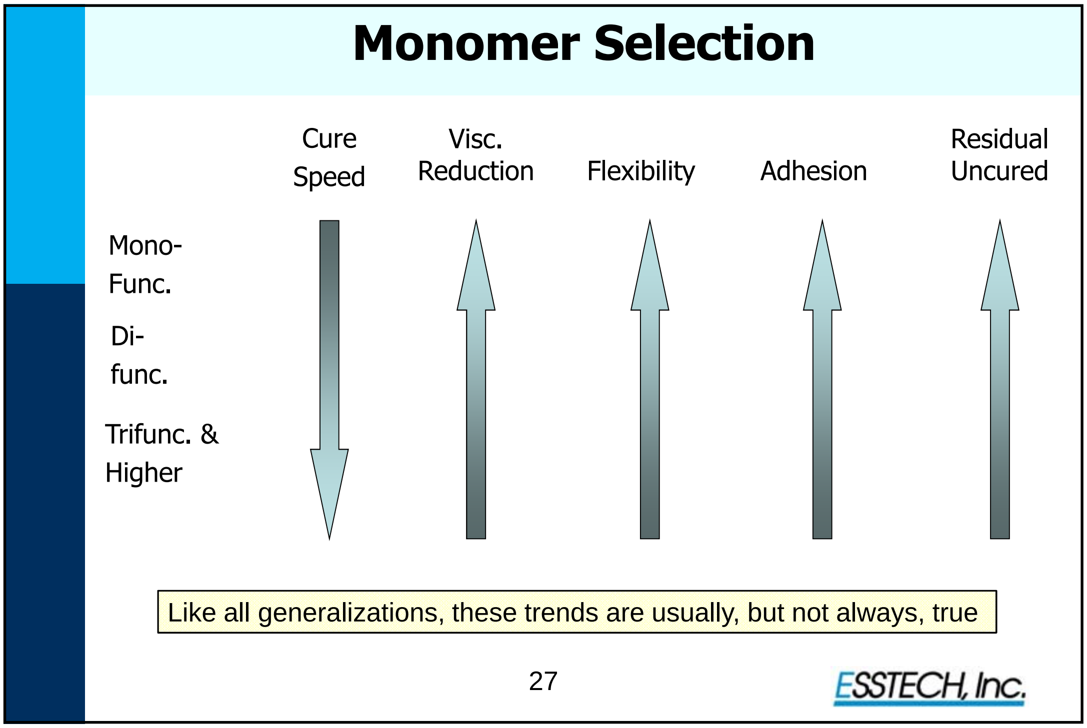
Monomer Selection
Cure Speed
Visc. Reduction
Flexibility
Adhesion
Residual Uncured
Mono-Func.
Di-func.
Trifunc. & Higher
Like all generalizations, these trends are usually, but not always, true
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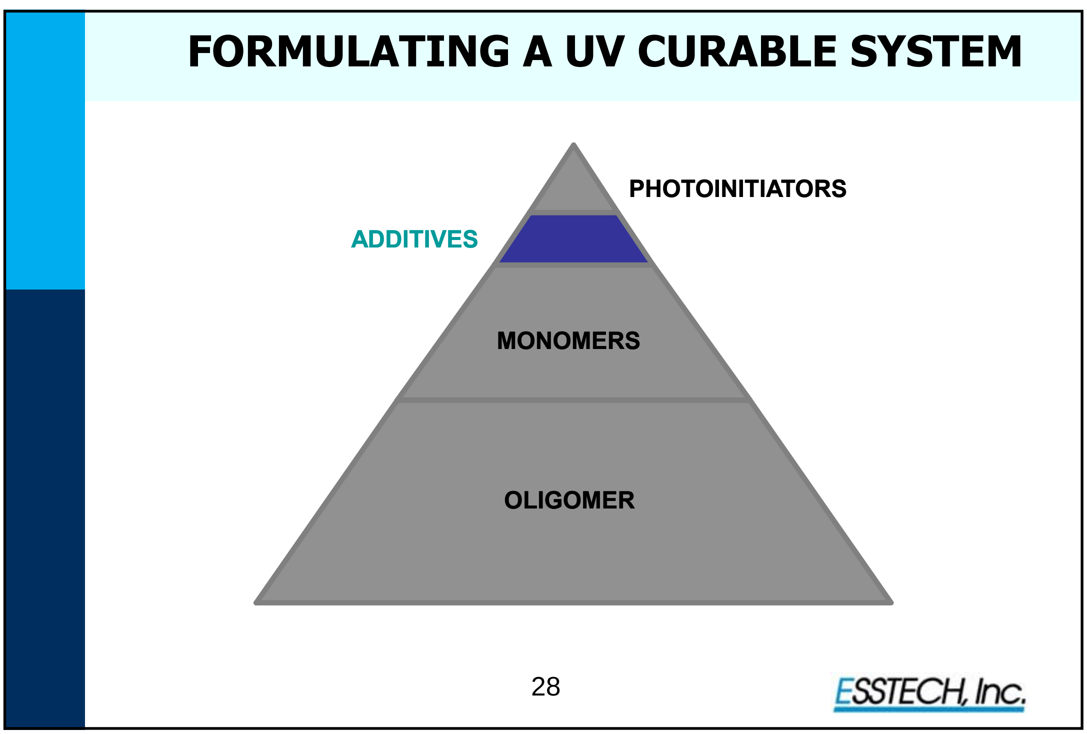
FORMULATING A UV CURABLE SYSTEM
PHOTOINITIATORS
ADDITIVES
MONOMERS
OLIGOMER
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ADDITIVES

- Pigments
- Fillers
- Defomers
- Flatting Agents
- Wetting Agents
- Slip Aids

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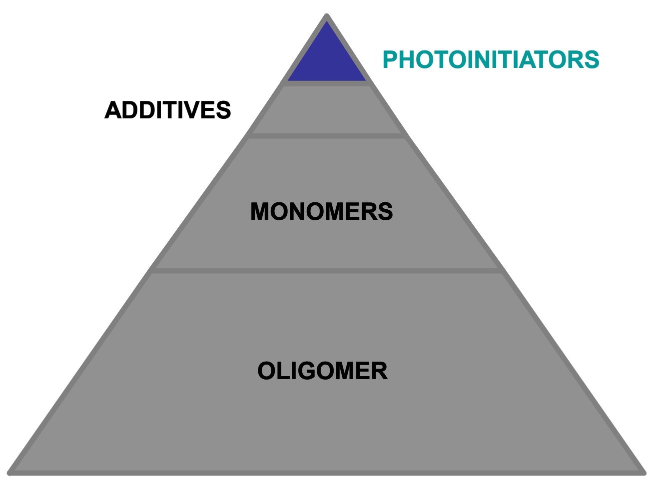
FORMULATING A UV CURABLE SYSTEM



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Photoinitiators

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Terms/Glossary

λ_{max} (pronounced "lambda max")	The wavelength at which photoinitiator absorbs the most energy; also known as peak absorbance
absorbance	The amount of light a material takes in as opposed to reflecting or transmitting it
cure	The conversion of unreacted material to reacted material; transformation of monomers and oligomers to a polymer network; in practical terms, usually the point at which the wet material reaches a mar free state (or any other property of interest)
photons	A quantum of light; a packet of light energy
polymerization	The reaction by which monomers (and oligomers) are converted to high molecular weight materials (polymers)
radical	AKA free radical, molecule fragment with 1 unpaired electron. Not an ion (has no charge)
transmission	The amount of light passing through a material; the ratio between the outgoing (I) and the incoming intensity (I_o), $\%T = (I/I_o) \times 100$

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Why Are PI Necessary?

- **PI Characteristics**
  - Absorb UV light or electrons to form active species (radicals or acids)
  - Add to monomer/oligomer to start cure process (polymerization)
  - Different PI absorb UV light at different wavelengths
  - Match PI λ_{max} with UV lamp output
  - Only reacts with UV-Vis energy, not heat
  - Long pot life/shelf life

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UV Radical Polymerization

- **Initiation**
  - System is irradiated, reactive species (free radicals) created
- **Propagation**
  - Oligomers and monomers add to the growing polymer chain, creating a high MW network
- **Termination**
  - Two radicals combine to stop the chain reaction

- Photoinitiators can be a factor in initiation and termination

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Initiation

- **Initiation Process**
  - System is irradiated and the photoinitiator absorbs some of the incoming energy
  - Photoinitiator forms one or more free radicals
  - A free radical then combines with an acrylate to form a new radical that is the active species for the growing polymer
  - UV polymerization is line-of-sight only – shadowed areas very hard to cure

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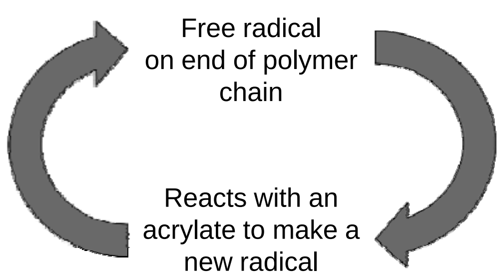
Propagation

- **Propagation Process**



- Referred to as a chain reaction

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Termination

- **Termination Process**
  - Two radicals (active species, growing chains, PI fragments) combine and the polymerization stops
  - If PI concentration is too high, the radicals from the PI can contribute to a high termination rate
  - A high termination rate can lead to
    - Greater levels of unreacted material
    - Poor physical properties (e.g. low adhesion, greater marring, poor tensile properties)

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Summary

•Initiation	I	$\xrightarrow{\text{UV Energy}}$	2 I•
	I• + M	$\longrightarrow$	IM•
• Propagation	IM• + M	$\longrightarrow$	IMM•
	IMM• + M	$\longrightarrow$	IMMM•
	IMMM• + M	$\longrightarrow$	IMMMM•
• Termination	P~M• + •M~P	$\longrightarrow$	P~M-M~P
		-OR-	
	P~M• + •I	$\longrightarrow$	P~M-I

I = Initiator M = Monomer (or any acrylate) P = Polymer chain

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Classes of Photoinitiators

- **Photocleavage (unimolecular PI)**

  a-cleavage PI - Adsorbs light and fragments to form the radicals which initiate polymerization.

- **Photoabstraction (bimolecular PI)**

  Hydrogen abstraction PI - Adsorbs light and abstracts hydrogen from another molecule (photoactivator) which produces radicals.

  Amine synergist (photoactivator) - Donates a hydrogen to the photosensitizer to produce the radicals which initiate polymerization.

Photoinitiator, photosensitizer, and photoactivator are often used as different words for photoinitiators even though they are not the same

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Photoinitiator Mixtures (liquid blends)

- Liquids are easier to handle in a plant (but often $$)
- PI blends offer advantages
  - Absorb over a larger range of wavelengths – better chance of avoiding interference from e.g. pigments and make use of more of the available UV energy
  - Combination of PI for surface and through cure

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Photoinitiator Selection

- Absorption characteristics of photoinitiator and formulated system
- Pigmentation
- Spectral output of UV lamps
- Oxygen inhibition
- Weatherability (yellowing)
- Handling (liquid vs. solid)
- Toxicity
- Cost

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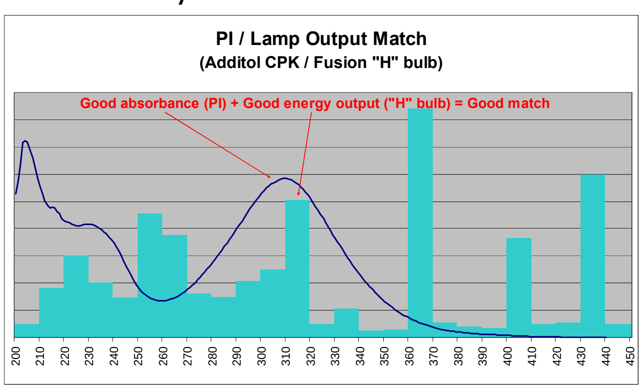
Matching PI with UV lamp

- Different UV lamps emit energy in different part of the spectrum
- Need to match absorbance of the PI with the output of the lamp for highest efficiency



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Oxygen inhibition

- Oxygen can inhibit (slow down) the cure speed of coatings and inks, especially in thin layers

- Solutions:
  - Amine synergists
  - Cure under an inert (N_2) atmosphere

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Cationic Cure

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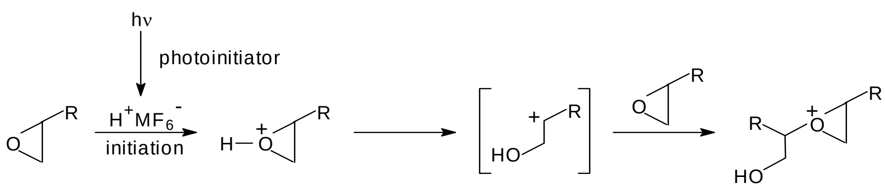
CATIONIC CURING MECHANISM

Initiation (Light & Heat)



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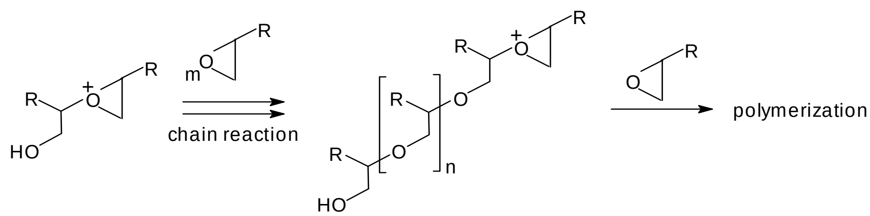
CATIONIC CURING MECHANISM

Polymerization (Chain Reaction; Heat)



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Radical vs. Cationic

Radical	Cationic
wide variety of raw materials	more limited raw materials
inhibited by oxygen	not inhibited by oxygen
not inhibited by high humidity	inhibited by high humidity
not inhibited by basic materials	inhibited by basic materials
full cure in seconds	full cure in hours
shrinkage - greater	shrinkage - less
adhesion - less	adhesion - greater
depth of cure - greater	depth of cure - less
cost - less	cost - greater
UV/EB market share - 92-94%	UV/EB market share - 6-8%

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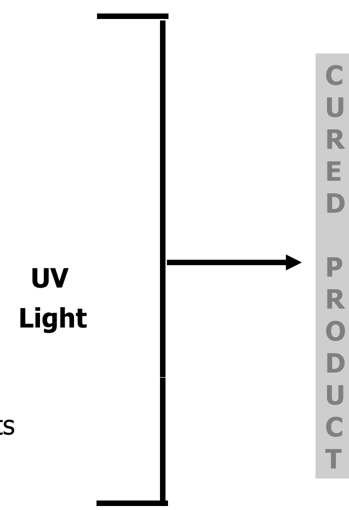
UV Cationic Curing

- **Cycloaliphatic Epoxide(s)**
  basic coating properties
- **Polyol(s)**
  crosslinking, flexibility
- **Epoxy/Vinyl Ether Monomer(s)**
  viscosity reduction
- **Additives**
  performance fine tuning
- **Photoinitiator Package**
  cation generation - commonly sulphonium salts



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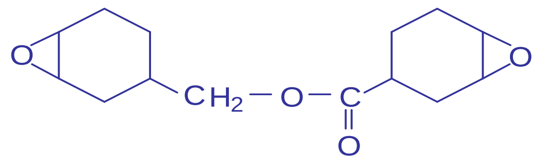
Epoxides

Cycloaliphatic Epoxides

- Major Component of the formulation
- Builds properties of the film
- Other components are modifiers



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Electron Beam

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ELECTRON BEAM

Ionizing radiation or low energy electrons (e^-)

- have sufficient energy to break bonds in coating, and generate free radicals
- can penetrate into and through a coating/ink, and through some substrates
- are not affected by pigmentation or transparency of coating/ink or substrate
- generate little to no heat
- dose can be precisely controlled
- enable high through put

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E BEAM PARAMETERS

- Voltage = Electron Penetration
  - Equals Thickness Penetrated
  - units are e^- volts: MeV, keV
- Amperage = Beam Current
  - Equals Exposure Intensity
  - units are amps
- Dose = Absorbed Energy
  - Expressed in kGy (kiloGray) or Mrad (mega rad)

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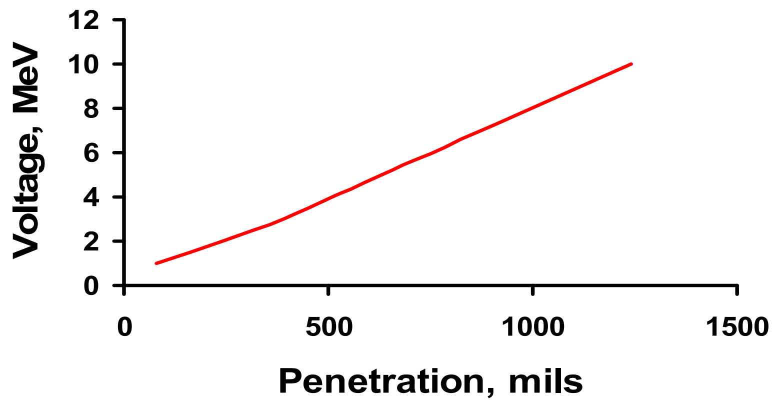
High Voltage E BEAM PENETRATION



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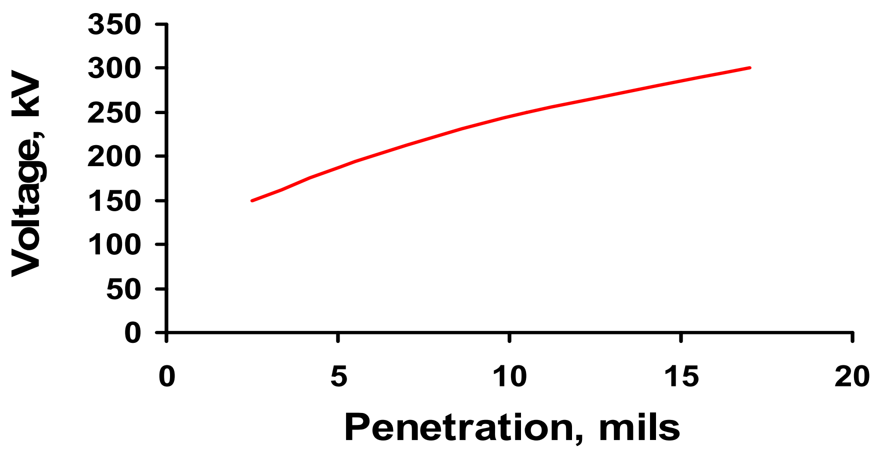
LOW VOLTAGE E BEAM PENETRATION



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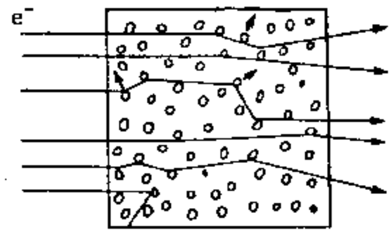
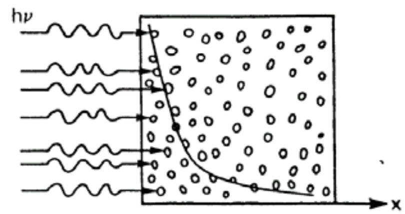
e⁻ AND hν PENETRATION





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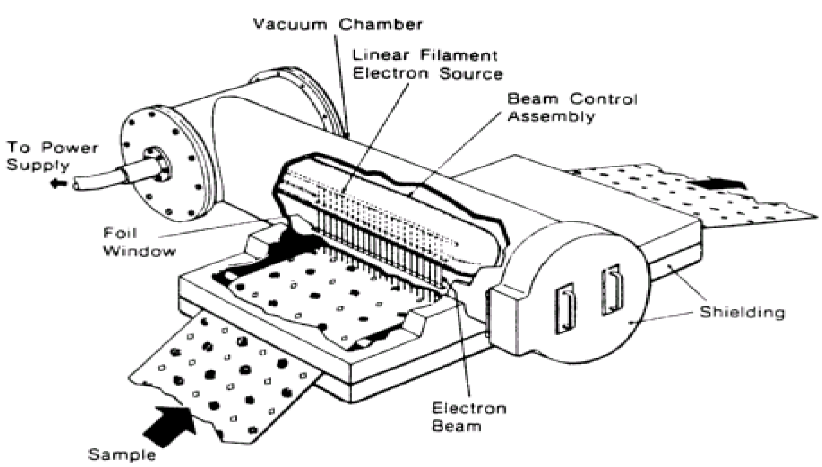
LOW VOLTAGE E BEAM



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Thank You!

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