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DRYING & CURING MECHANISMS INCLUDING ENERGY CURABLE MATERIALS 2026 NPIRI Summer Course

- James Ford
- Flint Group

AGENDA

- Introduction to Drying & Curing
- Basics of Energy Curing
- Raw Materials for Energy Curing
- Photoinitiator Basics
- Interactions of Lamps, Photoinitiators, and Energy Curable Materials
- Formulating and Testing

How does ink go from a liquid to a solid? **Absorption, Evaporation, Reaction**

Absorption of carrier (oil, solvent, water, monomer) into the substrate leaving solids on surface.

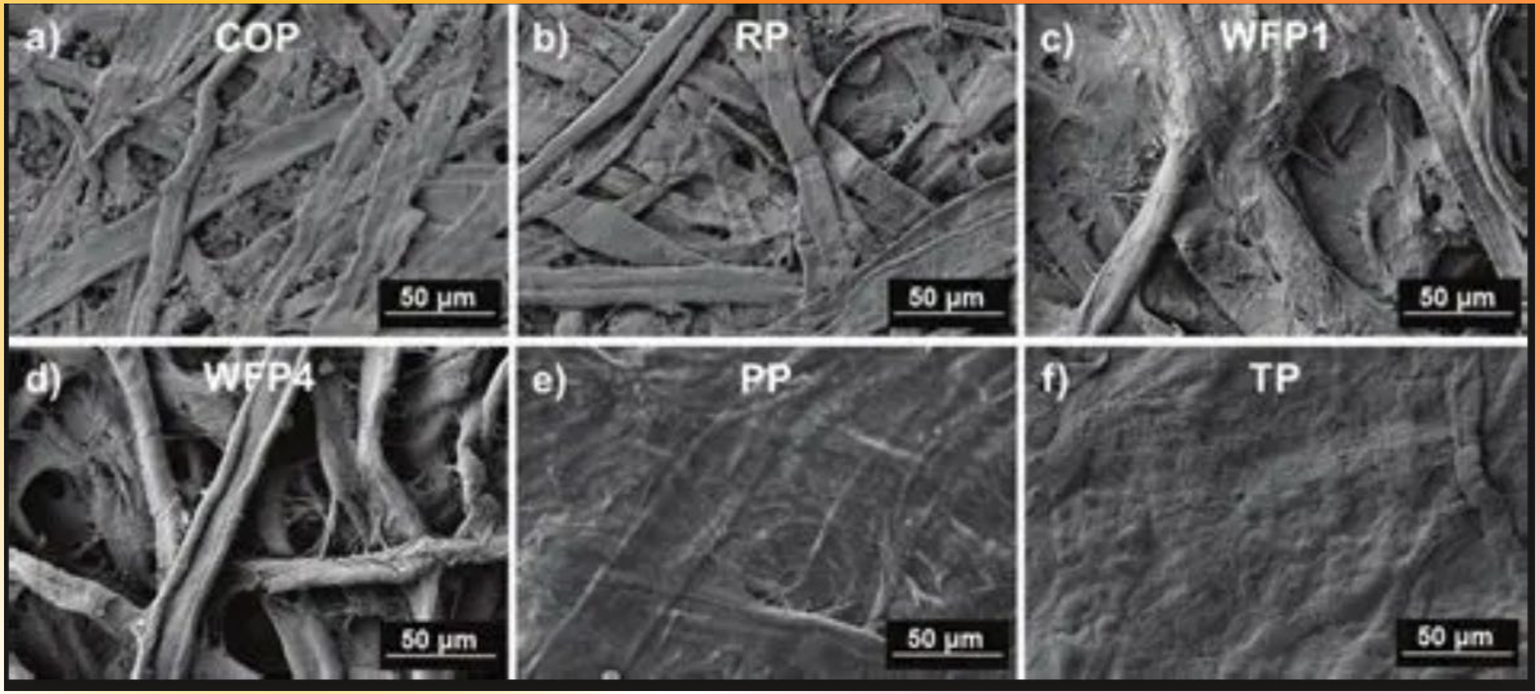
Evaporation of carrier from ink to air

Reaction of ink to environment or external factor (visible, UV, LED, time, temperature, etc)

Sometimes, a combination of all the above.

Absorption

Absorption depends upon substrate structure, treatment, viscosity of ink, fluid dynamics, etc..
Leaves solids on surface



Evaporation

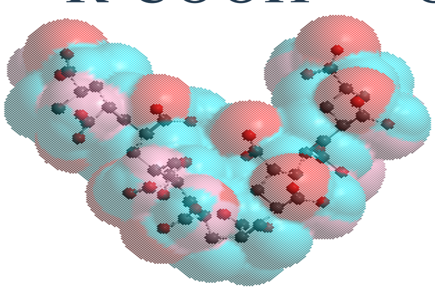
Evaporation of the carrier will be conducted by means of air, heated air, or other means to remove volatile components of the ink, leaving the solids on the surface. This will be influenced by the evaporation rate of the components, the speed of the press, and temperature/humidity conditions,

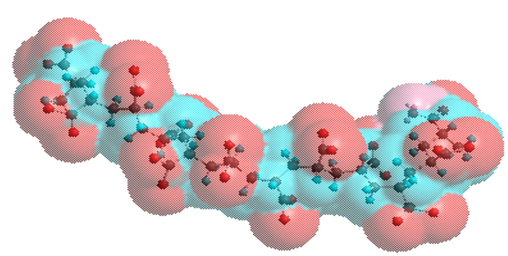
And don’t forget that these components have to be efficiently removed from the surface.

Evaporation may not just be the solvent

Consider a conventional acrylic water-based ink. The resins are not soluble in pure water. They need to be neutralized to go into solution. The addition of pH adjuster makes the resins soluble, and when the ink dries and the pH adjuster evaporates, the resin reverts to an insoluble coating.

$$R\text{-}COOH + OH^{(-)} \Rightarrow R\text{-}COO^{(-)} + H_2O$$





Reaction

In some cases, the ink can be applied to the substrate and be reacted in a way to solidify the ink on the surface. Absorption or evaporation not necessary. This can be done by crosslinking the polymer backbone to form the solid surface.
UV and UV/LED are common, but visible light can also be used, as well as electron beam. Could also be precipitation of resins due to exposure to moisture in Heatset.

Combinations

Some ink types may use multiple means of drying, such as waterborne UV inks. Ink is applied in a water carrier which needs to be removed, followed by a curing process to set the ink.

Dry Rate / Cure Rate Testing

Many ways to measure dry rate and/or cure rate
Manual, Mechanical, DSC, Moisture testing, MEK rub, KMnO4, etc

Troubleshoot Drying/Cure

High humidity	Moisture film on the ink surface retards oxygen penetration. Each 10% increase in relative humidity above 60% roughly doubles the drying time for some ink formulations. Above 80% RH, some inks may not dry reliably at all.	In humid conditions (especially June–September in Mumbai): reduce pile height, increase anti-setoff powder quantity, use inks with higher drier content or humidity-resistant formulations. Do not attempt to laminate or UV coat until drying is confirmed by rub test.
Low temperature	Oxidative polymerisation is temperature-dependent, the reaction rate approximately doubles with every 10°C increase in temperature. A press room at 18°C dries much more slowly than one at 28°C.	Maintain press room temperature above 20°C. In cold press rooms (air-conditioned below 20°C), use inks with faster drying drier systems or increase drier concentration.

Troubleshoot Drying/Cure

Excessive ink coverage (high TIC)	Thick ink films (from heavy coverage or high TIC) require oxygen to diffuse further into the film to achieve through-cure. Films above 3–4 microns dry significantly more slowly than standard thin films.	Manage TIC within substrate limits (see CMYK guide). Where heavy coverage is unavoidable, reduce pile height and extend drying time before finishing.
Coated paper substrate	Coated paper's sealed surface prevents ink vehicle from absorbing into the substrate, more vehicle remains on the surface and drying relies entirely on oxidative curing rather than the partial absorption mechanism that accelerates setting on uncoated stock.	Accept longer drying times on coated stock. Use IR delivery dryers. Ensure press room ventilation is adequate to supply oxygen to the delivery pile.

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- Raw Materials for Energy Curing
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- Interactions of Lamps, Photoinitiators, and Energy Curable Formulations
- Formulating and Testing

ENERGY CURE UV/EB USE IN PACKAGING

- Inks, Coatings, Overprint Varnishes (OPV), Laminating Adhesives, Silicone Release Coatings, Primer Coatings
- All Printing Processes:
  - Offset, Flexo, Letterpress, Screen, Digital, and Inkjet
- Food and Non-Food Applications (FCN 772)
- Substrates:
  - Porous substrates
    - Paper and board stock
  - Non-porous substrates
    - Flexible and rigid plastics
    - Metallized foils
    - Aluminum and can stock

Properties of an ink

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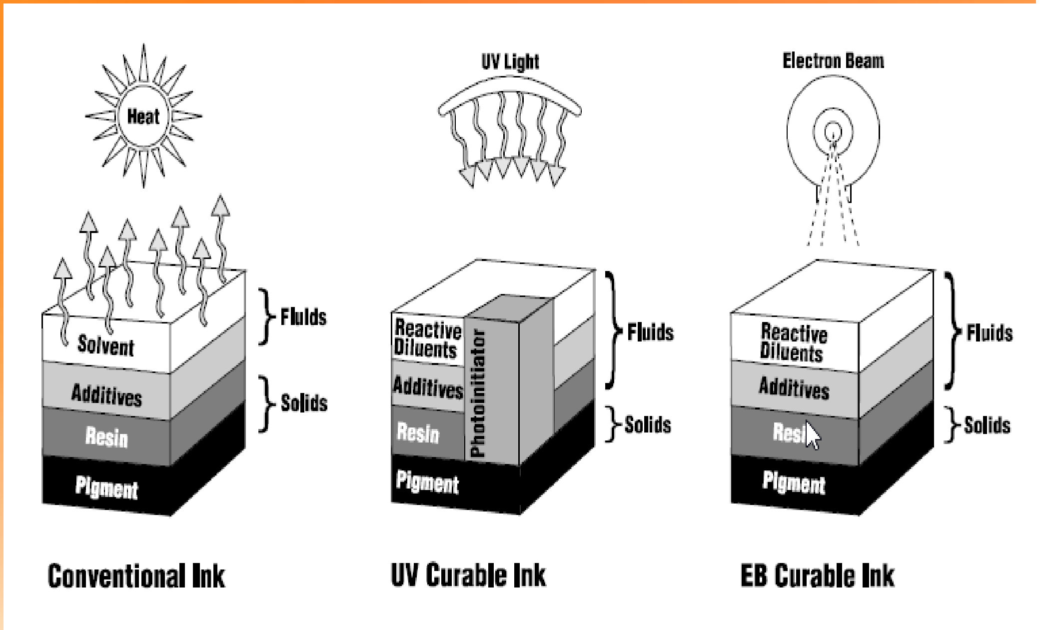
- Adhesion to substrate
- Optics (Color, Gloss, Reflectance, Opacity/Transparency)
- Functional
  - Resistance to Abrasion (Rub)
  - Resistance to Environment (water, humidity, chemicals, etc.)
  - Slip/Friction Aspects
- Performance
  - Dry Speed
  - Resolubility
  - Stability
  - Other (foaming, pinholing, etc.)



What is Energy Curing?

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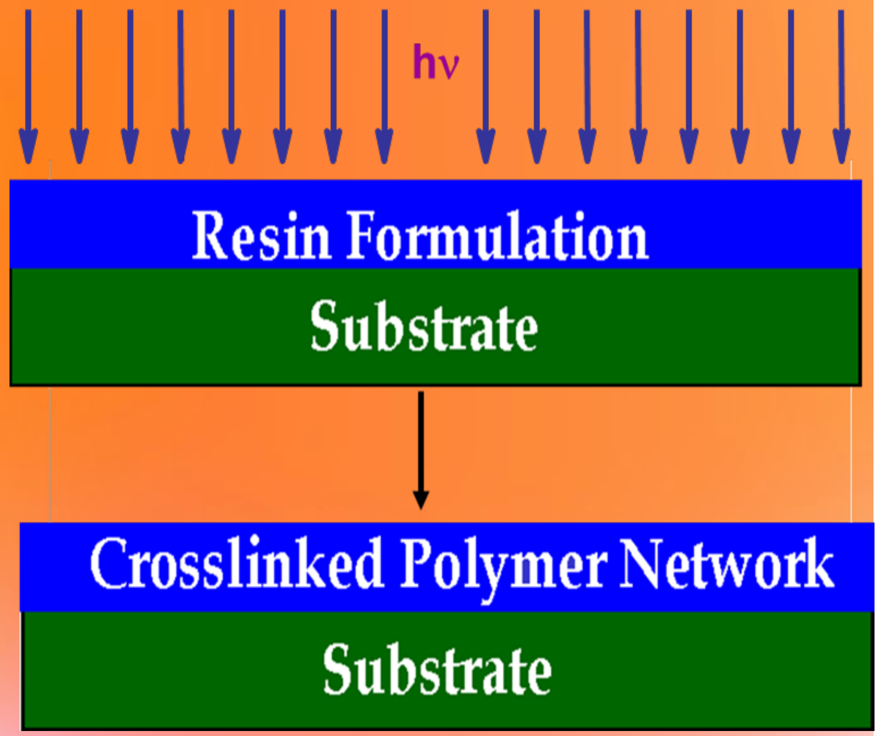
Using UV energy, visible light, or high energy electrons as opposed to thermal, evaporative, or oxidative (air-dry) cure to form a coating, film or ink

Types of energy used for energy curing:

- Ultra Violet (UV): 200 – 400 nm
- Visible light: typically 380 - 450 nm
- Electron beam: high energy electrons

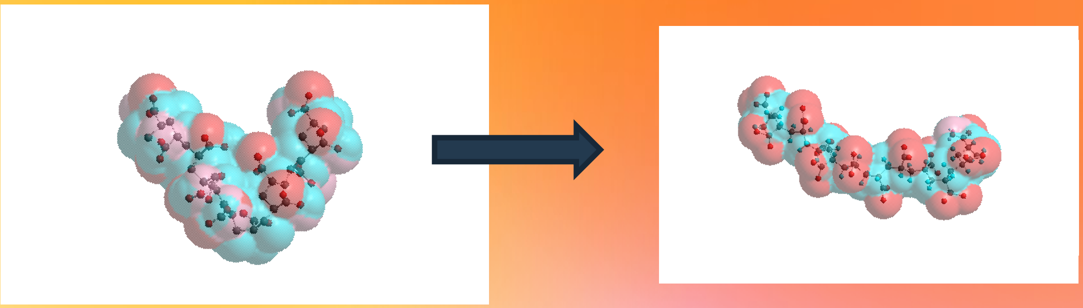


Why is Energy Cure different?

Component	Solvent Inks	Water Inks	Oxidative	UV / EB
Color	Pigments	Pigments	Pigments	Pigments
Binder	Solvent soluble solid polymer	Emulsion Polymers, plus	alkyds, etc.	Reactive Oligomer
Diluent	solvents (toluene, alcohol, acetate)	Water	oil	Monomer
Additives	Waxes, surfactants, etc	Waxes, surfactants, etc	Waxes, surfactants, etc	Waxes, surfactants, etc
Catalyst	None	None *	Oxygen	Photoinitiators (Not needed EB)
Neutralizer	None	Base (ammonia, amine, etc.)	None	None *

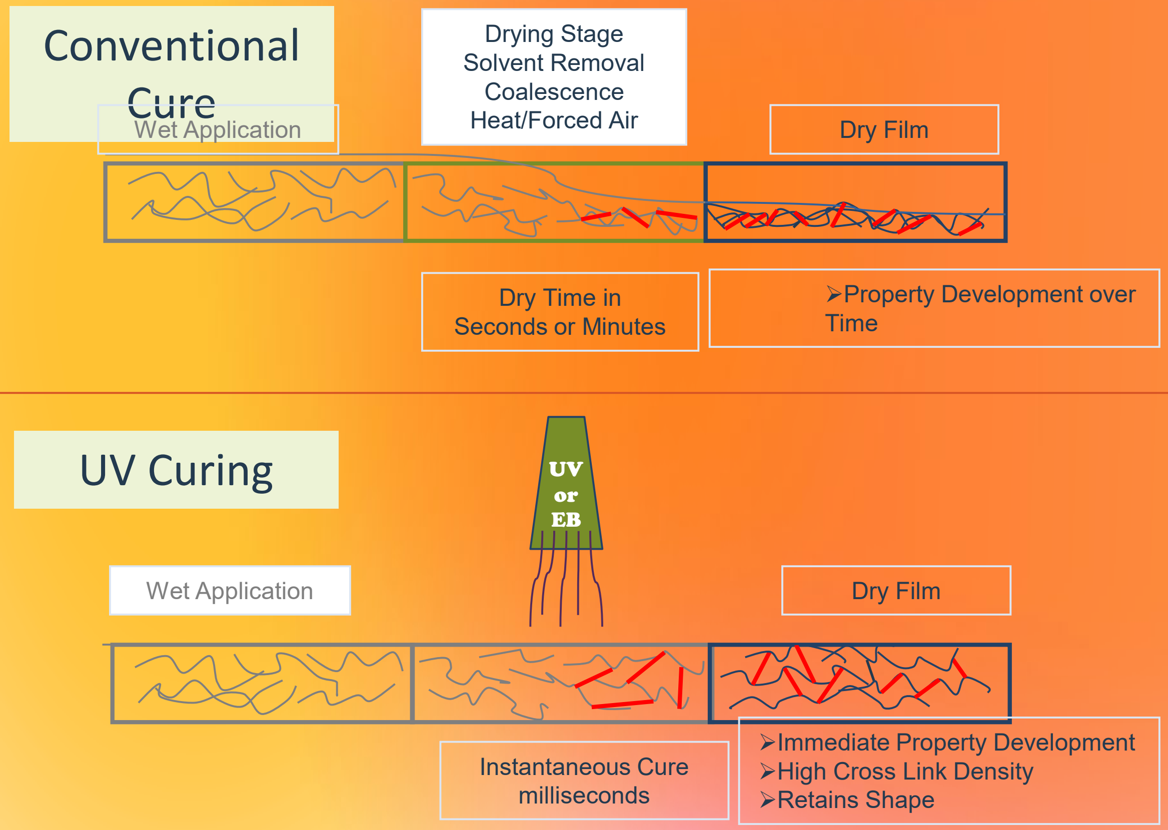
Versus Water Inks

- Water-based inks usually start with an already formed polymer either dispersed or formed in water.
- Most water-based inks are based upon acrylic polymers, but styrene/acrylics, SBR, and various natural resins are also common.
- Polyacrylic acid is unstable at low pH and is not soluble in water. As base (pH adjuster) is added, polymer becomes more stable and is more resoluble.

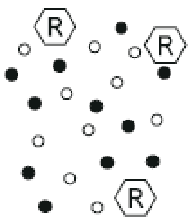


- That is why pH is so important in water inks!

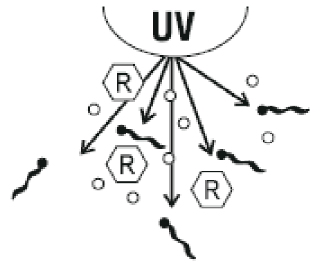
Dry Film Formation



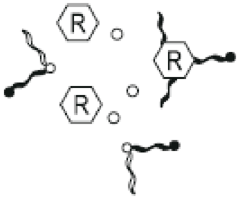
1. Ink before UV light energy.



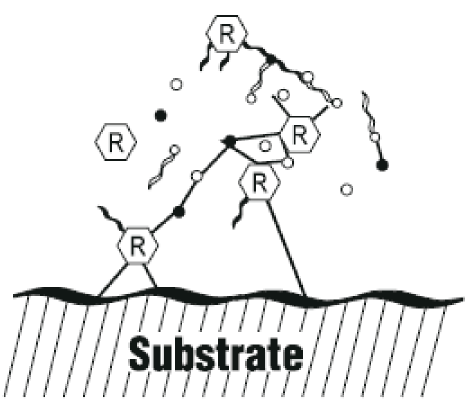
2. UV light exciting photoinitiator and creating "free radicals."



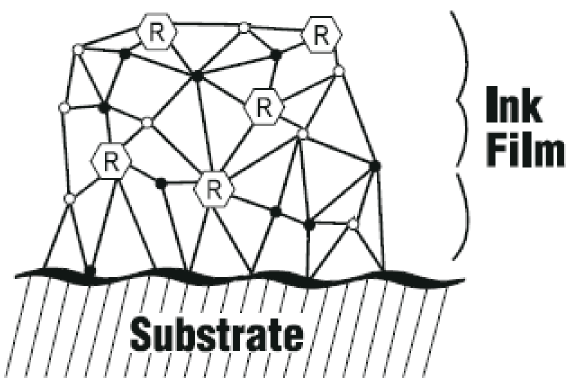
3. Chain reaction begins. Components are attracted to free radicals. Note new position of free radicals.



4. Reaction continues or "propogates;" the chemical bonding is called polymerization.

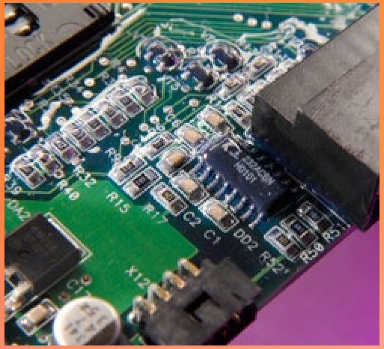


5. Completed chemical reaction. Note strong chemical network.



Why Use Energy Curing?

- Productivity, Productivity, Productivity
  - Seconds to cure vs. minutes or hours, press stability
- 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



WHY ENERGY CURE?

- Improved properties for inks and coatings
  - Higher gloss
  - Control ink/coating thickness; 100% solids
  - Better solvent resistance
- Environmentally friendly?
  - Very low VOC -- safer work environment
  - Fully cured ink can be incinerated or disposed in landfill
  - Reduced or no hazard reporting

WHY Energy Cure?

- Press ready inks that don't dry in ink train
  - Consistent printing and color
  - Reduced time for clean-up; fewer wash-ups
  - Faster start-up; reduced substrate waste
  - Extended pot life

- Instant drying
  - Reduced floor space needed for drying
  - Ability to "convert" in-line
  - Low temperature drying

- End result: Increased Productivity (Lower Cost)

WHY NOT UV/EB ?

- Additional capital cost
  - Retrofitting is difficult for offset, but getting easier with new lamps (especially UV LED)
  - EB is expensive, but is becoming more cost competitive

- Inks and coatings are more expensive
  - Cost may be offset by improvements in productivity, superior appearance, and better resistance properties

- Re-training of press operators
  - UV/EB inks perform differently on press vs others

  - Regulatory issues with monomers and PI’s

ENERGY CURING

- Types of Energy

<u>UV: ultraviolet light</u>

- Non-ionizing radiation
- Photons
- 220 nm - 400 nm

<u>EB: ionizing radiation</u>

- High to mid energy electrons
- 300 KeV max

ENERGY CURING

- Types of Chemistry

  Free Radical
  - Polymerization through double bonds
  - Acrylate double bonds most common functionality

  Cationic
  - Polymerization through epoxy groups
  - Cycloaliphatic epoxies most common functionality
  - Not widely used
    - Metal deco is exception
  - More expensive, and fewer raw materials

ENERGY CURING

- Chemistry of Polymerization: Curing, Drying

Free Radical - UV

- Photoinitiator absorbs UV light, and generates free radicals
- Free radicals react with double bonds, causing chain reaction and polymerization

Free Radical - EB

- Electrons break bonds to generate free radicals - no photoinitiator is required
- Free radicals react with double bonds, causing chain reaction and polymerization

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TYPES OF REACTIVE DOUBLE BONDS
FREE RADICAL CHEMISTRY

ACRYLATE $R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2$

METHACRYLATE $R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$

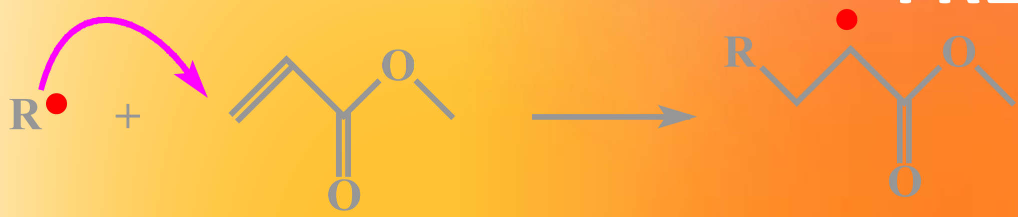
ALLYL $R{-}CH_2{-}CH{=}CH_2$

VINYL $R{-}CH{=}CH{-}R$

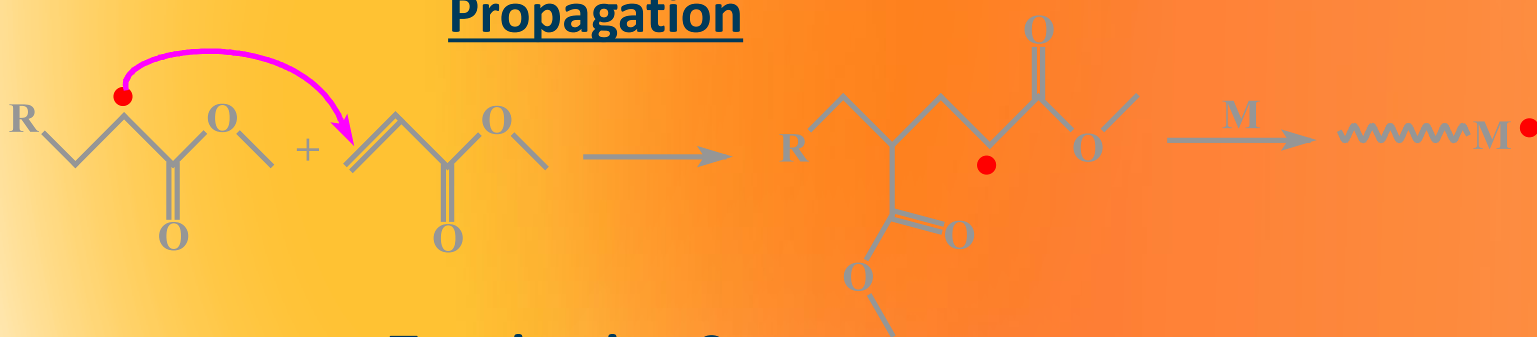
$R{-}CH{=}CH_2$

FREE RADICAL CURING

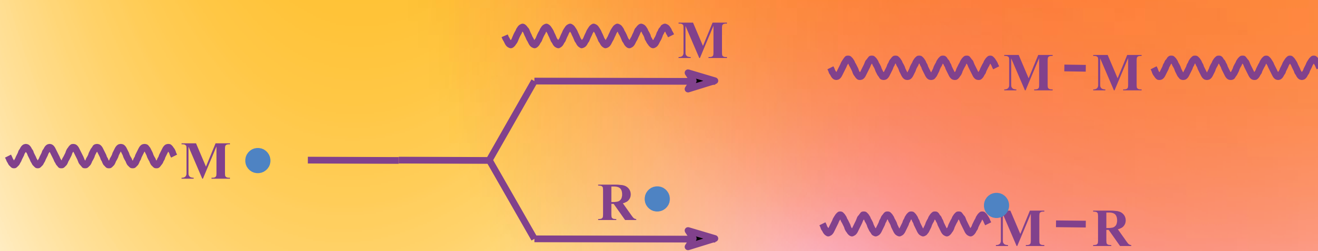
Initiation Step



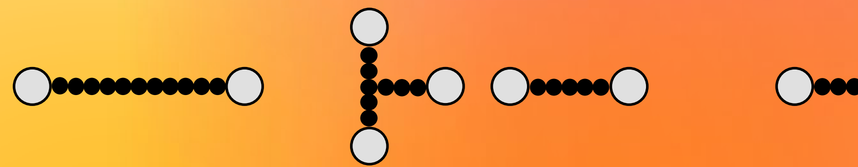
Propagation



Termination Steps



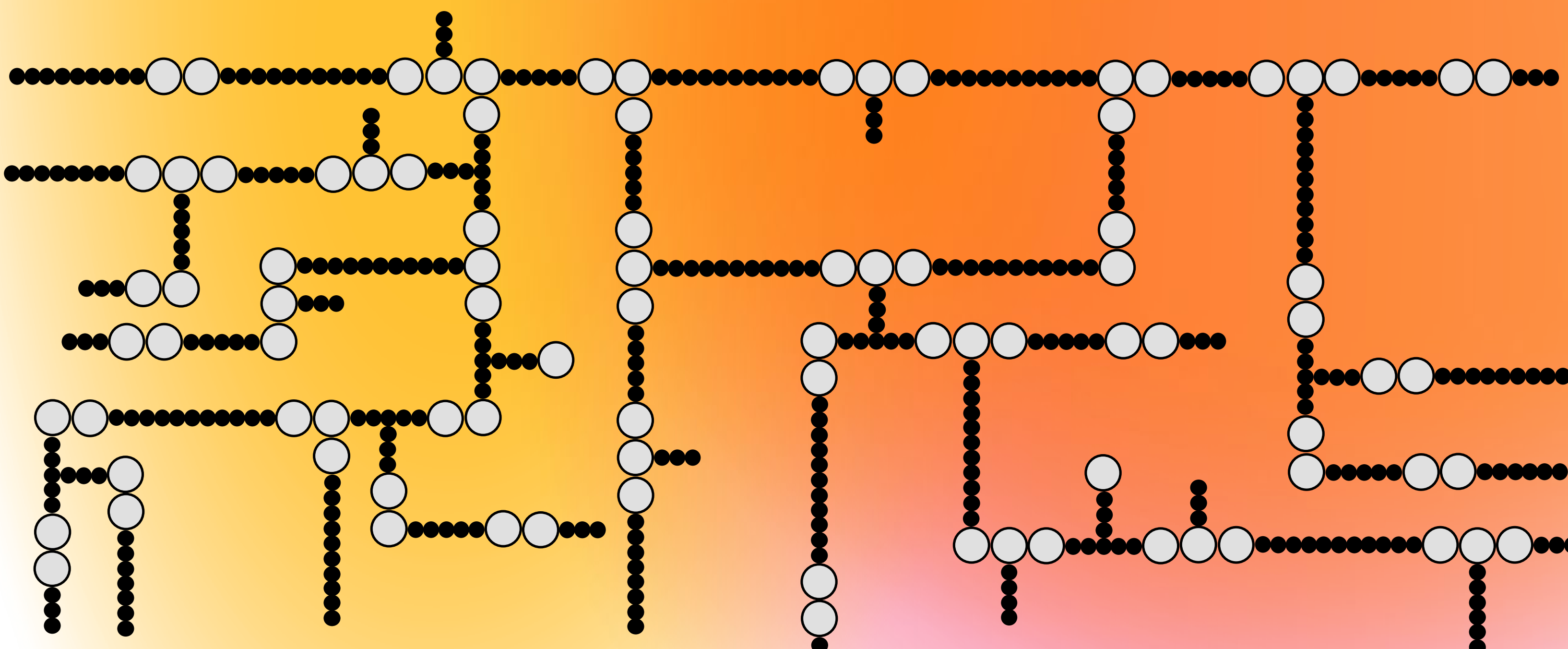
FREE RADICAL CURING



Oligomer

Multifunctional Monomers

Monofunctional Monomers



INHIBITION OF PREMATURE POLYMERIZATION

Storage Stability

- 500-1000 ppm of a radical scavenger
  - Quinones
- Oxygenated systems
- Generally no effect on cure speed
- May impact labeling
  - New GHS regulations

POLYMERIZATION vs. CONVERSION

Adequate cure (polymerization) is defined by the end use

- Cured state (% conversion) that provides the coating or ink with the required properties:
  - Tack free state (thumb twist)
  - Specified solvent resistance (MEK Rubs)
  - Scratch and/or abrasion resistance specifications
  - Analytical techniques (extractables)
    - FTIR/LC/GC-MS : Food packaging (migration / extraction

POLYMERIZATION vs. CONVERSION

100% conversion

- Complete consumption of double bonds
- Generally not achieved
- Vitrification limits mobility of free radicals
  - Crosslinking or hinders mobility

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Component	Inks	UV Inks
Color	Pigment	Pigment
Vehicle	Polymer	Oligomer
Diluent	Water, Solvent	Monomer
Additives	Waxes, Surfactants	Waxes, Surfactants
Catalyst	None	Photoinitiator
Neutralizer	Ammonia, Amine	None

UV FREE RADICAL CURING FORMULATION

Acrylated Oligomer(s), Epoxies, etc.
basic coating properties

Monofunctional Monomer(s)
viscosity reduction, flexibility

Multifunctional Monomer(s)
viscosity reduction, crosslinking

Additives
performance fine tuning

Photoinitiator Package
radical generation

UV →

CURED PRODUCT

EB FREE RADICAL

Acrylated Oligomer(s)
basic coating properties

Monofunctional Monomer(s)
viscosity reduction, flexibility

Multifunctional Monomer(s)
viscosity reduction, crosslinking

Additives
performance fine tuning

Electrons →

CURED PRODUCT

ACRYLATED OLIGOMERS (PREPOLYMERS, RESINS

- High viscosity
  - Usually require dilution
- High molecular weight
  - 500 - 5,000
- Provide much of the overall performance of cured film or ink
- Functionality ranges from 2 - 6
- Oligomer additives can affect performance and/or labeling:
  - Catalysts, inhibitors

HEALTH & SAFETY

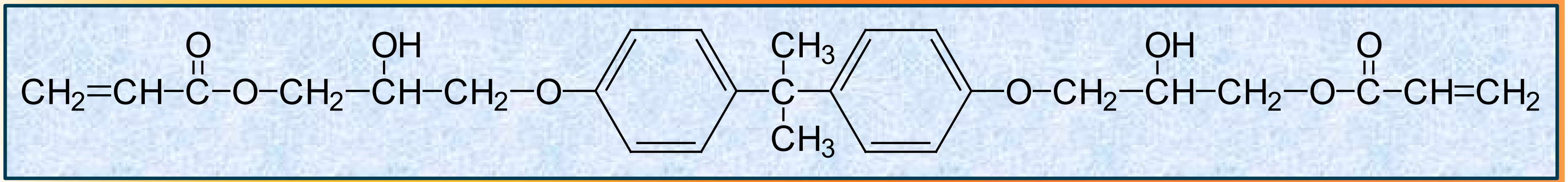
(METH)ACRYLATES in general:

- Non-toxic
- May be irritants
  - Skin
  - Eye
- Low vapor pressure
- Good industrial/lab hygiene
  - Review SDS's
  - Avoid skin contact
  - Wear appropriate PPE
    - Safety glasses
    - Gloves
    - Lab coats

ACRYLATED OLIGOMERS

(Meth)Acrylated	Characteristics
Epoxies	Economical, fast curing, hard, solvent resistance; BPA issue
Aliphatic Urethanes	Flexible, tough, non-yellowing, best weathering properties
Aromatic Urethanes	Flexible, tough, lower cost than aliphatic urethanes
Polyesters	Good pigment wetting properties, lower viscosities, good printing properties
Specialty Polyesters	Good adhesion, special applications
Amines	Faster cure speed; mitigate oxygen inhibition
Acrylics	Good weathering; low shrinkage

ACRYLATED EPOXY OLIGOMER



Bisphenol A Diglycidyl Ether Diacrylate

diglycidyl ether + acrylate functional organic acid

BPA derived

ACRYLATED EPOXY OLIGOMERS

Basic BPA Epoxy Acrylate

- Economical
- Very fast cure response
- Poor pigment wetting
- Good hardness
- Excellent solvent and chemical resistance
- High tensile strength, low elongation
- Moderate shrinkage
- High viscosity
- Low oxygen inhibition
- OH groups available for additional reactions
- BPA derived

MODIFIED EPOXY OLIGOMERS

Fatty Acid Modified Epoxy Acrylates

- Improved Pigment Wetting
- Slower Cure Speed
- Less Solvent Resistance
- Higher Cost
- BPA derived

ACRYLATED EPOXY OLIGOMERS

Other Epoxy Acrylates

Epoxidized Oils: soya, linseed, castor

- Relatively low viscosity
- Good flow and wetting properties
- Improved flexibility
- Slower cure
- Softer ink film
- No BPA impurities

ACRYLATED EPOXY OLIGOMERS

In Litho Inks

- Lower cost oligomer
- Higher ink tack
- Lower ink misting
- Lower ink flow
- Narrow ink-water balance
- BPA limits use in food packaging

ACRYLATED EPOXY OLIGOMERS

In Overprint Varnishes (OPV's)

- Oligomer of choice
  - BPA impurities impacting this
- Economical
- Excellent reactivity
- Hardness
- Chemical and solvent resistance

ACRYLATED POLYESTER OLIGOMER

$$(CH_2{=}CH{-}C({=}O){-}O)_2{-}R{-}O{-}C({=}O){-}R'{-}C({=}O){-}O{-}R{-}(O{-}C({=}O){-}CH{=}CH_2)_2$$

Polyester Tetra-acrylate

Reaction product of polyol and polyfunctional organic acids

Polyols include: ethylene glycol, diethylene glycol, glycerol, NPG, TMP and others

Organic acids include: Phthalic, isophthalic, adipic, and fatty

Can be designed for food packaging compliance

ACRYLATED POLYESTER OLIGOMERS

General Characteristics

- Engineered for pigment wetting and low viscosity (fatty acid modification); Can also be designed for food packaging compliance

- Viscosity range: 100's - 100,000's cP

- Moderate to high shrinkage
- Moderate to very fast cure response
- 2 - 6 functional
- 300 - 3000 MW

(ACRYLATED) POLYESTER OLIGOMERS

- **Acrylated**
  - Most popular and useful
  - 2 - 6 functional
  - Moderately hard and low elongation after cure
  - Must balance low viscosity with pigment wetting and flow
- **Non-acrylated**
  - Adhesion promoters
  - Formulation extenders
- **BPA impurities MAY be present**
  - Confirm with supplier

(ACRYLATED) POLYESTER OLIGOMERS

Specialty

- Low shrinkage
- Good adhesion
- Moderate to fast cure response

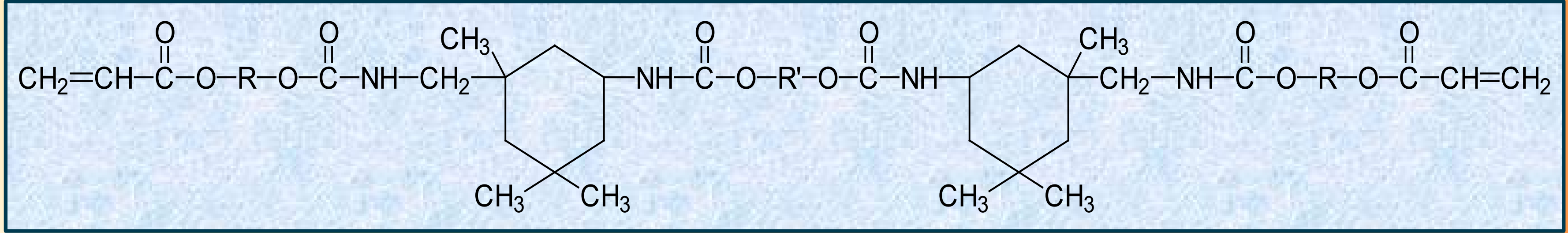
- **Chlorinated**
  - Non-acrylate functional
  - Adhesion to polyolefins and metals
  - Chlorine under regulatory pressure; non-chlorinated versions available
- **Acidic**
  - Non-acrylate functional
  - Adhesion to polyolefins and metals

(ACRYLATED) POLYESTER OLIGOMERS

In Litho Inks

- Preferred oligomer type
- Provides
  - Pigment wetting
  - Color development
  - Reactivity
  - Ink-water balance
  - Printability
  - Adhesion to non-porous substrates
  - Food packaging compliance

ACRYLATED URETHANE OLIGOMERS

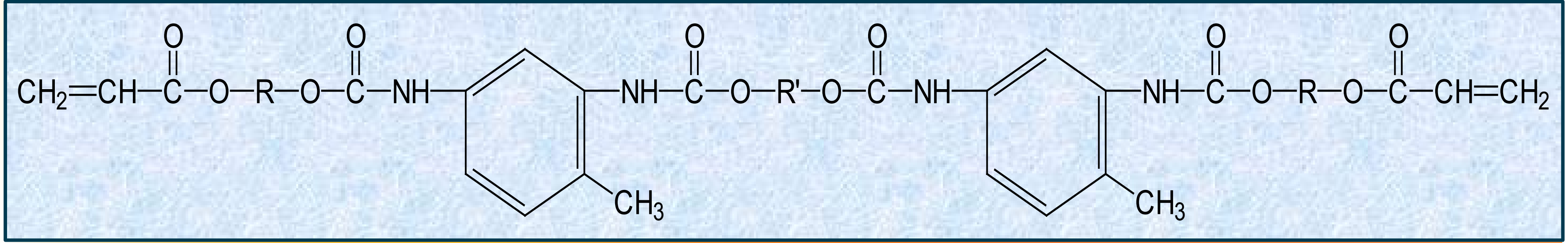


Aliphatic Urethane Diacrylate

Reaction product of isocyanate (NCO), polyol, and hydroxy-functional acrylate (HAA)

Non-yellowing
IPDI, typical diisocyanate

ACRYLATED URETHANE OLIGOMERS



Aromatic Urethane Diacrylate

Reaction product of isocyanate (NCO), polyol, and hydroxy-functional acrylate (HAA)

Yellowing

TDI, typical diisocyanate

ACRYLATED URETHANE OLIGOMERS

Properties of a given urethane acrylate are controlled by compositional elements

Compositional Variable	End Property
Polyol type	Viscosity
Diisocyanate type	Cure speed
Functionality	Tensile strength
MW distribution	Tensile modulus
Urethane content	Elongation
HAA type	Hardness
	Adhesion
Inhibitor (MEHQ/HQ labeling)	Solvent Resistance
Catalyst (tin types regulated)	Flexibility

ACRYLATED URETHANE OLIGOMERS

In Litho Inks

- Difunctional urethane acrylates
  - Increase flexibility
  - Enhance adhesion
  - Can be designed for food packaging compliance

- Multi-functional urethane acrylates
  - Enhance reactivity
  - Increase hardness
  - Improve chemical and solvent resistance
  - Can be designed for food packaging compliance

OLIGOMER PERFORMANCE

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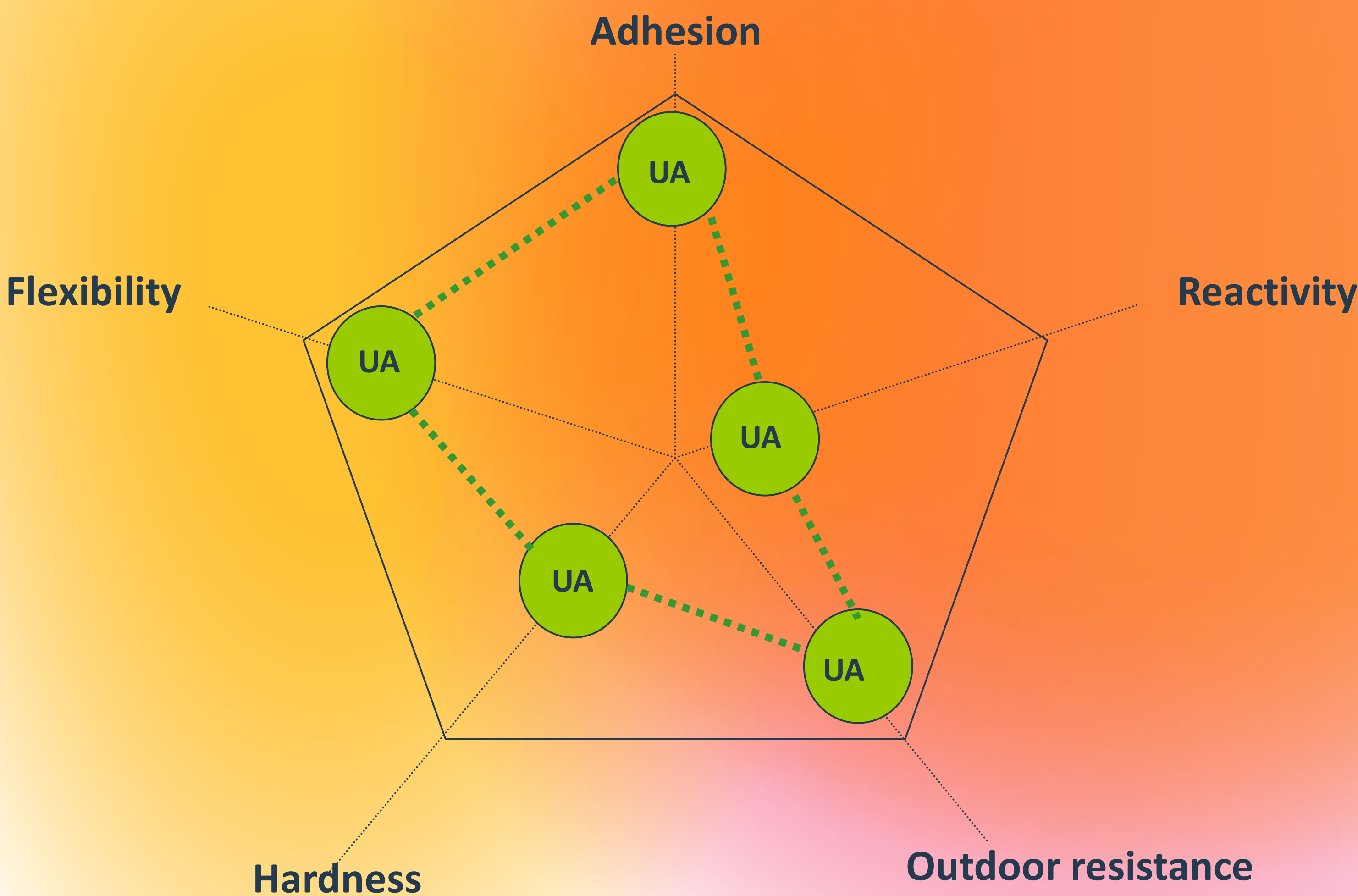
Oligomer backbone chemistry : Urethane



OLIGOMER PERFORMANCE

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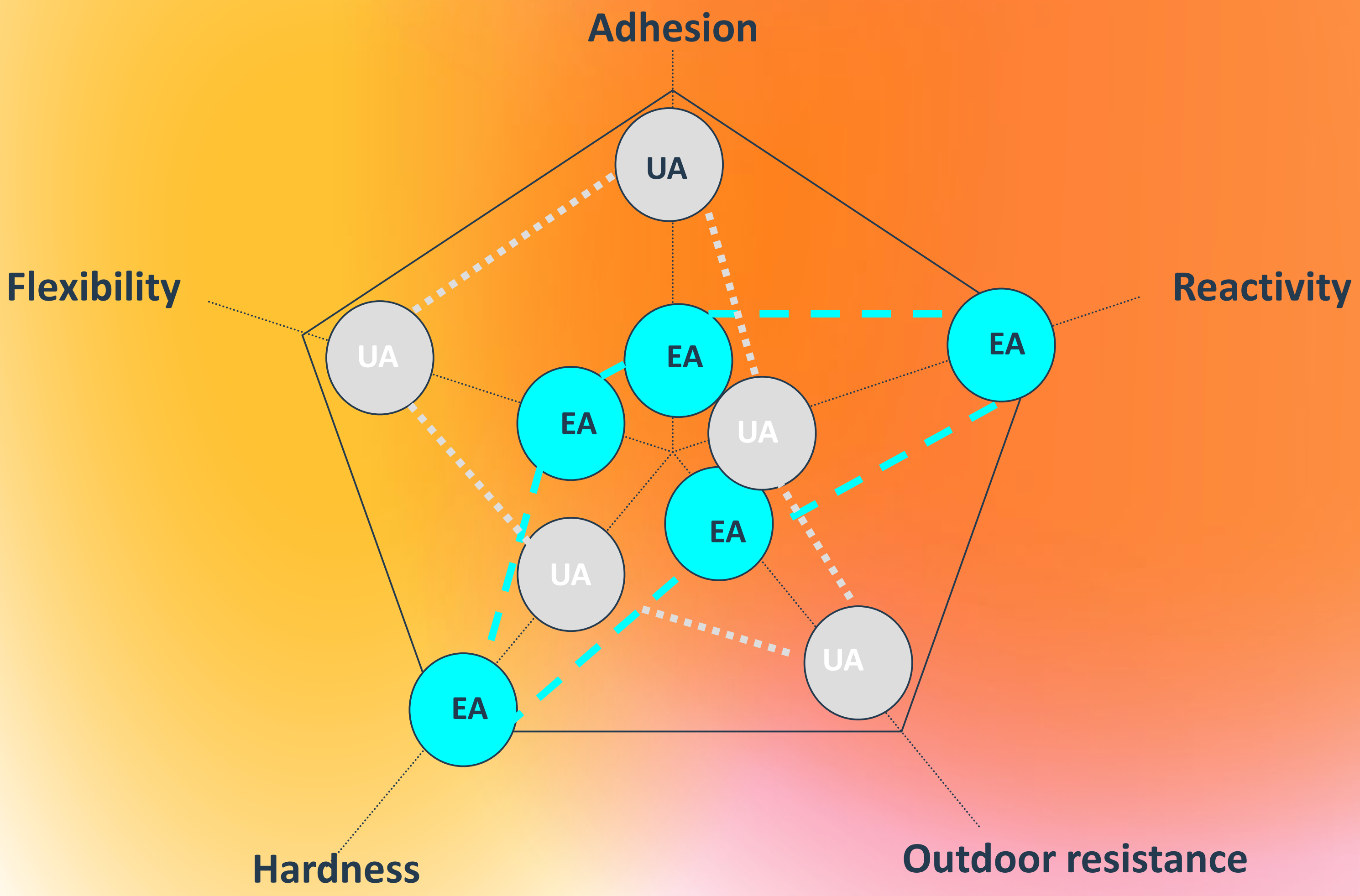
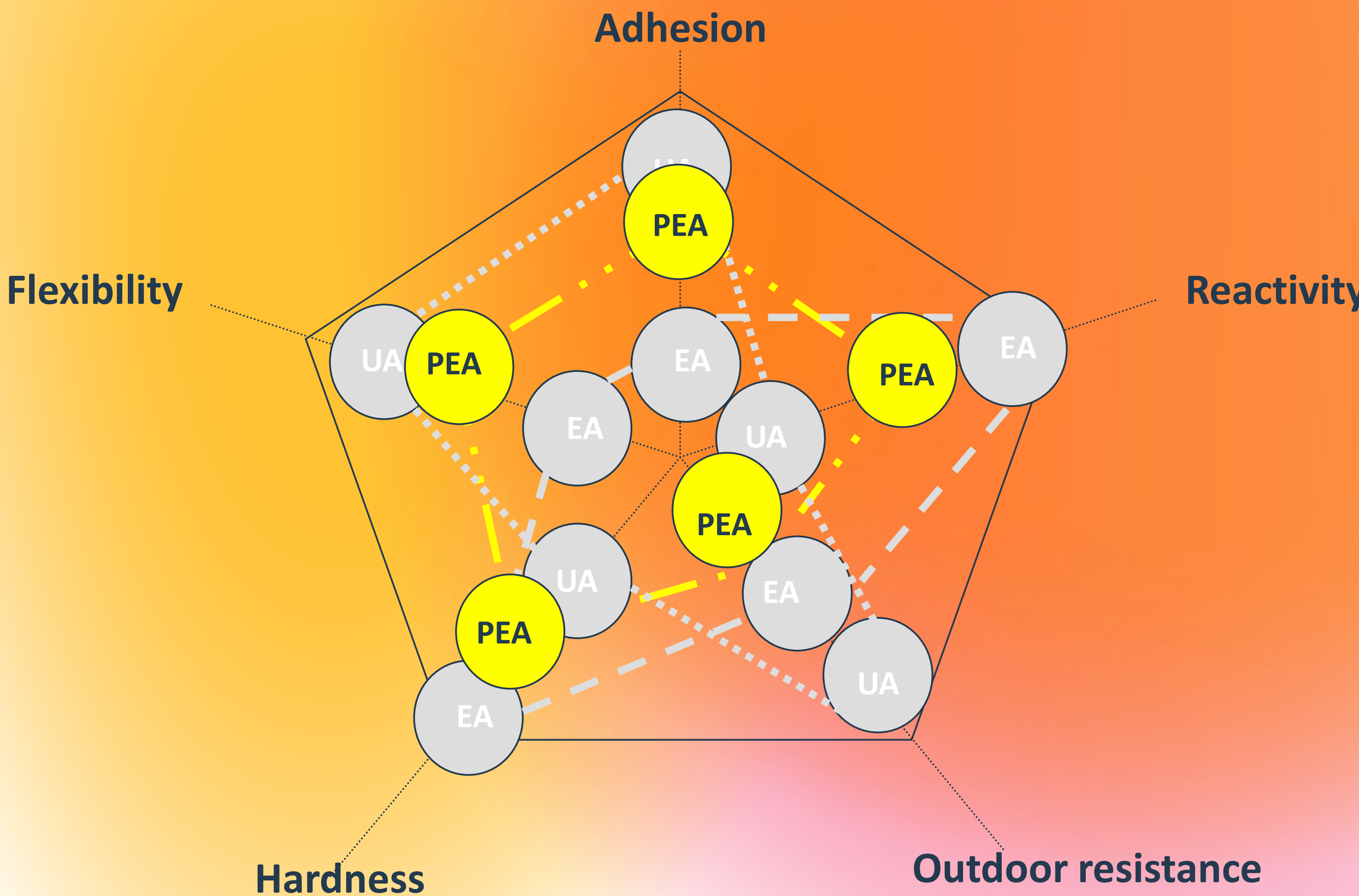
Oligomer backbone chemistry : Epoxy

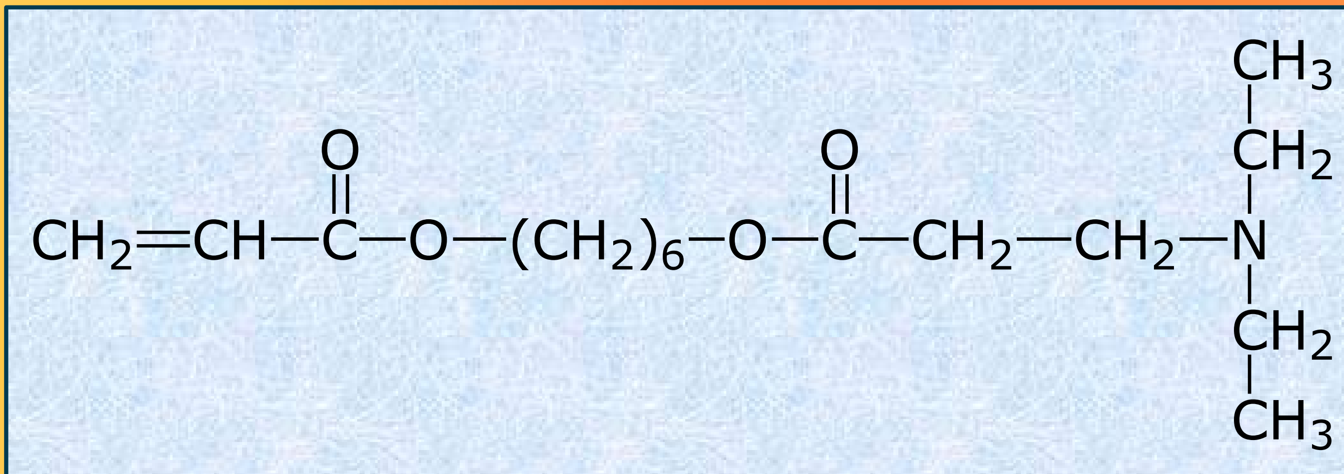


OLIGOMER PERFORMANCE

Oligomer backbone chemistry : Polyester



ACRYLATED AMINE OLIGOMERS



Amine Synergists (co-initiators)

Decrease oxygen inhibition and increase cure speed

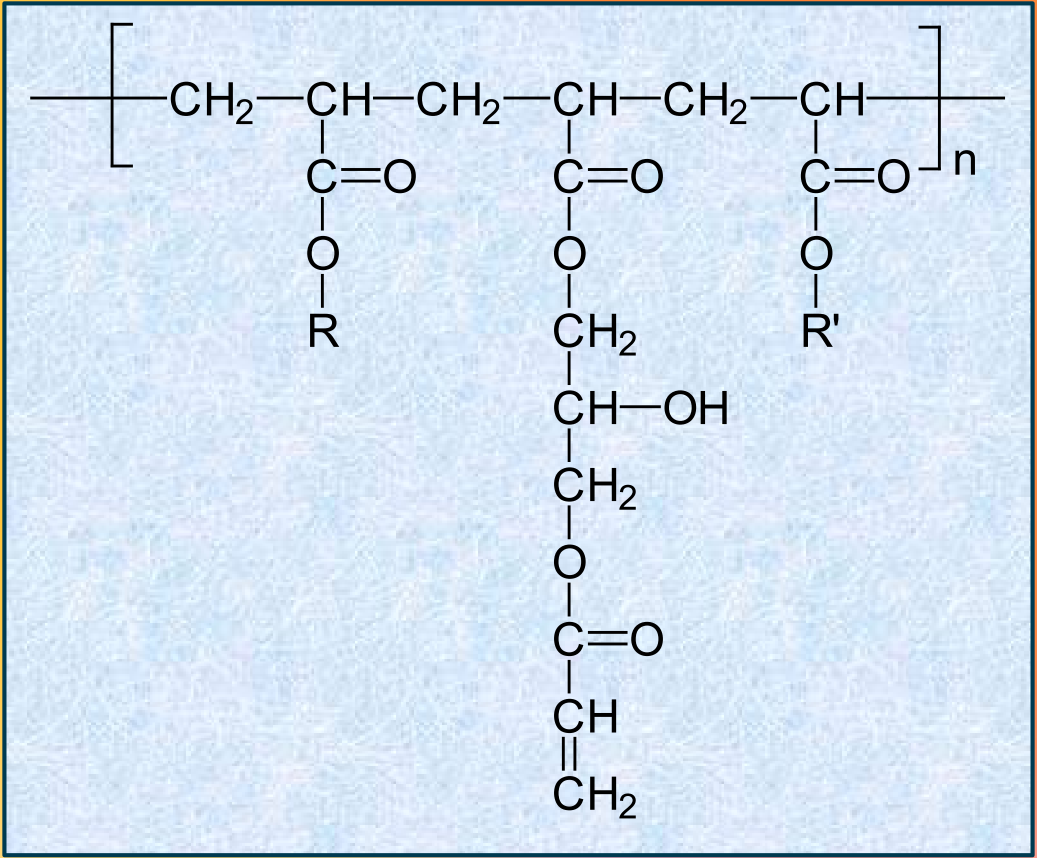
Not used in litho inks because of acidic fountain solutions

Useful in OPVs

ACRYLATED AMINE OLIGOMERS

- Compared to non-acrylated amines:
  - Low odor
  - Low extractables
  - No blooming or discoloration
  - Food packaging compliant
- Not principal oligomer
  - Poor mechanical properties
  - High cost
- Avoid use with acidic materials
- Useful in UV LED cure to mitigate oxygen inhibition

(ACRYLATED) ACRYLIC OLIGOMERS



Acrylated Acrylic

(ACRYLATED) ACRYLIC OLIGOMERS

- Free radical polymerization of monofunctional acrylates (BA, AA), methacrylates (MMA), and vinyls (styrene)

- Broad range of physical & mechanical properties
  - Tg: sub zero to >60°C
  - Soft and flexible to hard and brittle
  - Good to excellent weatherability

- Two Types
  - Acrylated
    - Improve adhesion without sacrificing cure speed
  - Non-acrylated
    - Detract from cure speed
    - Improve adhesion (reduce shrinkage)

(ACRYLATED) ACRYLIC OLIGOMERS

In Litho Inks

- Generally good pigment wetters
  - Functionality of pendant groups affect pigment wetting and adhesion
- Additive to improve adhesion
- Limited use due to misting tendencies
- Some types meet food packaging regulations

NON-ACRYLATED OLIGOMERS

Saturated Resins

- Acrylics
- Polyesters
- Vinyls
- Hydrocarbons

- Dissolve in acrylated monomers
- Minimize shrinkage
- Increase adhesion
- Possible to meet food packaging regulations

UV FREE RADICAL CURING FORMULATION

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

$\xrightarrow{\text{UV}}$ CURED PRODUCT

DILUENTS

Polymerizable

- Acrylated Monomers
  - > Monofunctional
  - > Multifunctional (MFM'S)
  - > Polyol Polyacrylates
  - > Reactive Diluents

Non-Polymerizable

- Solvent
- Water

NAPIM SUMMER COURSE

Properties vs. Monomer Functionality

- Rate and Crosslink Density Increase with Monomer Functionality

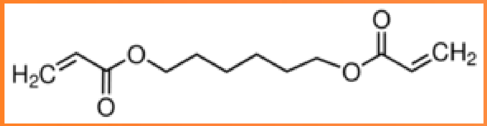
  Mono < di < tri < tetra < penta < hexa

- Conversion Decreases with Monomer Functionality

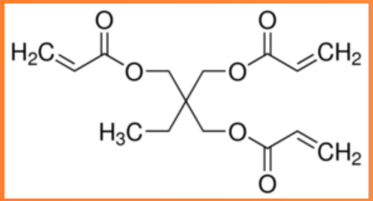
  Mono > di > tri > tetra > penta > hexa

- Viscosity Generally Increases with Functionality

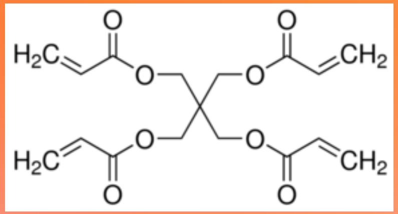
Hexanediol diacrylate(HDDA or HDODA)



Trimethylolpropane triacrylate(TMPTA)



Pentaerthritol tetraacrylate(PETA)



ACRYLATED MONOMERS

Choice of Monomer Influences

Liquid Properties

- Formulation Viscosity
- Cure Speed
- Surface Tension
- Volatility & Odor
- Stability
- Color
- Regulatory Constraints

Cured Film Properties

- Weatherability & Color
- Flexibility
- Hardness
- Adhesion
- Resistance Properties
- Tg, Tensile Strength & Modulus, Elongation
- Shrinkage
- Etc.

MONOMER SELECTION

Monofunctionals

- Lower cure speed
- Residual uncured; not for food packaging
- Impart flexibility; increase MW between x-links
- Improve adhesion
- Significantly reduce viscosity

- May cause swelling of photopolymer printing plates
- Rarely used in litho
- Increased labeling due to REACH testing

MONOMER SELECTION

Difunctionals

- Improve solvent resistance while maintaining flexibility
- Provide adhesion
- Reduce viscosity
- Propoxylates reduce surface tension and improve substrate wetting and increase flexibility
- Some are food packaging compliant

- Aggressive monomers may cause swelling of photopolymer plates (HDDA not used in litho)

ACRYLATED MONOMERS

Difunctional Monomer

$$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}(C_3H_6O)_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH{=}CH_2$$

TPGDA

Tripropylene Glycol Diacrylate

MONOMER SELECTION

Trifunctional and higher functionalities

- Best pigment wetter is propoxylated glycerol triacrylate (GPTA or OTA-480)
- Ethoxylates improve flow
- Increase cure speed but can make material brittle
- Typically higher in viscosity and not as effective at reducing viscosity
- Easier to meet food packaging regulations

UV-Cured Film Properties

Property	Monofunctional	Multifunctional
Tensile Strength	↓	↑
Elongation	↑	↓
Hardness	↓	↑
Flexibility	↑	↓
Impact Resistance	↑	↓
Abrasion Resistance	↓	↑

MONOMERS SPECIFIC TO LITHOGRAPHY

- Pigment wetting
  - GPTA, Propoxylated NPGDA
- Water balance
  - GPTA
- Food packaging
  - DPHA, alkoxylated PETA
- Use monofunctionals and aggressive difunctionals (such as HDDA) with caution due to roller and plate swelling
- Excessive monomer content adversely affects litho properties
  - Monomers are typically 5-10% of the formula
- Viscosity reduction is less important
  - Use higher viscosity reactive diluents such as ethoxylated bisphenol A or DiTMPTA

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Additives
performance fine tuning

Photoinitiator Package
radical generation

UV →

CURED PRODUCT

FORMULATING ENERGY CURABLE SYSTEMS

ALL COMPONENTS INFLUENCE FINAL PROPERTIES

Oligomer
Type
Molecular Weight
Functionality

Monomer
Reactive Diluent
Functionality

Photoinitiator
Type
Concentration

Other Components
Additives
Pigments

Formulator Expertise
Formulator Specific

Additives & Pigments

- Pigments
  - inorganic
  - organic
  - fluorescent
- Fillers
  - $CaCO_3$
  - $BaSO_4$
  - talc
  - clays
- Defoamers
  - silicones
- Flatting Agents
  - silicas
  - waxes (PE/PP/PTFE)
  - microspheres
- Wetting Agents
  - reactive silicones
  - silicones
  - fluorocarbons
  - polyacrylics
- Slip Aids
  - silicones
  - waxes (PE/PTFE/carnauba)

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UV →

CURED PRODUCT

PHOTOINITIATORS: 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**
Transmission	The amount of light passing through a material; the ratio between the outgoing (I) and the incoming intensity (I_o), $\%T = (I/I_o) \times 100$
Photon	**A quantum of light; a packet of light energy**
Free Radical	Molecule fragment with 1 unpaired electron, not an ion (has no charge)

WHY ARE PHOTOINITIATIORS NECESSARY

<u>Role of PI</u>

- Absorb UV light to form active species (free radicals)
- React with monomer/oligomer to initiate polymerization

- PIs absorb UV light at specific wavelengths
- Match PI λ_{max} with UV lamp emission (check TDS)
- Only reacts with UV-Vis energy, not heat
  - Thermally stable
  - Long pot life/shelf life

UV FREE RADICAL POLYMERIZATION

Steps in Free Radical Process

- **Free Radical Formation**
- **Initiation**
- **Propagation**
- **Termination**

- ***Photoinitiator type and concentration play a role in initiation and termination***

➢ ***UV polymerization is line-of-sight only – shadowed areas will not cure***

UV FREE RADICAL POLYMERIZATION

Free Radical Formation

- System is irradiated and the photoinitiator absorbs some of the incoming energy
- Photoinitiator forms one or more free radicals
- Number of free radicals created is dependent on PI concentration

Initiation Process

- A free radical then combines with an acrylate to form a new radical that is the active species for the growing polymer

UV FREE RADICAL POLYMERIZATION

Propagation Process

**Free radical
on end of polymer
chain**

**Reacts with an
acrylate to make a
new radical**

Also referred to as a chain reaction

UV FREE RADICAL POLYMERIZATION

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
  - Lower molecular weight polymers
  - Poorer physical properties (e.g. low adhesion, greater marring, poor tensile properties)

UV FREE RADICAL POLYMERIZATION

Oxygen Inhibition (Inhibition of Surface Cure)

Reactions of Oxygen in UV Free Radical Polymerization

Air contains 21% Oxygen

Causes Problems

- Tacky surfaces
- Reduced coating properties

- QUENCHING REACTION

$$PI^{\star} + O_2 \longrightarrow PI + O_2^{\star}$$

- SCAVENGING REACTION

$$R\bullet + O_2^{\star} \longrightarrow R\text{-}O\text{-}O\bullet$$

strong propagating radical

weak propagating radical

UV FREE RADICAL POLYMERIZATION

Oxygen Inhibition - Better Surface Cure from:

- Certain structural components = reactions with oxygen
- Lower weight per double bond = harder coating
- Increased viscosity = decrease in oxygen diffusion
- Increased coating thickness = decrease in oxygen diffusion
- Decreased distance from lamp to substrate = increased irradiance
- Increased exposure time = increased extent of cure
- Higher PI concentration = more initiating radicals
- Shorter wavelengths (UVC) = more absorbance at surface

PHOTOINITIATOR BASICS

Photoinitiator Classes

- Photocleavage (unimolecular PI) Type I
  - α-cleavage PI - Absorbs light and fragments to form the radicals which initiate polymerization.

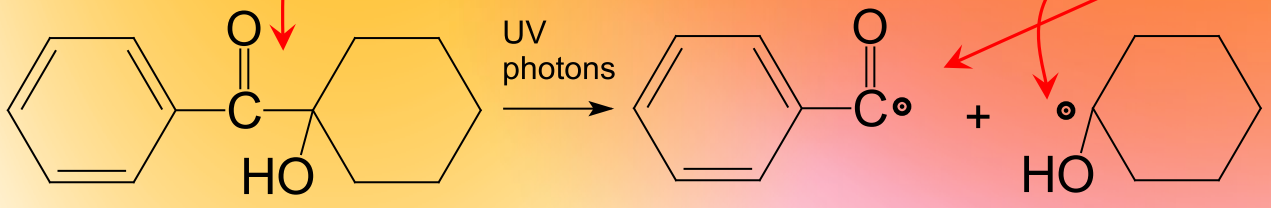
- Photoabstraction (bimolecular PI) Type II
  - Hydrogen abstraction PI - Absorbs light and abstracts hydrogen from another molecule (photoactivator) which produces radicals.
  - Amine synergist (photoactivator) - Donates a hydrogen to the photosensitizer to produce the radicals which initiate polymerization.

Photoinitiator, photosensitizer, and photoactivator are often used interchangeably even though they are not the same.

PHOTOINITIATOR BASICS

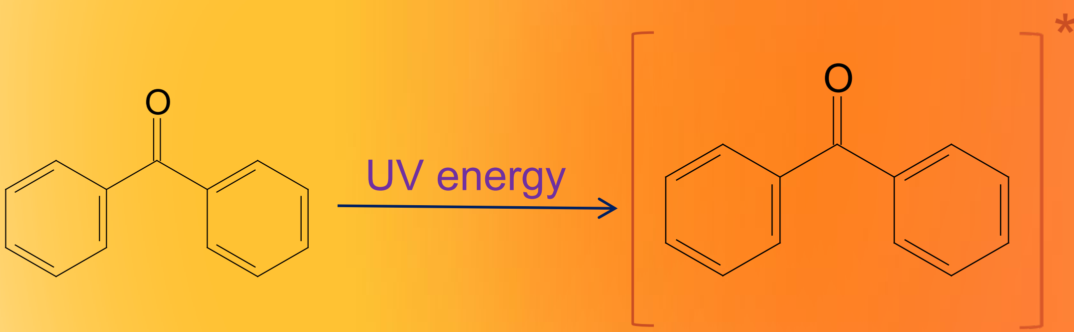
Photocleavage : Type I

After the molecule absorbs UV energy, *this bond* breaks apart to form two new *radicals* that can initiate polymerization (cure)

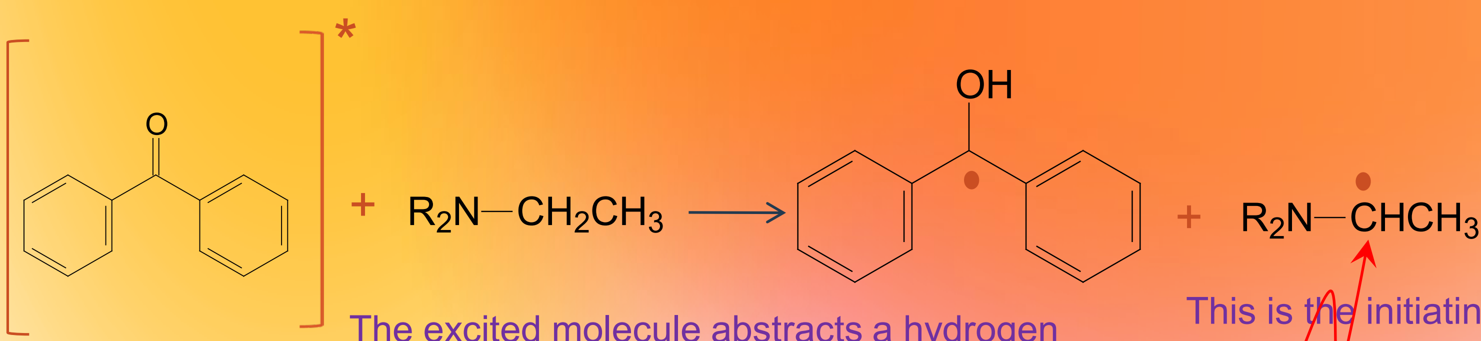


PHOTOINITIATOR BASICS

Photoabstraction



The molecule absorbs UV energy, and becomes *excited*

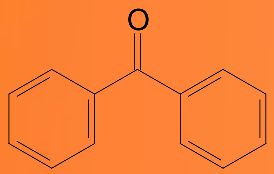


The excited molecule abstracts a hydrogen from another molecule (amines are good, ethers are OK too).

This is the initiating species.

Sensitization

- Some photoinitiators cannot absorb light directly, but require a second molecule to form a free radical.
- The additional required molecule is called a Sensitizer or Photoactivator.
- In this process, light is first absorbed by the sensitizer molecule
- Energy is then transferred to initiating molecule



Benzophenone

BP Flake

PHOTOINITIATOR SELECTION CRITERIA

- Absorption characteristics of photoinitiator and formulated system
- Pigmentation
- Spectral output of UV-Vis lamps
- Oxygen inhibition
- Weatherability (non-yellowing)
- Yellowing upon cure (photobleaching)
- Handling (solid vs. liquid)
- Migration of unreacted species
- Toxicity
- Food packaging approval
- Cost

NAPIM SUMMER COURSE

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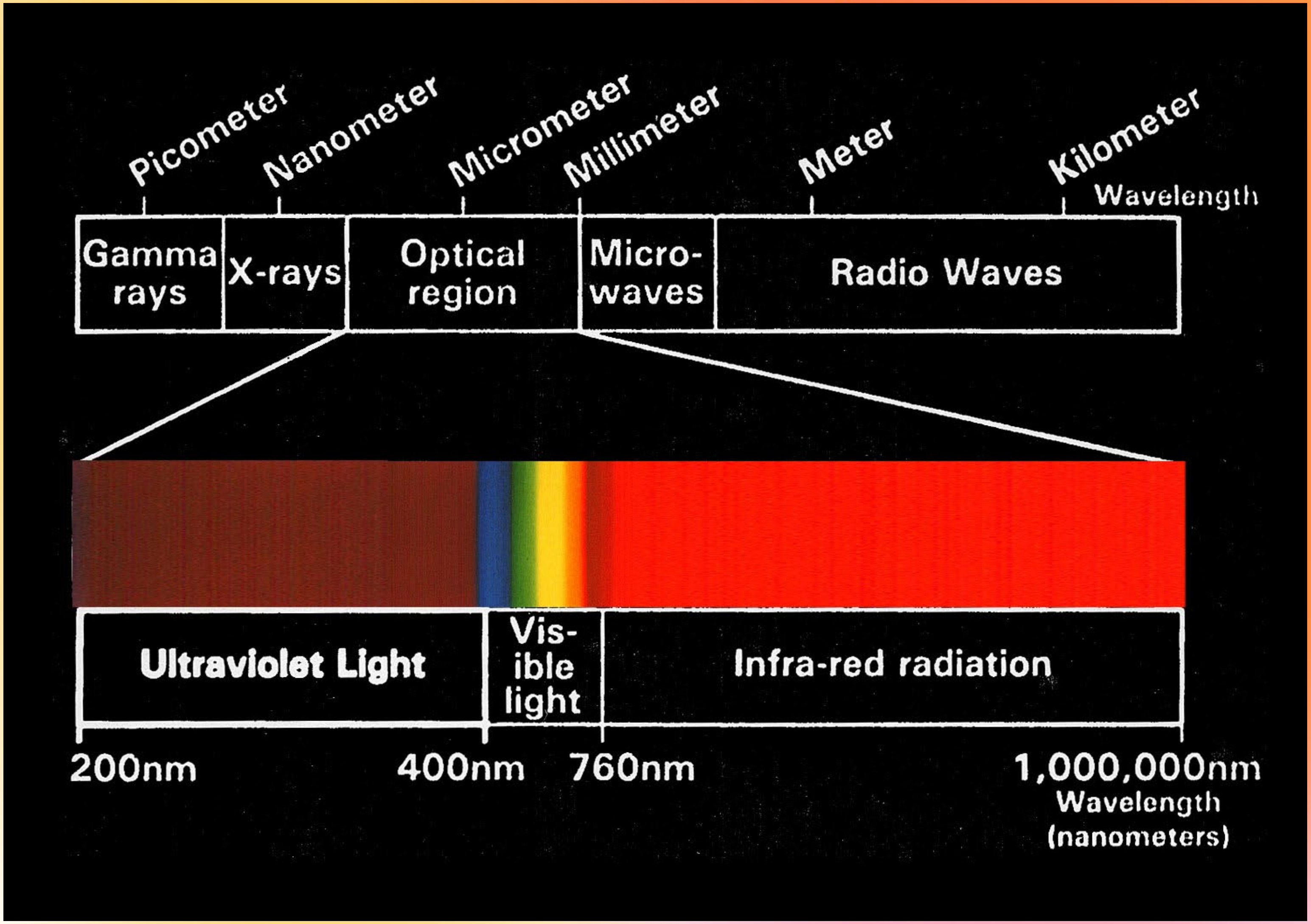
LAMP TYPES & AUXILIARY EQUIPMENT

- UV LAMPS
  - Standard Mercury Bulbs
  - Doped Mercury Bulbs (HUV)
  - UV LED Bulbs
  - Filters, Reflectors, and Optical Designs influence wavelengths and irradiance that reach the substrate

- ELECTRON BEAM

UV LIGHT SPECTRUM

NAPIM SUMMER COURSE

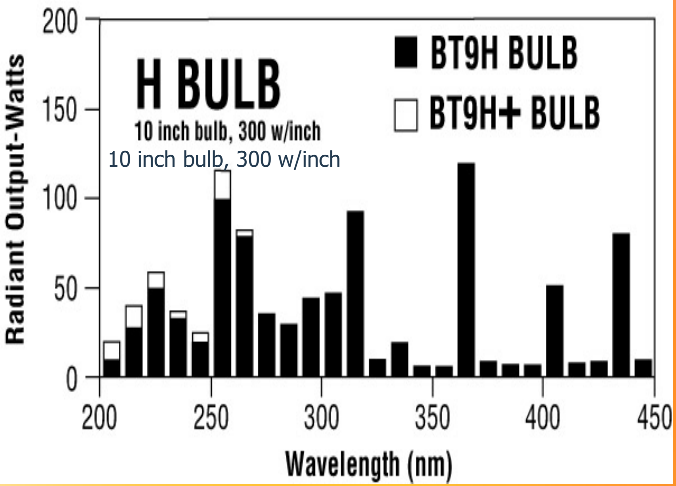


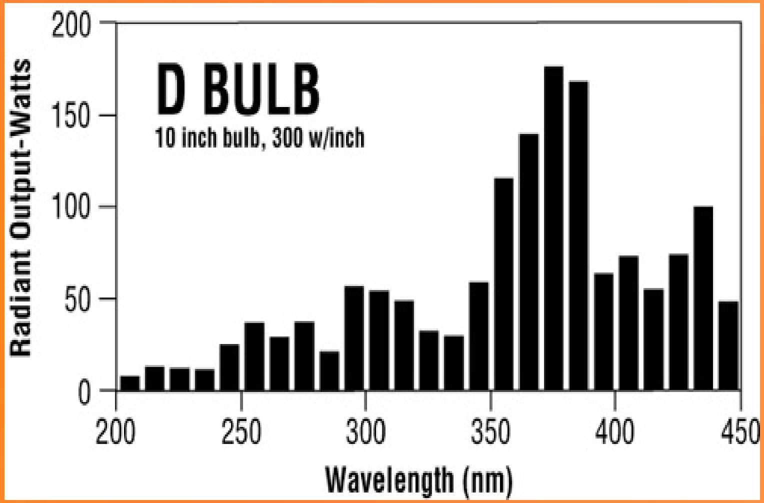
UV SPECTRUM CLASSIFICATION

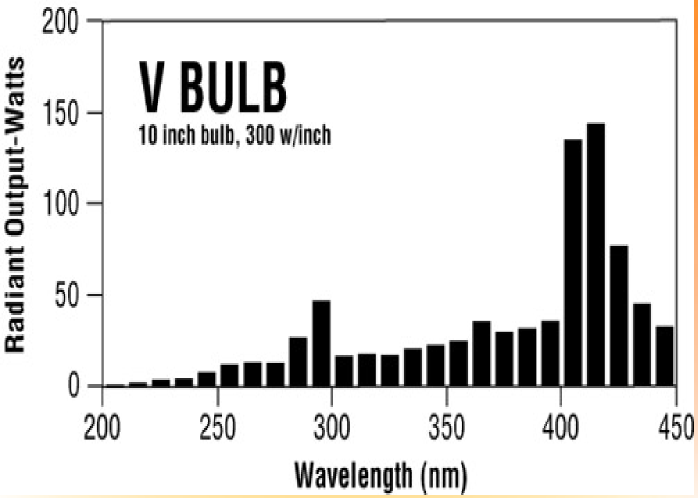
The UV region covers the wavelength range 100-400 nm and is divided into three bands:

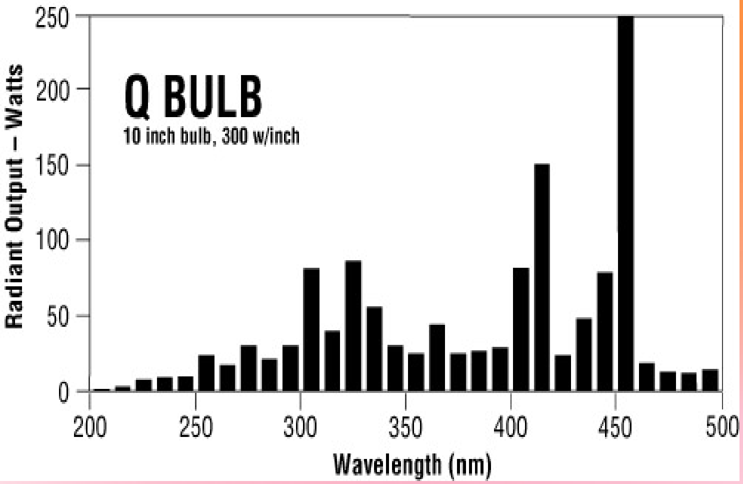
- UVA (315-400 nm) LED region
  - Long Wavelengths – Deep Cure; Adhesion
- UVB (280-315 nm)
  - Medium Wavelengths
- UVC (100-280 nm)
  - Short Wavelengths – Surface Cure
  - Important for Mitigating Oxygen Inhibition

SPECTRAL OUTPUT WITH DIFFERENT BULBS

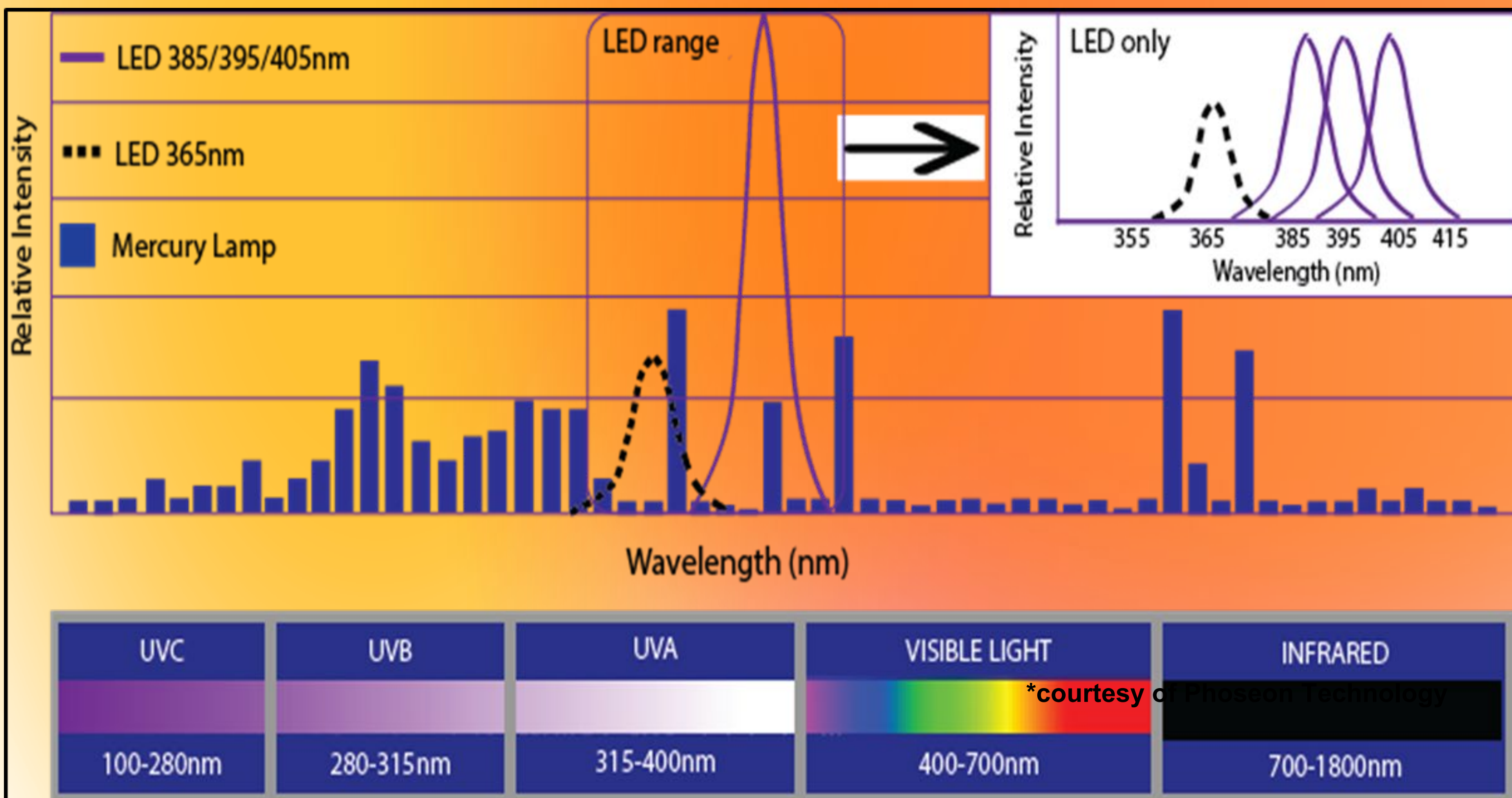




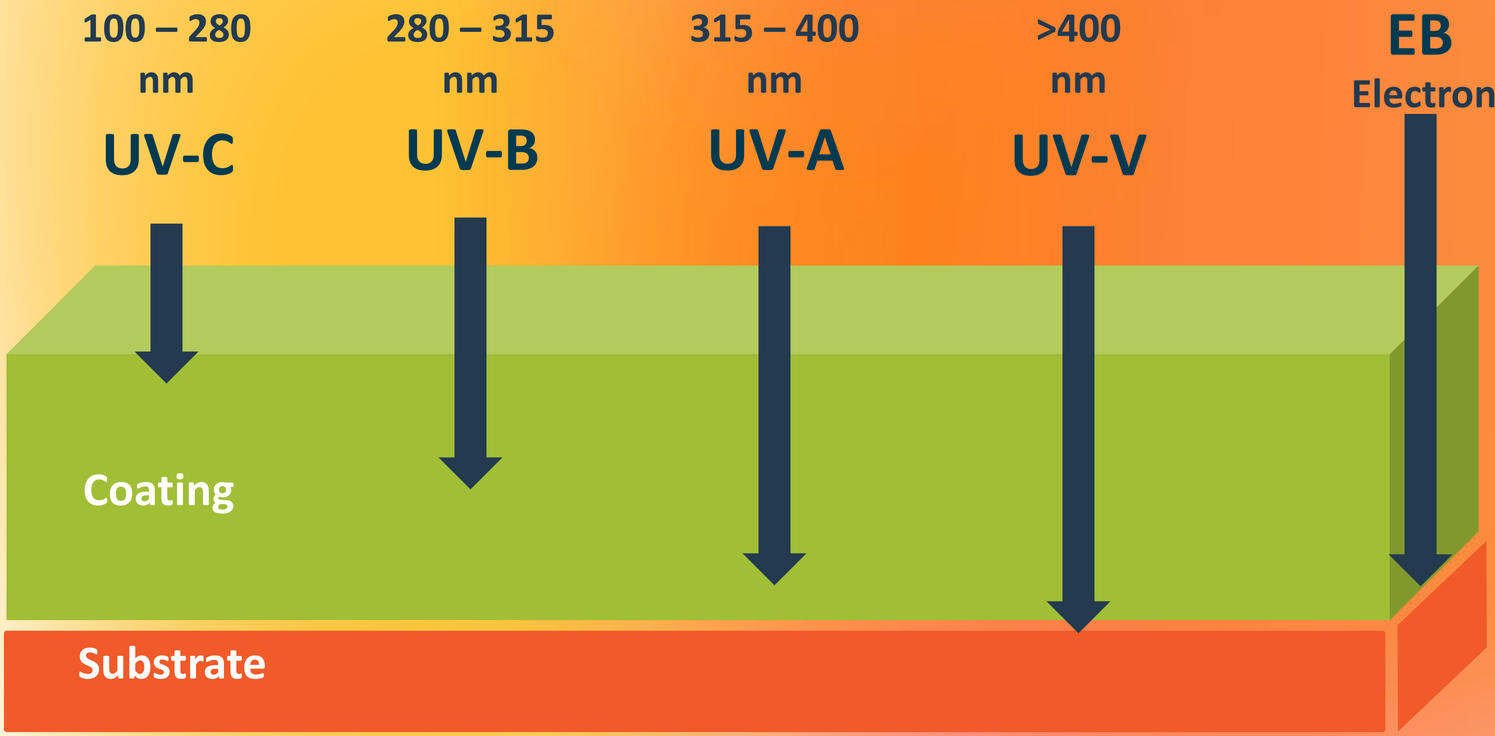




MERCURY LAMP AND LED EMISSION SPECTRA



EB/UV INTERACTIONS WITH COATINGS



- Different parts of the UV spectrum will penetrate to different depths of the coating
- The right photoinitiator(s) will initiate the reaction in the entire coating
- EB does not need a photoinitiator

LOW ENERGY/LONG WAVELENGTH LAMPS

- Do not produce ozone
  - No exhaust needed
  - Easier retrofits
- Less investment
  - Reduced number of lamps
  - Lower energy cost
- Generate less heat
  - Easier to print heat sensitive substrates
- Doped with iron to shift to high wavelengths
  - Reduces lamp life
  - Increases irradiance at substrate (300 watt/inch bulb)
    - >2.41 watts/cm^2 doped vs. 1.68 watts/cm^2 undoped
- Highly functional inks and coatings are required; oxygen inhibition effects
- Photoinitiators that absorb at higher wavelengths are required
  - More expensive
  - Color Issues

UV LED LAMPS

- UV LED is displacing HUV and similar lamps in both retrofits (50%) and new sheetfed offset presses (no regular UV on Komori presses today). Most still have Hg lamp in delivery to cure coating, but this is changing.
- 385-390 nm wavelengths are most popular (can also blend λs in array)
- Optical focusing is needed in sheetfed offset
- Similar value proposition to HUV lamps:
  - Much easier to retrofit (1 day installation)
  - No exhaust: no cleaning of lamps/reflectors; no static
  - Less energy to operate; less CO_2 production
  - Faster make-ready uses less ink; saves money
  - Less heat output for plastic substrates: less distortion and minimizes plasticizer migration. Can use thinner, less expensive plastic substrates
  - Better through cure = better adhesion
  - No/minimal lamp degradation = better quality control; possibility of food packaging applications
  - Long lamp lifetimes saves on lamp replacement costs

UV LED LAMPS

- Disadvantages of UV LED
  - Yellowing issues in thick coatings (had same issue with HUV in the beginning)
  - Photoinitiators are expensive
  - Need better photoinitiators (less yellowing)
  - Surface cure is lacking in some cases
  - Improved inks for surface cure can be more expensive

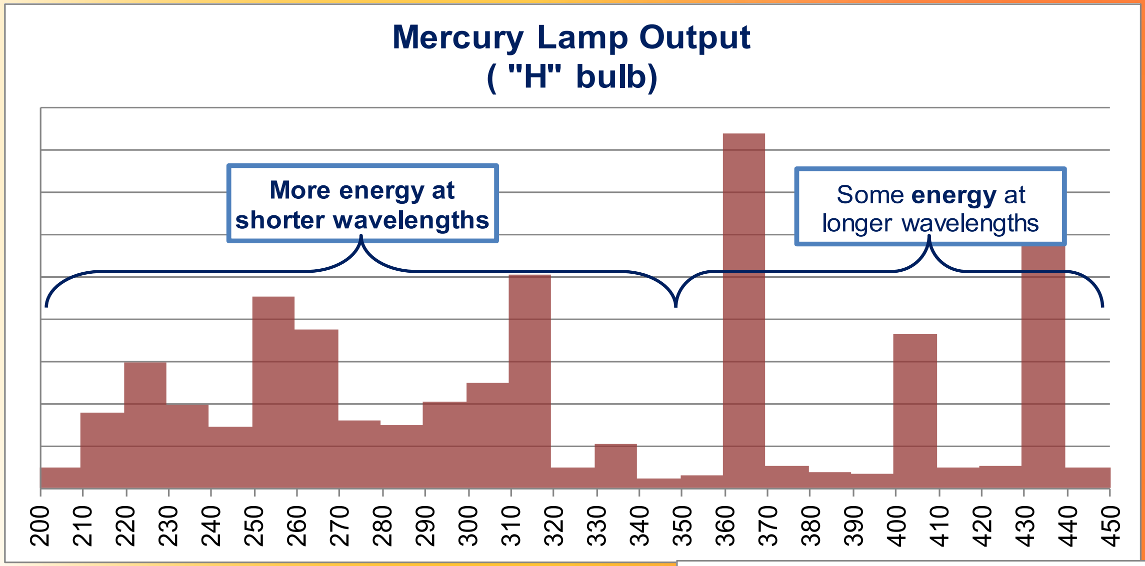
- Multiple suppliers in the sheetfed offset market today, some are:
  - Air Motion Systems
  - Benford
  - GEW

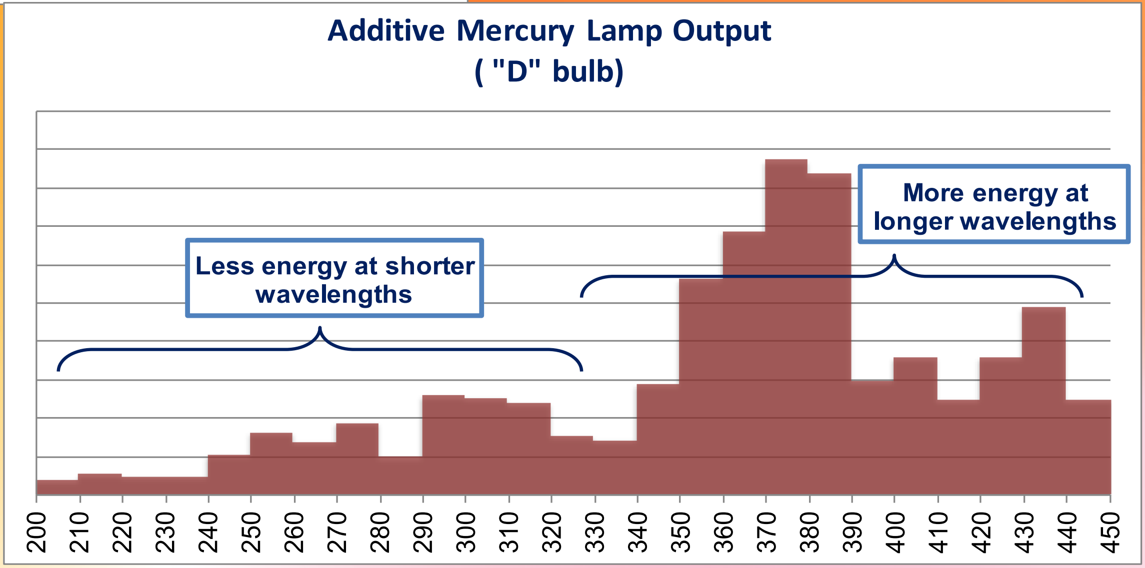
UV LAMP AND PHOTOINITIATOR SELECTION

- Different UV lamps emit energy in different parts of the spectrum
- It is essential to match the absorbance of the PI with the output of the lamp

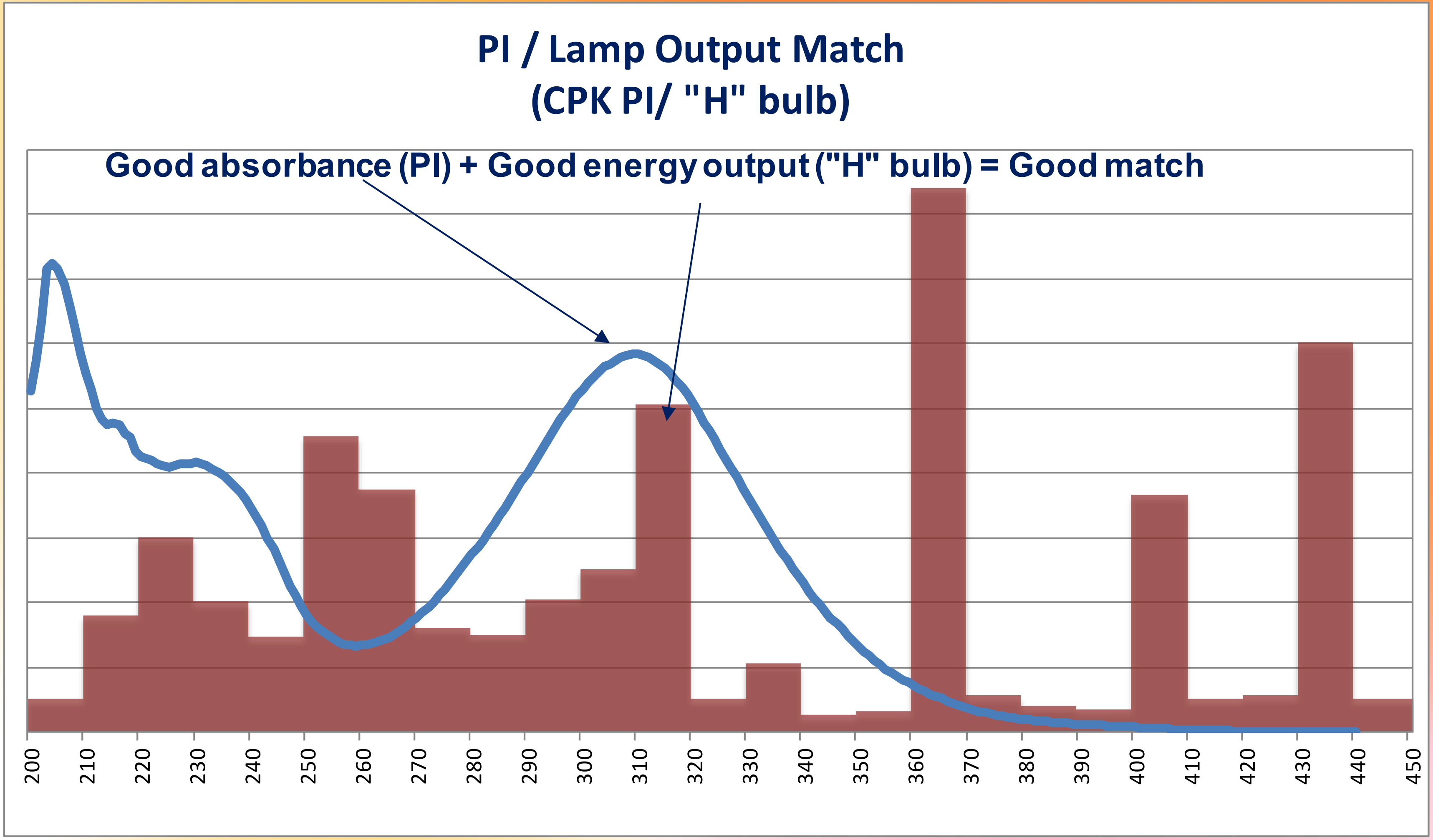
PHOTOINITIATOR CHOICE
UV LAMP EMISSION

napim NAPIM SUMMER COURSE

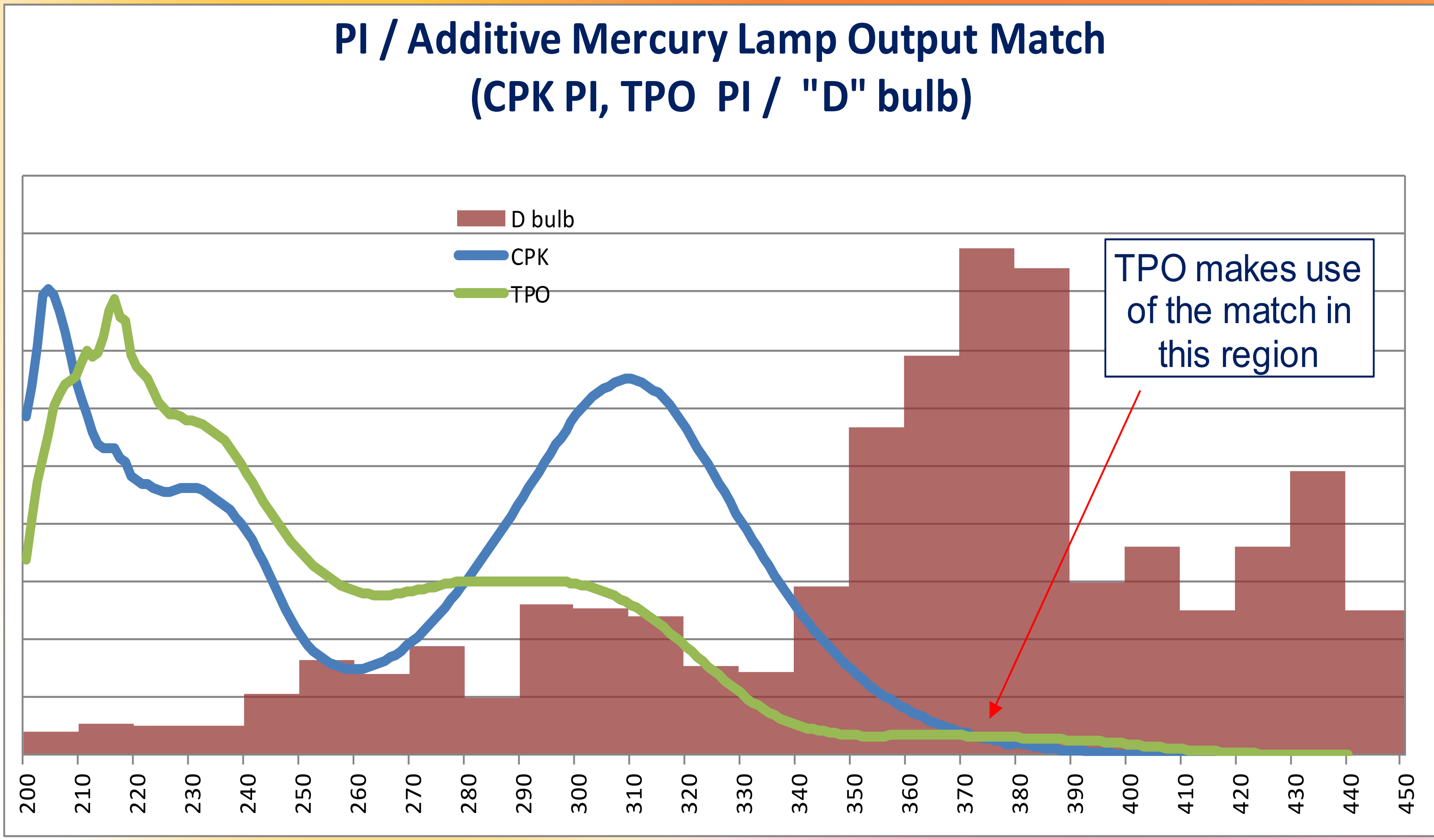




PHOTOINITIATOR : MATCH PI AND UV LAMP

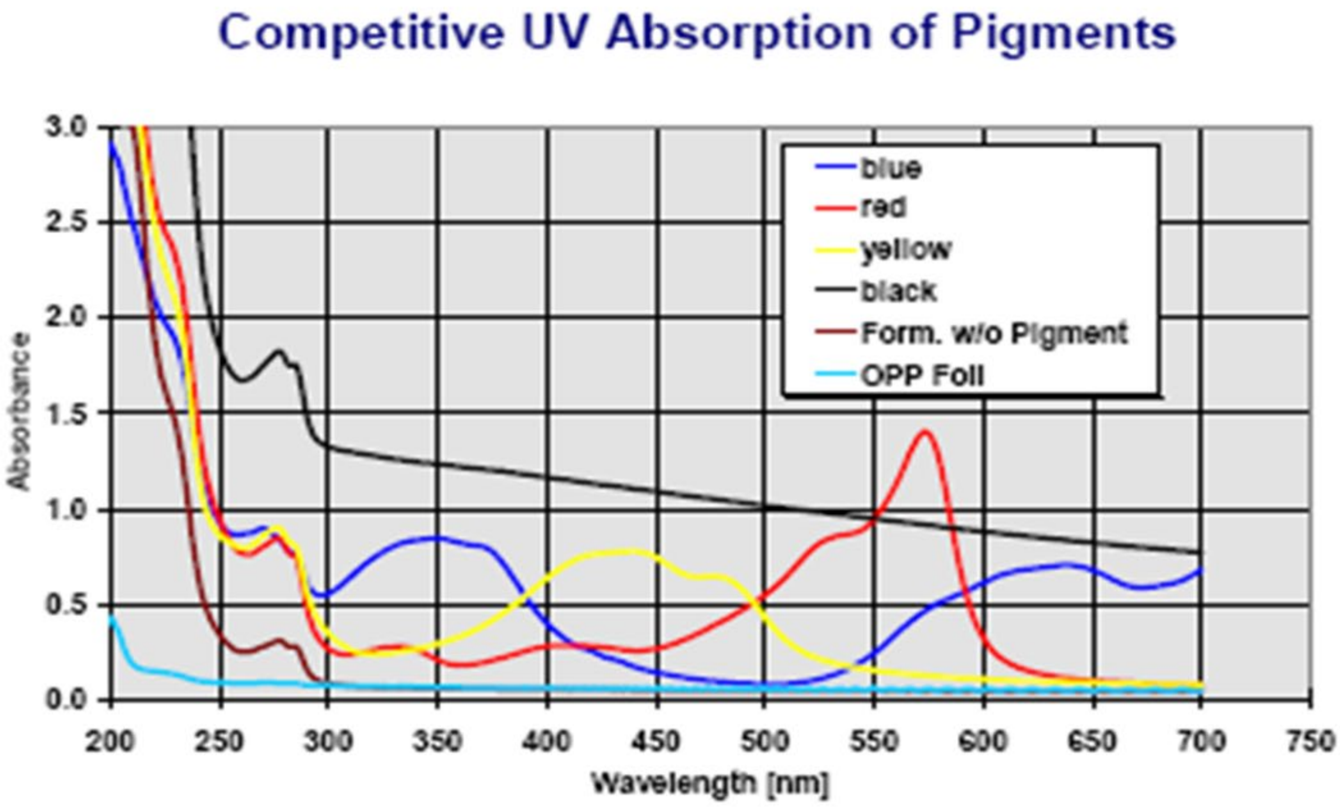


PHOTOINITIATOR SELECTION: MATCH PI AND UV LAMP

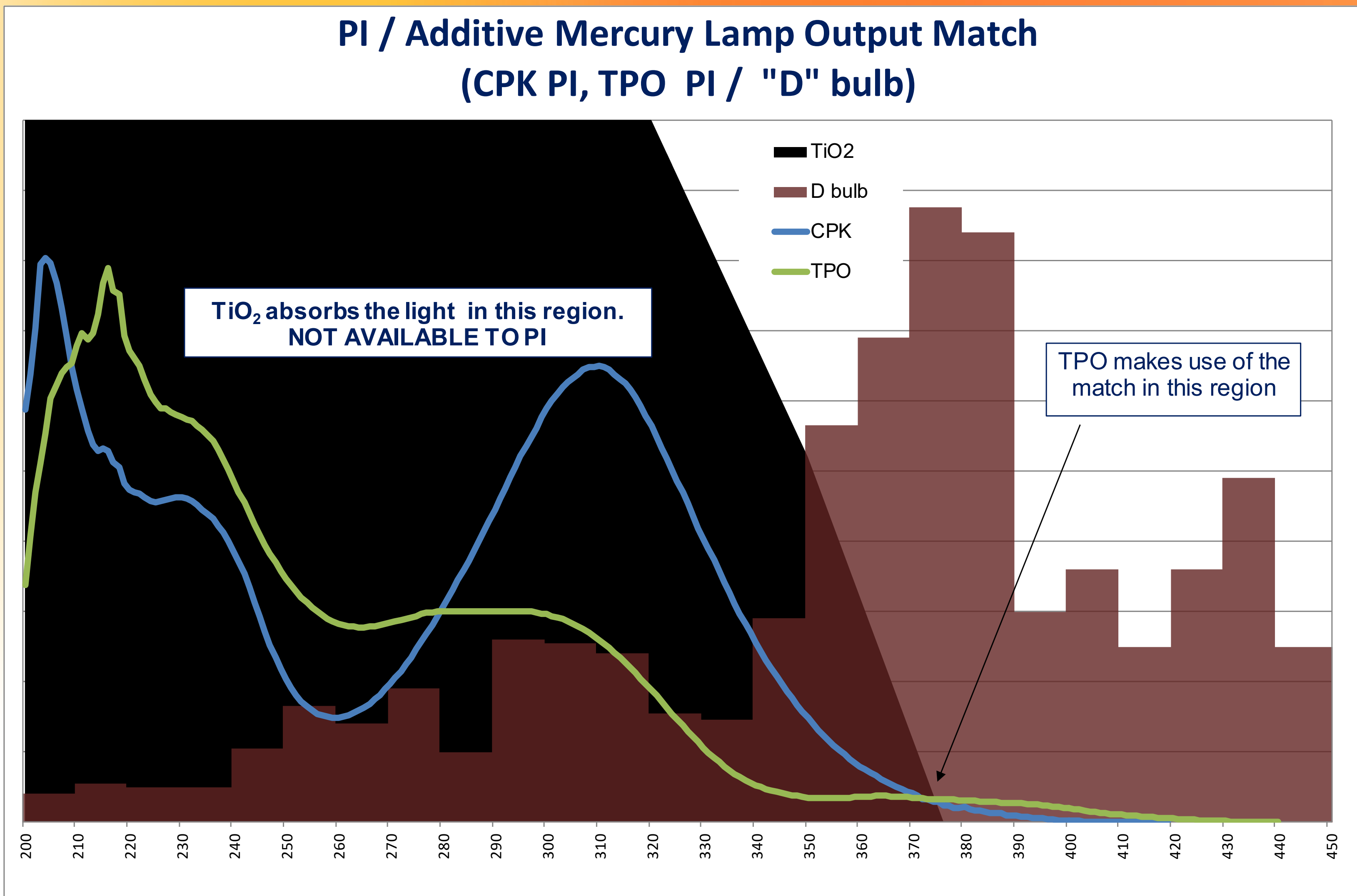


PHOTOINITIATOR SELECTION: UV ABSORPTION BY PIGMENTS

APPLICATION OF PI IN INKS



PHOTOINITIATOR SELECTION: UV ABSORPTION BY PIGM



PHOTOINITIATOR SELECTION: NO WORRIES WITH EB

AGENDA

- Introduction to Drying & Curing
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ENERGY CURABLE INKS: FORMULATION

Letdown

Oligomers,
Monomers,
Inert Fillers,
Additives, (PI)

Pigment Dispersion

Oligomers, Monomers,
Pigments, Dispersing Agents,
Stabilizers

UV CURABLE MILL BASE (PIGMENT DISPERSION)

Acrylated Oligomer (PEA, EA or combination for pigment wetting, flow, adhesion, cure speed)	50-60 %
Acrylated Monomer (GPTA or TPGDA)	5-10 %
Stabilizer	± 0.1 %
Dispersing Agent	1-5 %
Pigment	25-35 %

Mix together by hand; Triple Roll Mill until NPIRI grind is ≤ 3

UV CURABLE LITHO INK

Mill Base (Pigment Dispersion)	**50-60 %**	
Acrylated Oligomer (PEA, EA, UA or combination)	**10-20 %**	Ink Letdown – Blend Together
Acrylated Monomer	**0-5 %**	
Acrylated Oligomers (reactivity, hardness, flexibility)	**0-20 %**	
Additives (inert fillers, waxes, etc.)	**0-5 %**	
PI Package	**8-10 %**	

To prepare Ink:
mix Mill Base with
Ink Letdown
until homogeneous

Testing of Ink Properties

- Ink Tack
  - Thwing Albert Electronic Inkometer, 1200 RPM, 90°F, 1 minute
- Ink Misting
  - Thwing Albert Electronic Inkometer, 1200 RPM, 90°F, 1 minute
  - Color difference, ΔE; tendency to mist
- Reactivity
  - Radiant energy dose required to achieve mar-free surface (specified lamp)
- Adhesion
  - Tape test with 600, 610, or 810 tape
  - Cross hatch or tape pull

Testing of Ink Properties, continued

- Rheology (Yield)
  - Cone and Plate
- Flow
  - At a 45º angle, ink response to gravitational forces
- Ink-Water Balance
  - Various commercial instrumentation
- Printability
  - Evaluate on-press behavior
    - Productivity (make ready and clean up)
    - Appearance (image quality)
    - Gloss
    - Color density
    - Water window
    - Ink flow and transfer

FORMULATING GUIDELINES: ENERGY CURABLE PASTE INK

Formulate to achieve desired performance –

ink viscosity, tack, misting, reactivity and other properties

FORMULATING GUIDELINES

To increase tack ……………………………. Add high MW epoxy acrylate

To reduce tack ……………………………… Add low MW species or low viscosity PEA

To reduce misting …………………………. Add inert fillers or gelled vehicles

To increase reactivity ……………………. Add hexafunctional aliphatic UA

To increase flexibility ……………………. Add difunctional aromatic UA

ENERGY CURABLE LITHOGRAPHY MARKETS

General SPF for Porous Stock

Product	Yellow	Magenta	Cyan	Black	
Polyester Acrylate	25	22	24	18	Pigment wetting; ink water balance
Epoxy Acrylate	40	37	36	39	Reactivity; resistance properties
GPTA	2	4	2	3	Viscosity adjustment
Stabilizer	1	1	1	1	
Dispersing Agent				1.5	
Black Pigment				19	
Blue Pigment			17		
Red Pigment		18			
Yellow Pigment	14				
Pigment				1.5	
Dispersing agent	0,1				
Talc	5	5	6	3	Reduce tack and misting
Photoinitiator blend	8	8	9	10	
Wax	1	1	1	1	Improve scratch resistance
GPTA	4	4	4	4	Viscosity adjustment
Total	100	100	100	100	

ENERGY CURABLE LITHOGRAPHY MARKETS

General SPF for Non-Porous Stock

Product	Yellow	Magenta	Cyan	Black	
Chlorinated Polyester Acrylate	36	35	41	35	Adhesion
Urethane Acrylate	20	18	20	20	Increase reactivity and scratch resistance
TMPTA	5	6	-	4	Viscosity adjustment
Dispersing Agent		2		0-1	
Stabilizer	1	1	1	1	
Black Pigment				19	
Blue Pigment			17		
Red Pigment		18			
Yellow Pigment	14				
Pigment				1.5	
Dispersing Agent	0,1				
Talc	5	5	6	3	Reduce tack and misting
Photoinitiator blend	8	8	9	10	
Wax	2	2	2	2	Improve scratch resistance
Silicone Acrylate	0.5	0.5	0.5	0.5	Improve slip
TMPTA	5	4.5	4	4	Viscosity adjustment
Total	100	100	100	100	

ENERGY CURABLE FLEXO MARKETS

General SPF for Non-Porous Stock

Product	Yellow	Magenta	Cyan	Black	
Modified Epoxy Acrylate	15	15	17	15	Properties
Polyester Acrylate	20	20	20	20	Mill base
TPGDA	15	15	11	18	Viscosity adjustment
Dispersing Agent		2		0-1	
Stabilizer	1	1	1	1	
Black Pigment				12	
Blue Pigment			14		
Red Pigment		16			
Yellow Pigment	14				
Pigment				1.5	
Dispersing Agent	0,1				
TMPEOTA	20	20	20	20	
Photoinitiator blend	8	8	9	10	
Wax	2	2	2	2	Improve scratch resistance
Silicone Acrylate	0.5	0.5	0.5	0.5	Improve slip
TMPTA	5	4.5	4	4	Viscosity adjustment
Total	100	100	100	100	

Thank you!

James Ford
Flint Group
James.ford@flintgrp.com