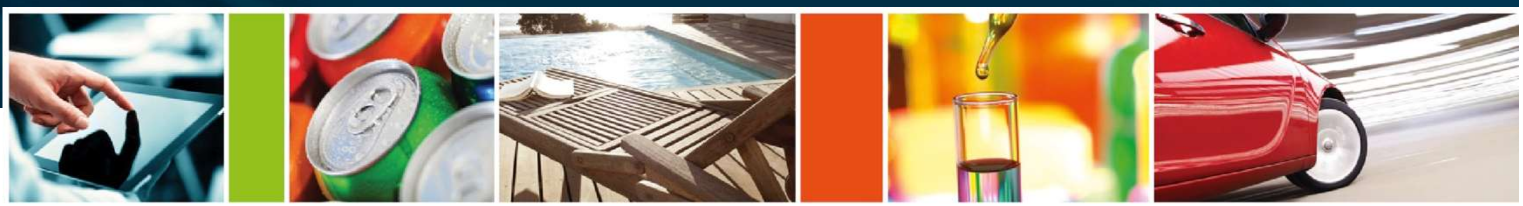
23 June 2020

Curing of (Meth)Acrylates

Allnex, Belgium
Technical Service & (New) Business Development



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Photochemical Curing of (Meth)Acrylates

UV / EB Radiation

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The Coating Resins Company

UV Formulation Technology

100% formulations

- **EBECRYL© Resin(s) (oligomers)**
  - basic coating properties
- **Monofunctional Monomer(s)**
  - viscosity reduction, flexibility
- **Multifunctional Monomer(s)**
  - viscosity reduction, x-linking
- **Additives**
  - performance fine tuning
- **Photoinitiator (Package)**
  - radical generation

Waterbased formulations

- **UCECOAT© Resin(s)**
  - basic coating properties
- **Additives**
  - performance fine tuning
- **Photoinitiator (Package)**
  - radical generation

- **EBECRYL** resins have in general a high viscosity
- Reactive **MONOMERS** are used to reduce the viscosity

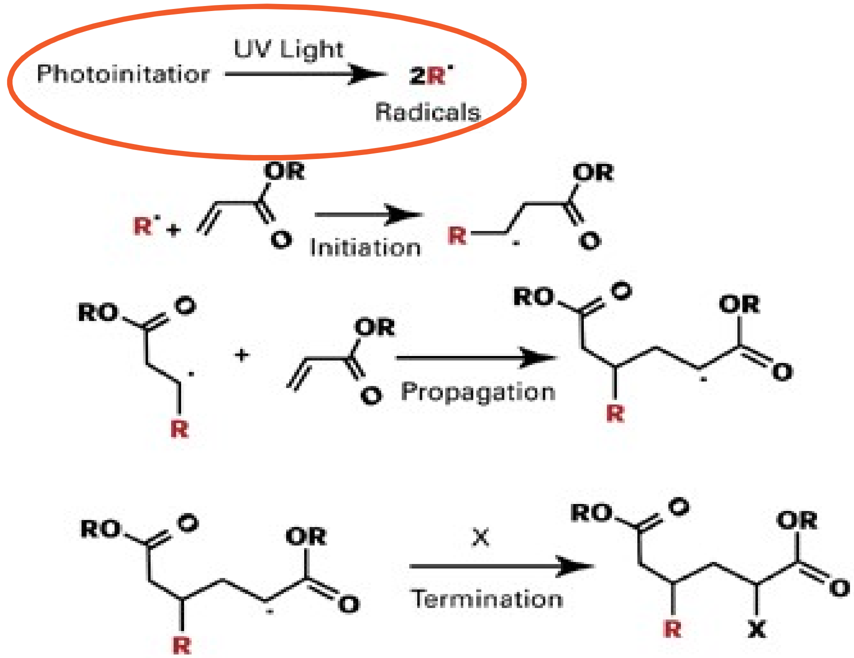
Application

100% reactive	UV Waterbased

• Solventless formulation
• Viscosity of resin is usually high
  - Viscosity reduction is likely needed
• Curing can be done short after application
• Full Properties are developed immediate after curing
	• H2O is used as medium
	• Viscosity of resin is low
	  - Thickening might be needed
	• H2O needs to be evaporated before curing.
	  - Sufficiently low residual H2O content is required
	• Full Properties are developed immediate after curing

UV light initiated Radical Reaction

- The acrylate resin **does not react** by exposure to UV light



- The present **photoinitiator absorbs the UV light** and generates radicals
- These **radicals initiate the reaction** at a C=C …

Types of Photoinitiator

- **Photocleavage (unimolecular PI)**

  α-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

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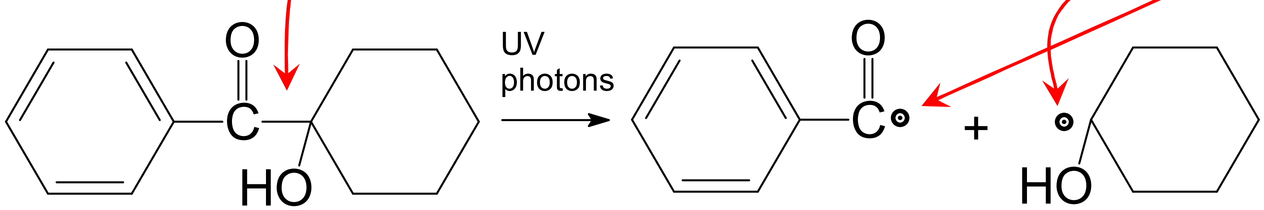
Photocleavage

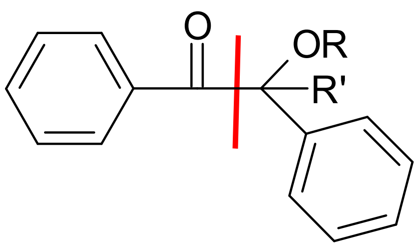
$$A - B \rightarrow A^{\bullet} + B^{\bullet}$$

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

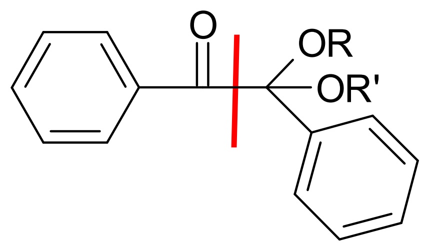


Photocleavage: different types

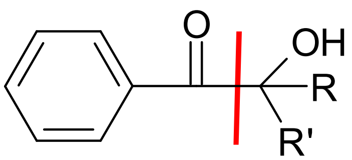
Benzoin ethers



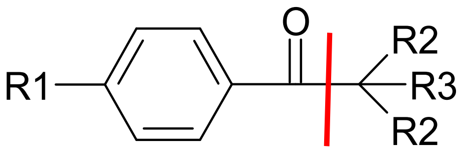
Benzil ketales

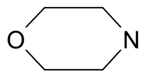


α-hydroxyalkylphenones

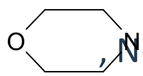


Aminoxyalkylphenones



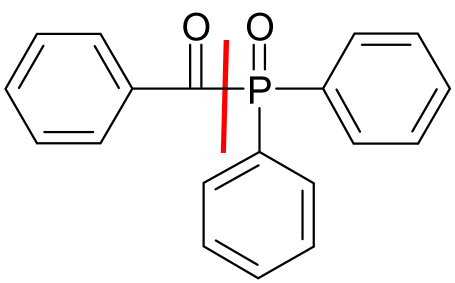
R1 = H_3CS, 

R2 = CH_3, CH_2Ph, C_2H_5

R3 = 

, $N(CH_3)_2$

Acylphosphine oxides



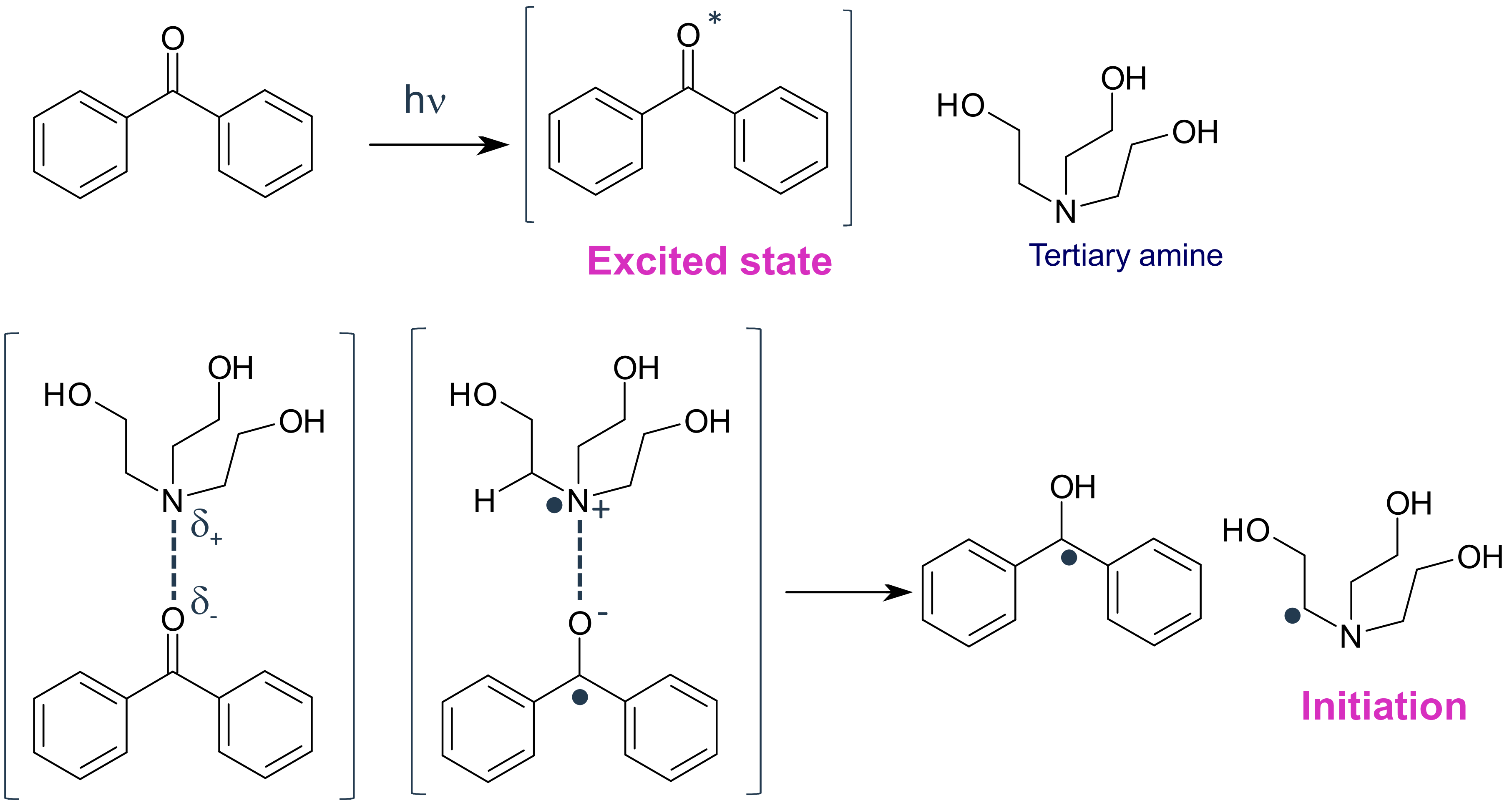
Hydrogen Abstraction

INTERMOLECULAR HYDROGEN ATOM ABSTRACTION

$$RX \rightarrow RX^{*}$$

$$RX^{*} + R'H \rightarrow RXH^{\bullet} + R'^{\bullet}$$

Hydrogen Abstraction

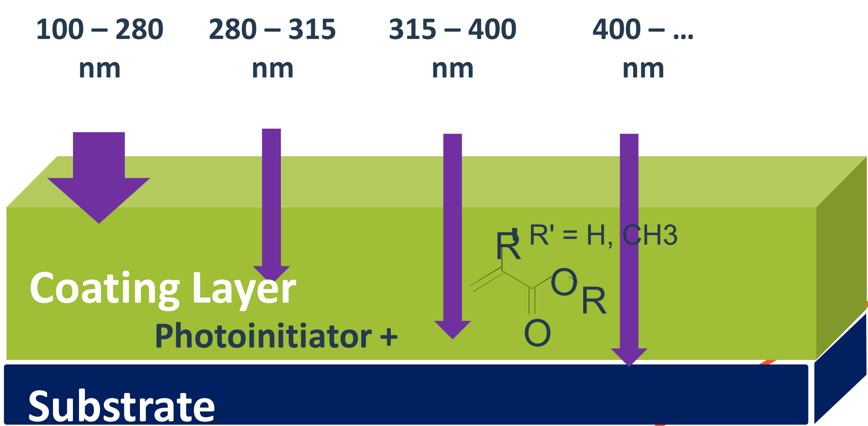


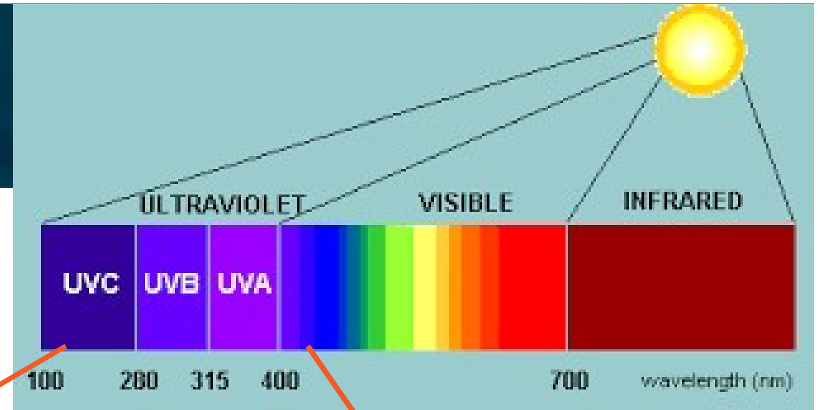
Exciplex

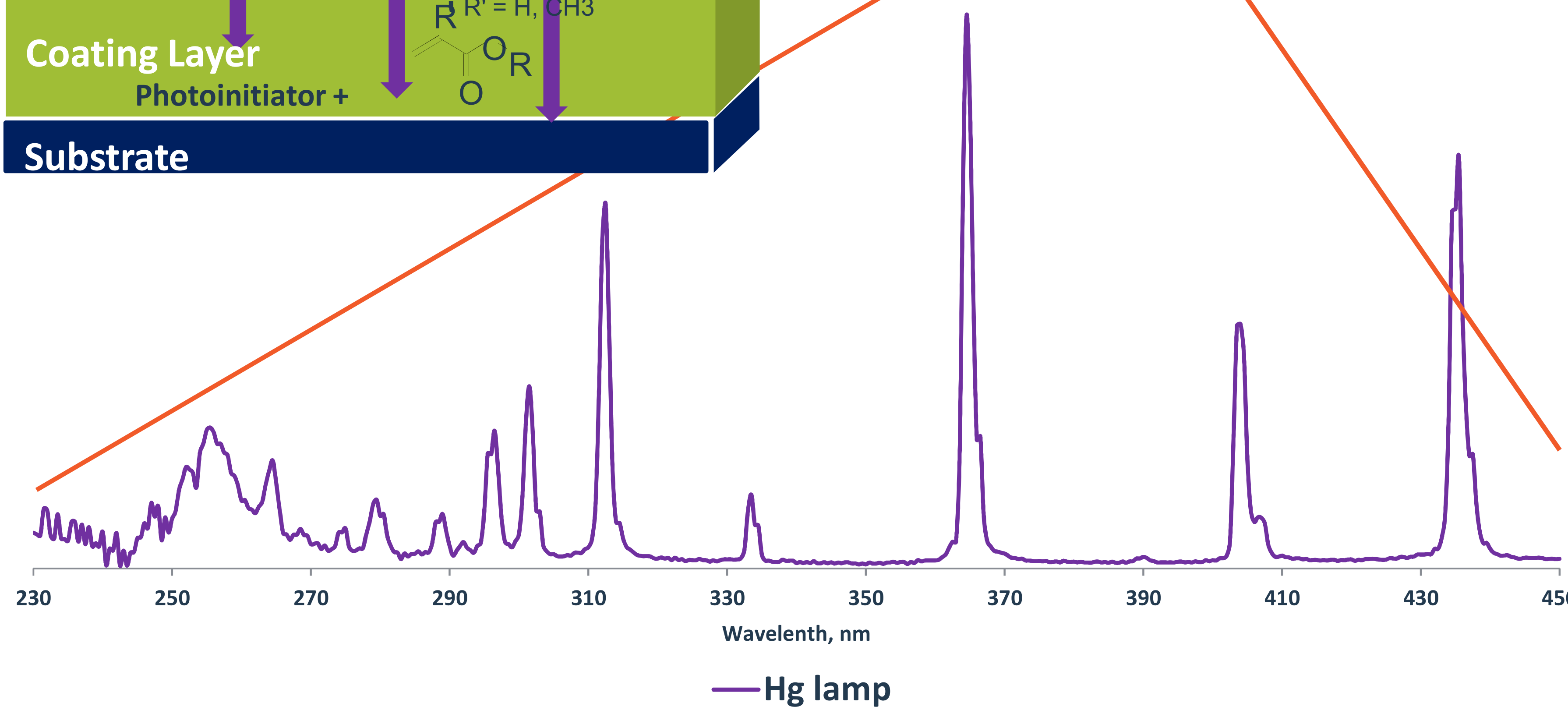
Photoinitiator selection

- UV equipment available
  - Hg, Fe or Ga lamp – UV LED
  - Aligning Absorption to Emission
- Surface cure vs. in depth cure
  - Absorbance vs penetration of light
- Film thickness
  - Absorbance vs penetration of light
- Pigmentation level
  - Light absorption
- Liquid vs. solid (handling)
  - Processing
- Toxicity: PI and PI-fragments
  - Food packaging, cosmetics, migration topic
- Cost
  - Always important

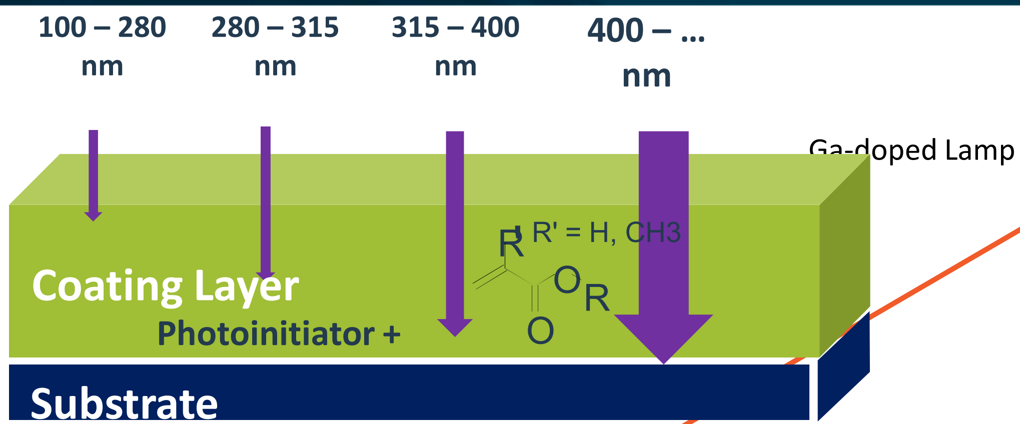
UV source: Lamp Spectrum & Use

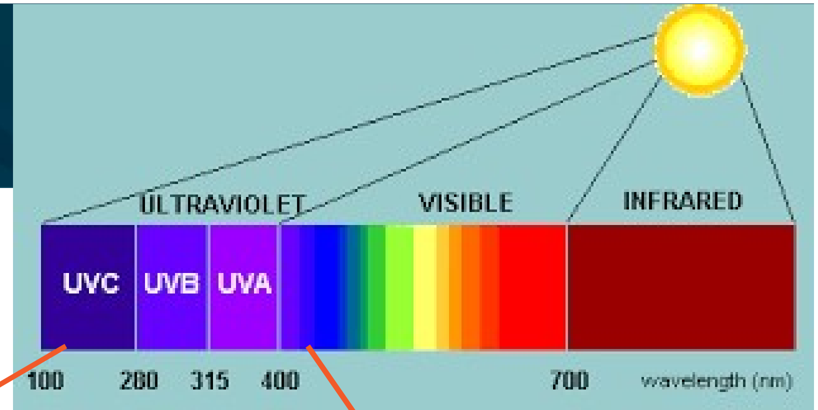


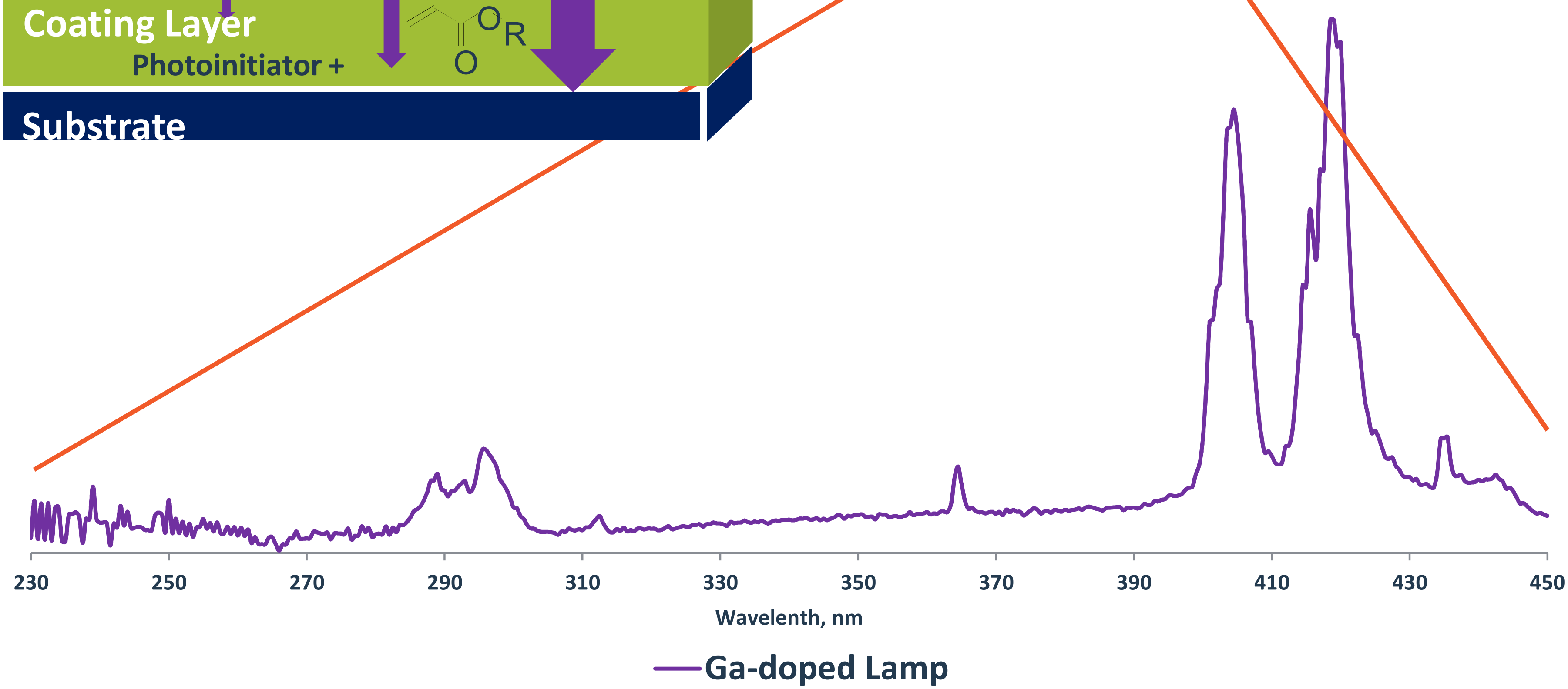




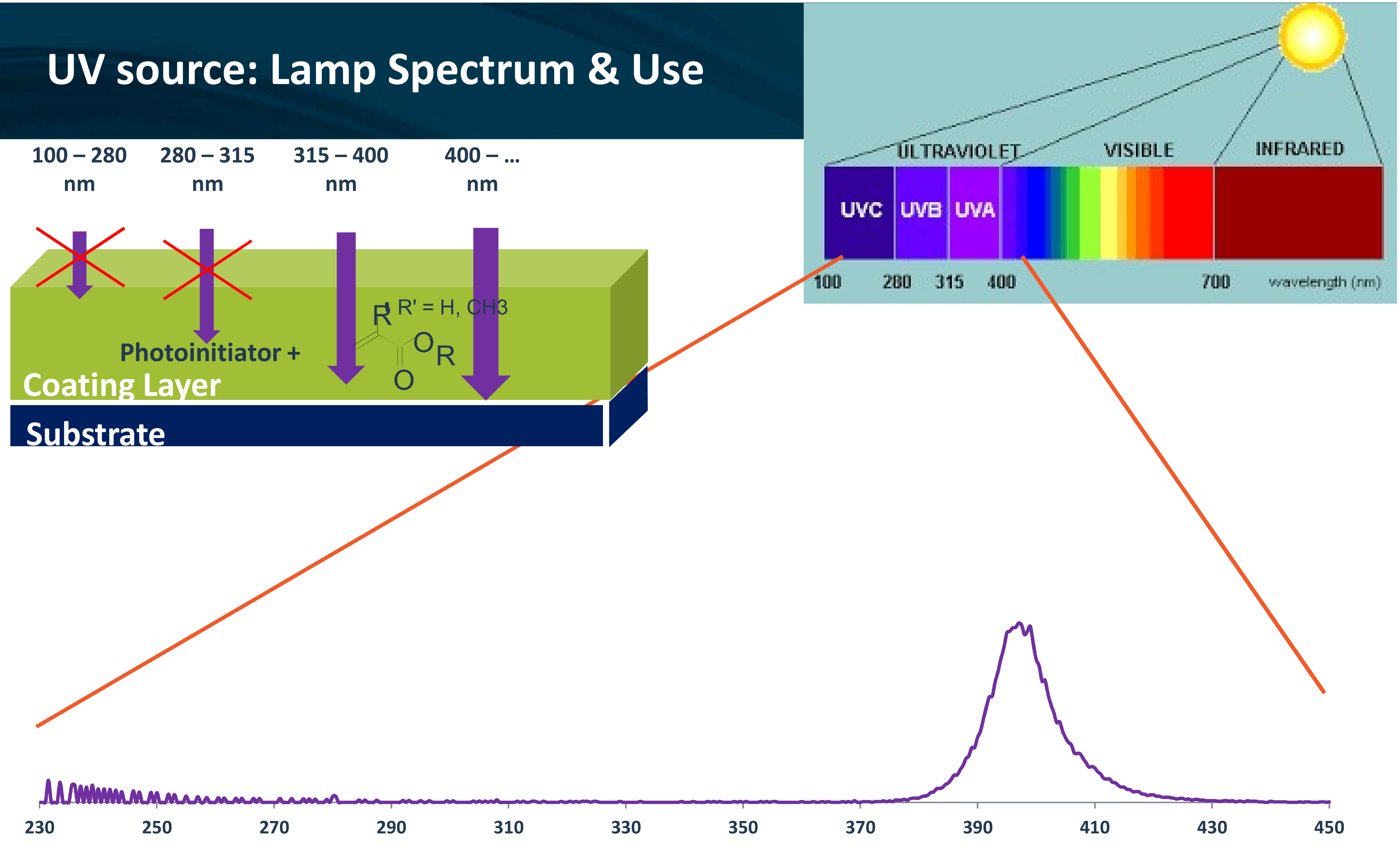
UV source: Lamp Spectrum & Use





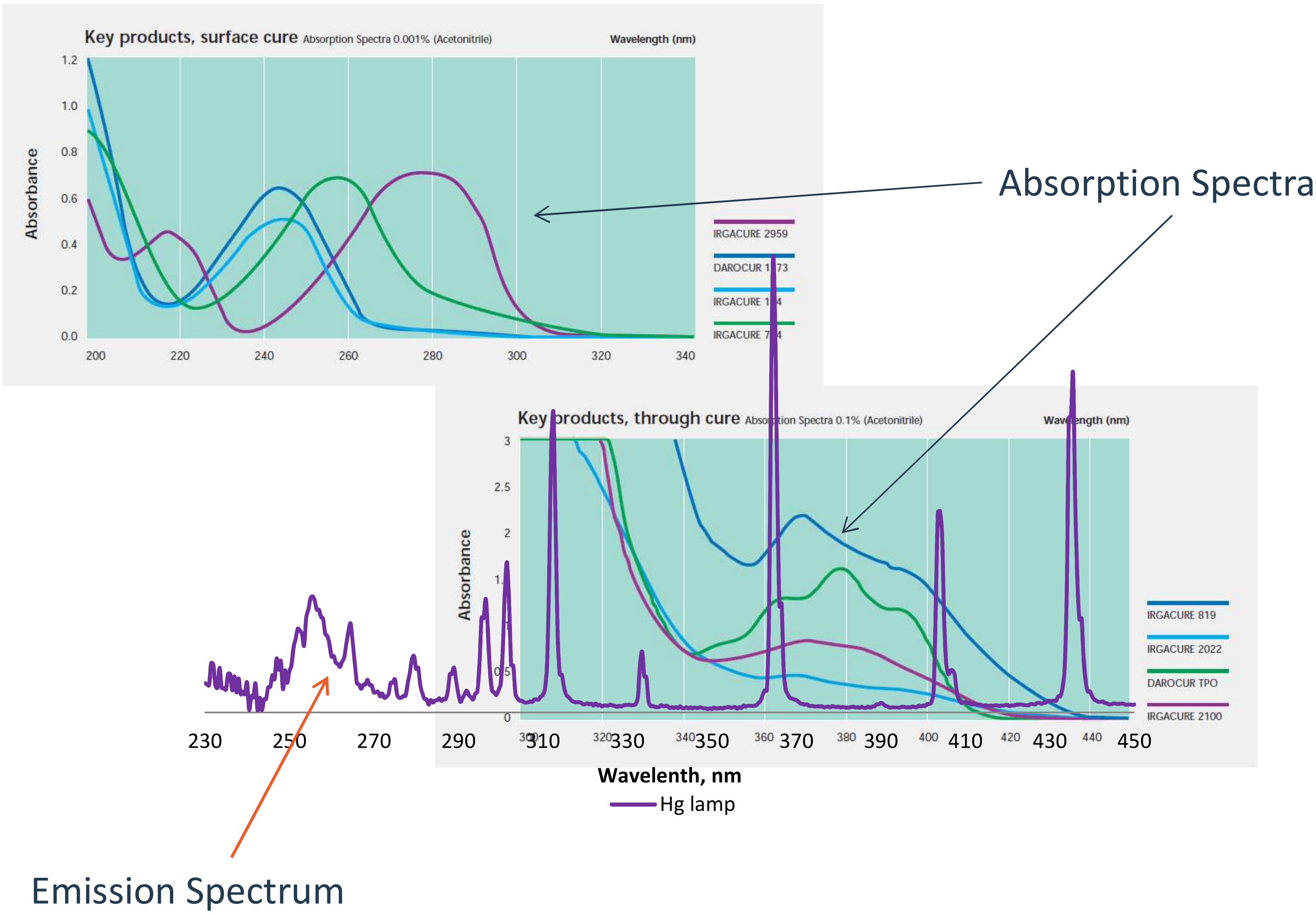


UV source: Lamp Spectrum & Use

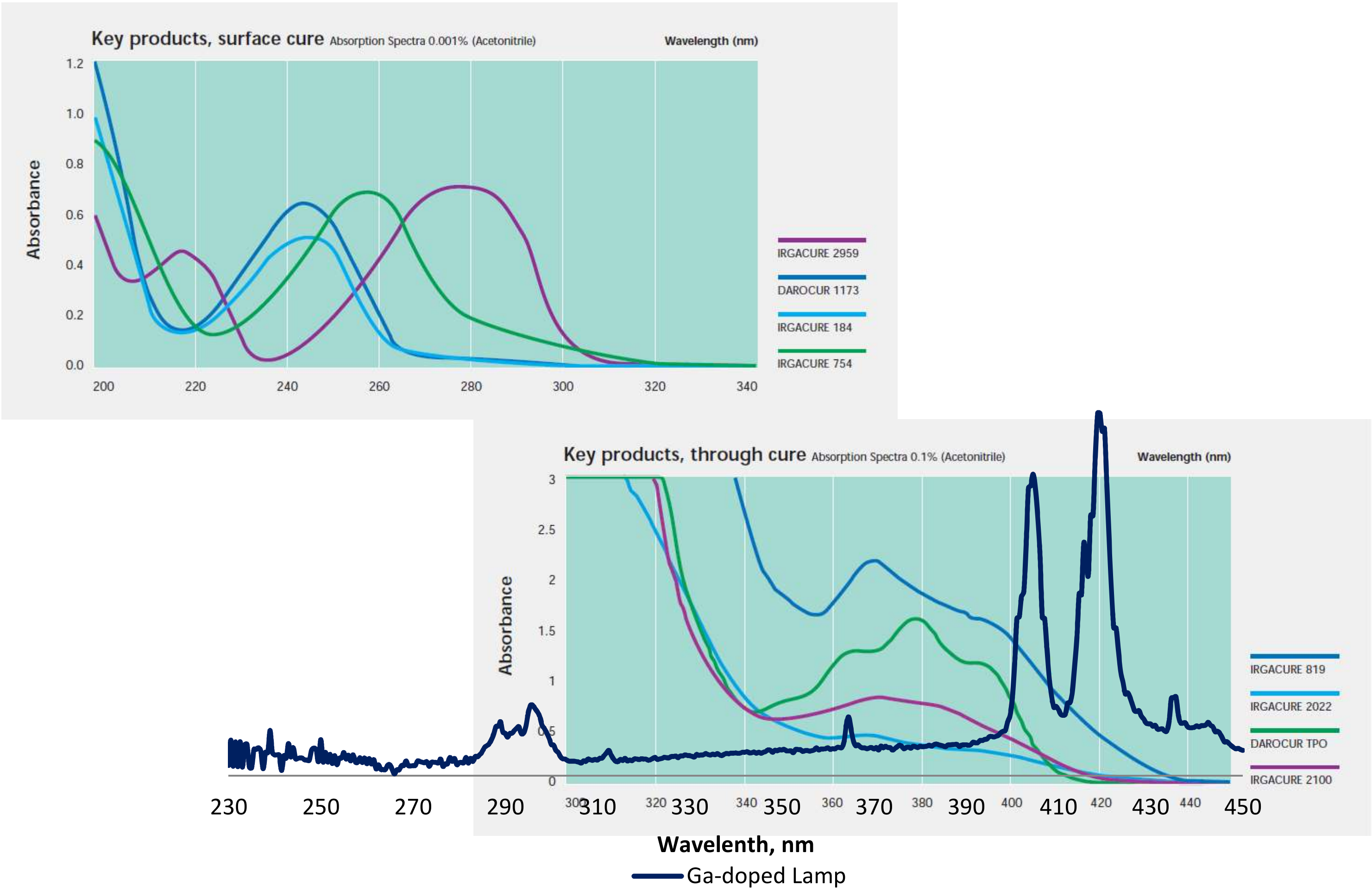


- UV LED – 395nm

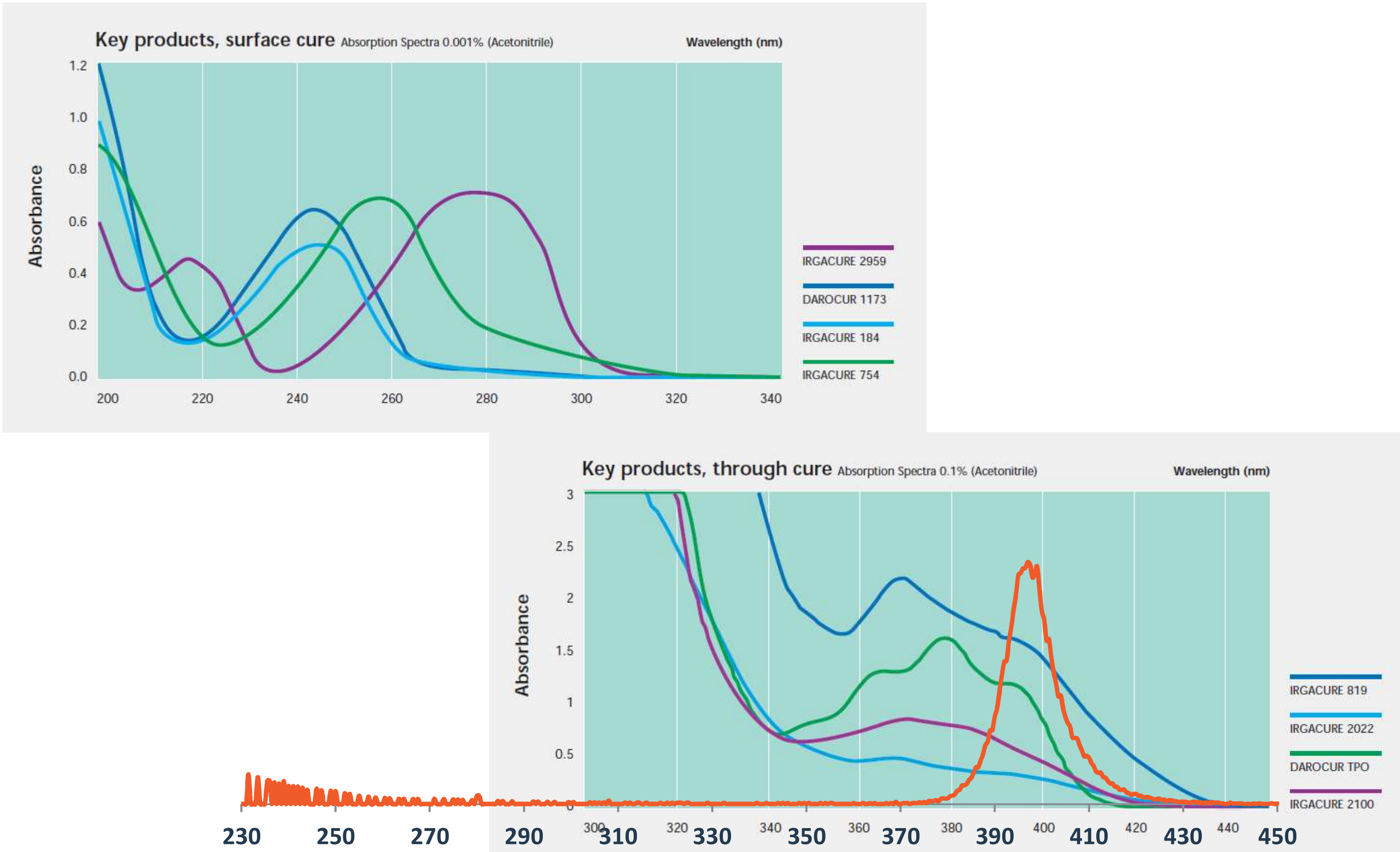
Choice of Photoinitiator, Matching UV spectrum



Choice of Photoinitiator, Matching UV spectrum



Choice of Photoinitiator, Matching UV spectrum



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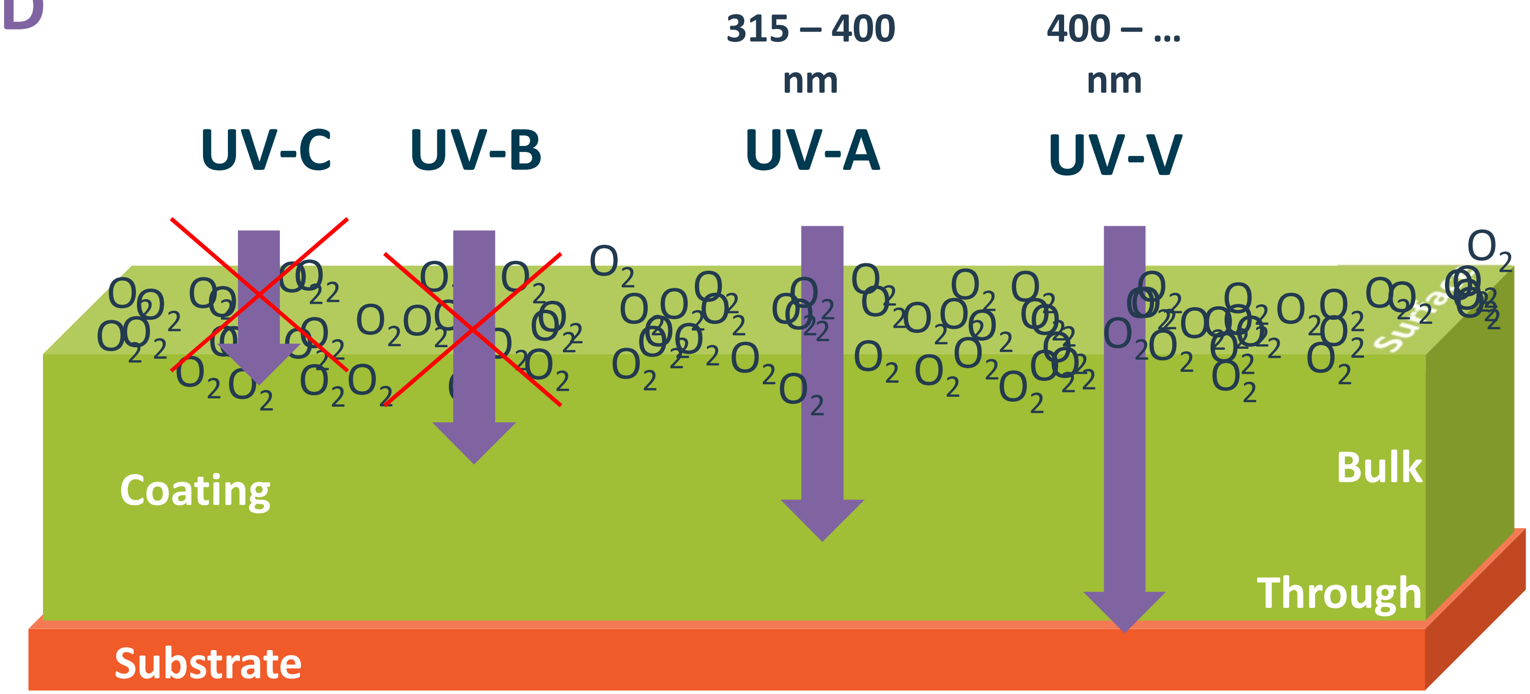
Oxygen Inhibition

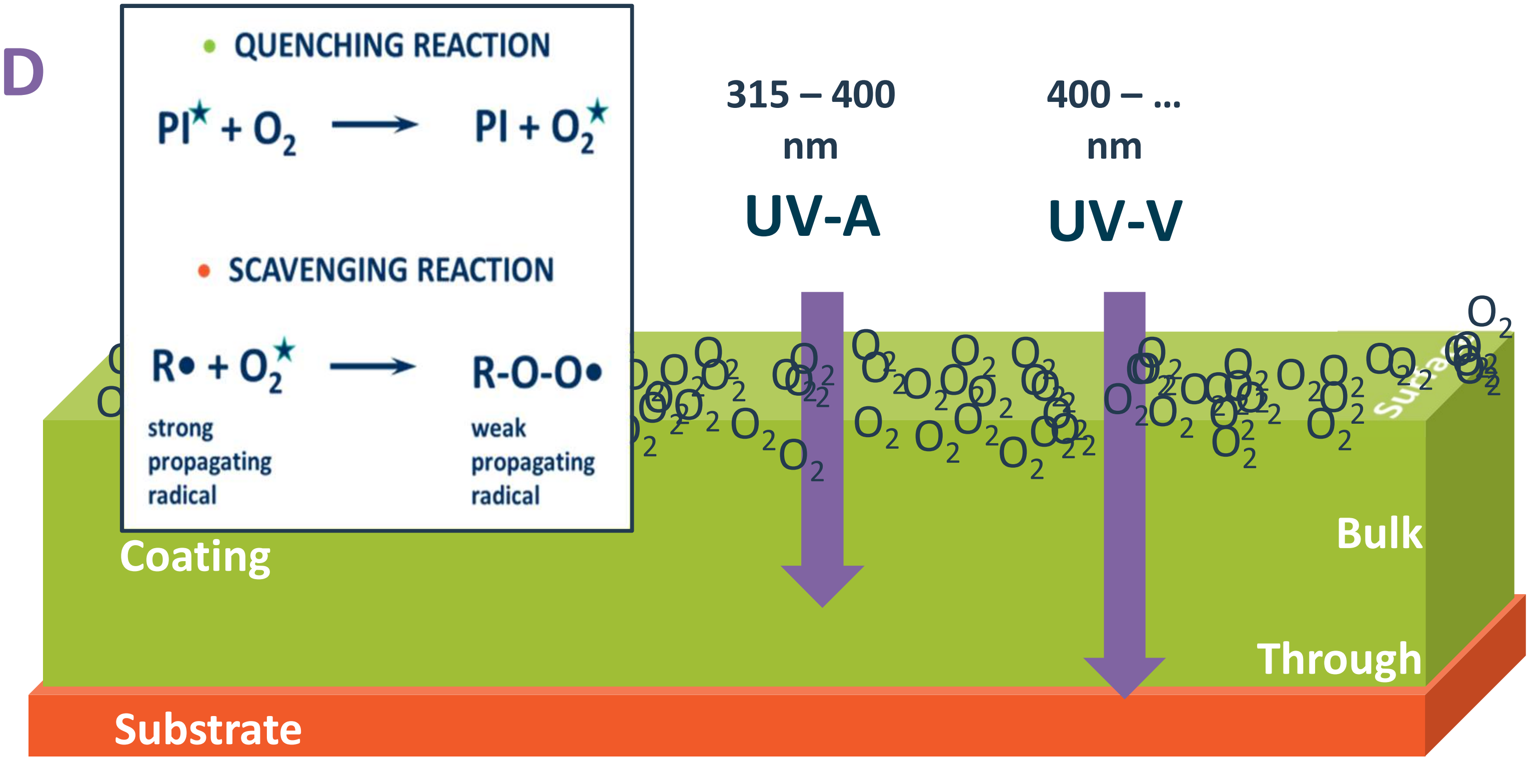
UV LED



= SURFACE CURE ISSUES

Oxygen Inhibition

UV LED



= SURFACE CURE ISSUES

How to keep Oxygen from Interfering at the Coating Surface during UV LED cure

Method
Chemical modification: (Abstractable) Hydrogen donors

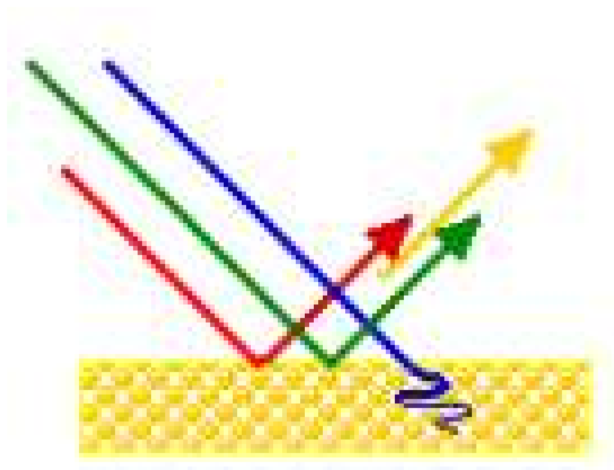
Thiols > Amines > Ethers

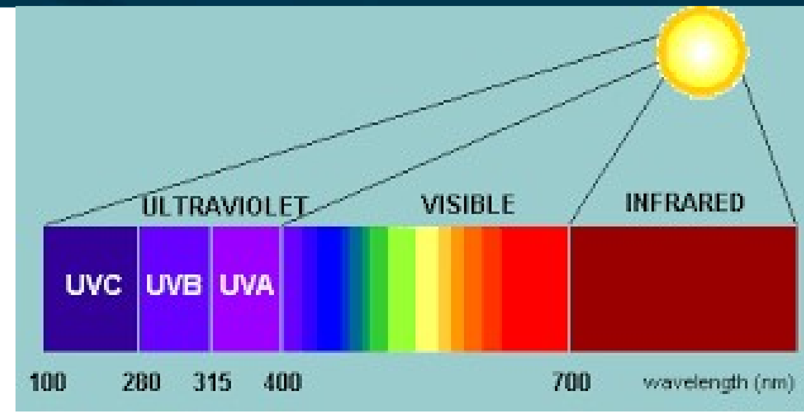
$$\text{Mon-O-O}^{\bullet} \xrightarrow{\text{R-H}} \text{Mon-O-O-H} \quad + \text{R}^{\bullet}$$

$$\text{R}^{\bullet} \xrightarrow{\text{Mon}} \text{R-Mon}^{\bullet} \xrightarrow{\text{Mon}} \ \xrightarrow{\text{Mon}}$$

Influence of Colours

RGB
(White light)



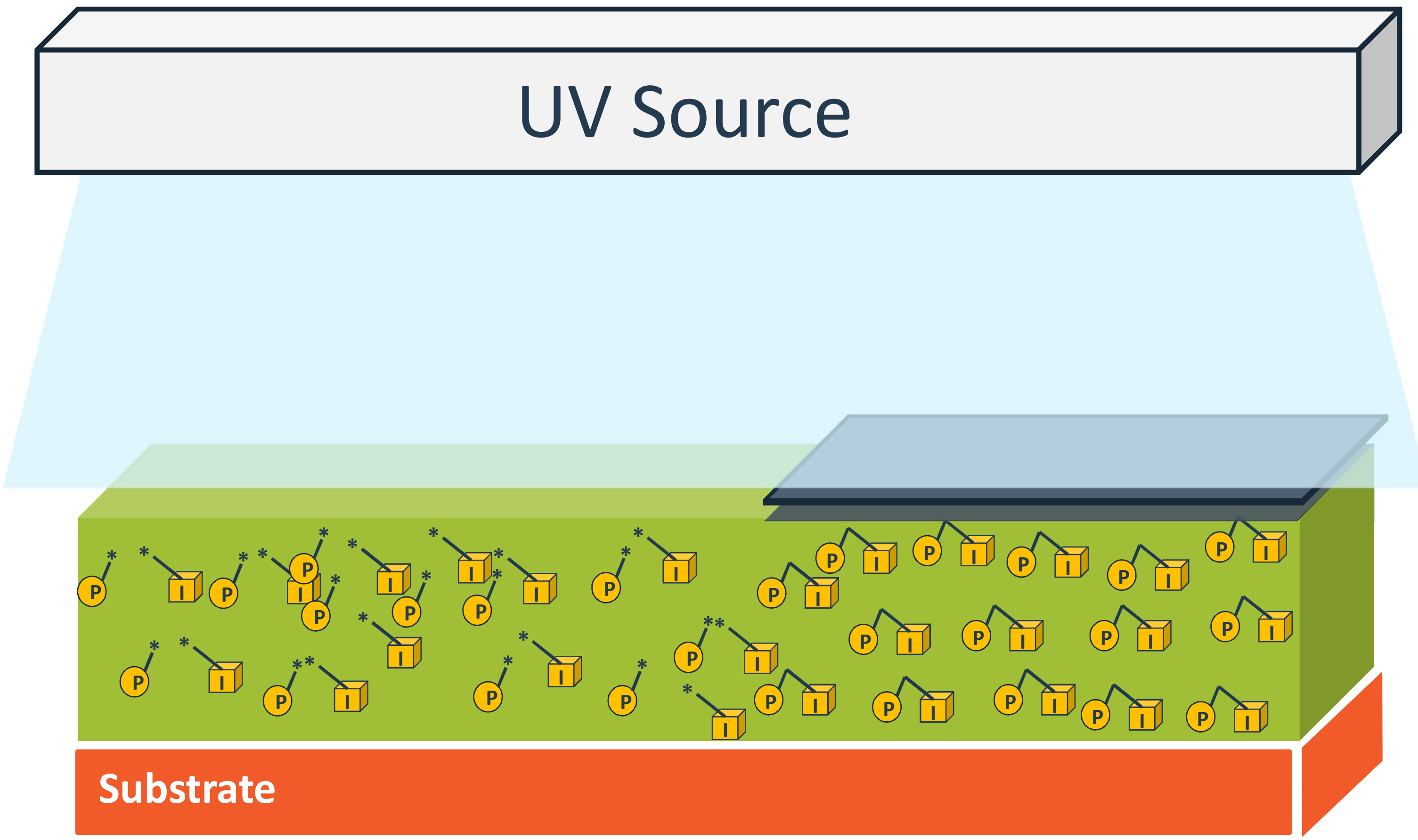


- Yellow pigment absorbs the blue
- Yellow pigment reflects red and green to be combined to Yellow

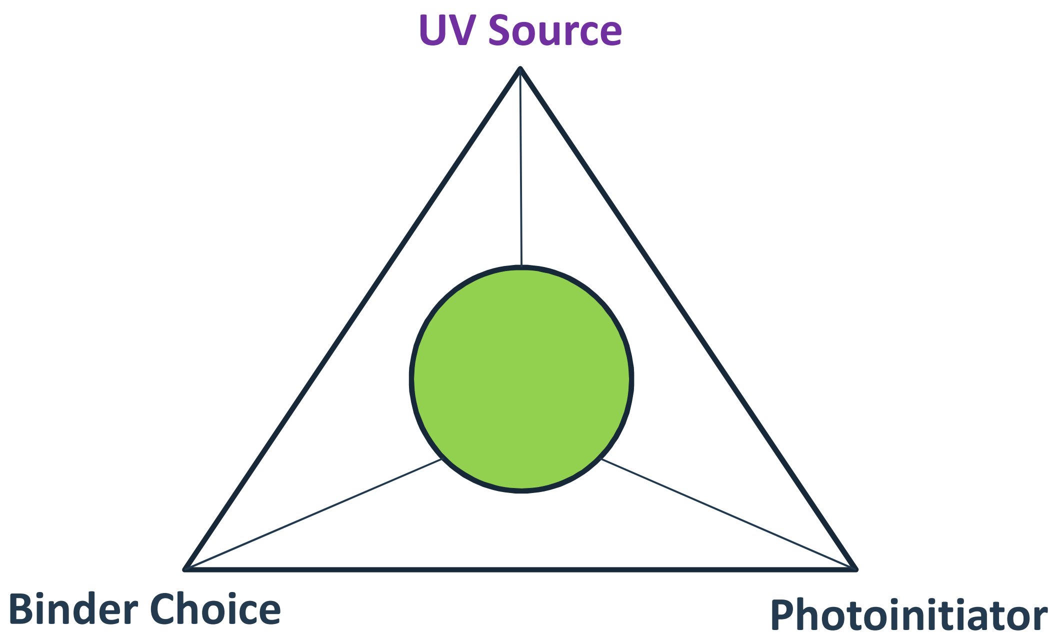
The (Ultra)Violet light is absorbed by pigment and photoinitiator

This phenomenon makes it more challenging to efficiently cure pigmented (coloured) coatings

Line of Sight curing…



Efficient UV curing is all about aligning the UV source type, the photoinitiator and the binder formulation

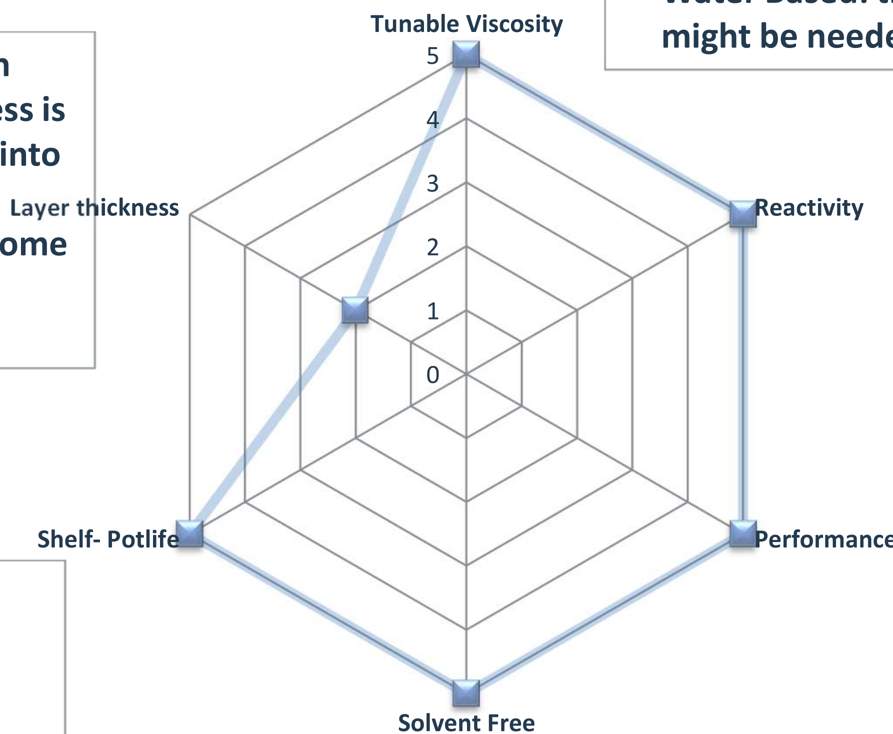


This efficiency makes it possible to cure within seconds

Why using Photochemical curing…

- Because of Radiation Curing, layer thickness is a parameter to take into account
- Also colours can become difficult

- Well selected reactive monomers as diluents.
- Water Based: thickener might be needed



- Possibility of curing in seconds
- Limited manufacturing footprint
- Possibility of stacking immediately after curing

- Single Component System
- Without light, no reaction
- Acceptable stability at elevated temperatures

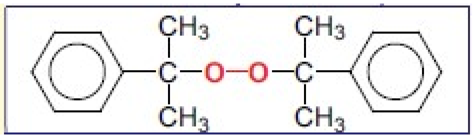
- Most common solvents can be used
- Waterbased dispersion / emulsions are available

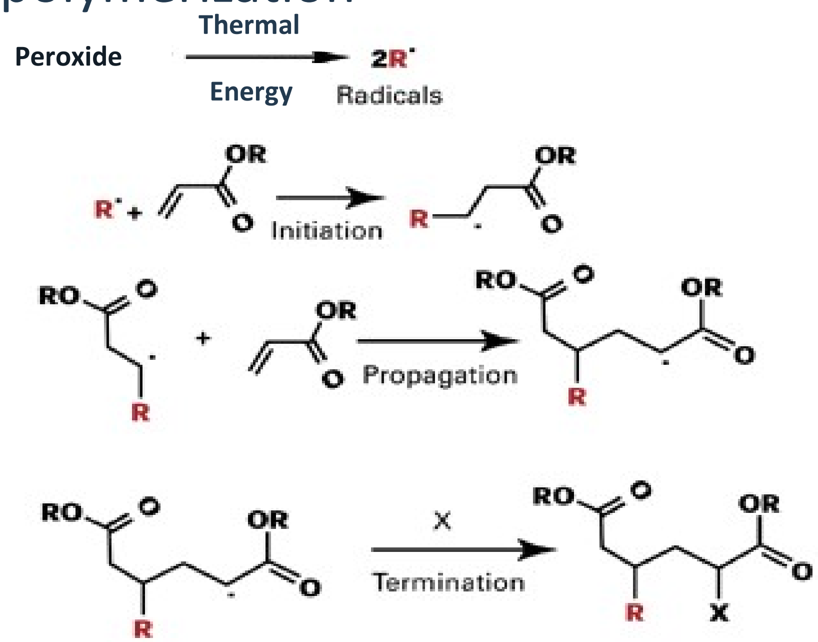
- Hardness - Flexibility
- Scratch resistant
- Chemical resistance
- Outdoor - Indoor
- …

Curing with Peroxides

Peroxide Curing, Mechanism

- Radicals are generated by decomposition of the peroxide
  - By heat: >80°C
  - By accelerators: <80°C
    - > Amine accelerated
    - > Cobalt accelerated
- These radicals react with (meth)acrylate groups (or other C=C bonds like vinyl or allyl) and initiate the polymerization
  - This curing mechanism is similar to UV curing





Peroxide Curing, Parameters

- Formulation and curing is a 2K – process
  - A peroxide in combination with (meth)acrylates will always imply a pot-life

- Type of peroxide to be used will be based on cure temperature and the shelf life / pot life of the formulation

- Key property is the half-life temperature
  - Temperature at which half of the radicals are generated in a given period of time
  - A vast choice of different type of peroxides exist

	1 min Half-Life Temp (°C)	10 min Half-Life Temp (°C)	1 hour Half-Life Temp (°C)
BP-50-FT1	130	91	72

Example – Benzoyl Peroxide

	1 min Half-Life Temp (°C)	10 min Half-Life Temp (°C)	1 hour Half-Life Temp (°C)
BP-50-FT1	130	91	72

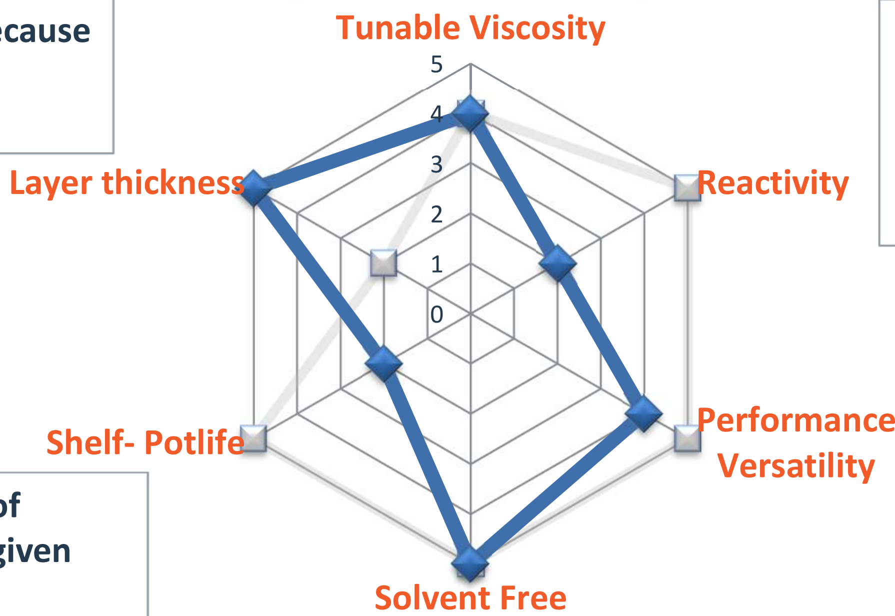
- At room/ambient temperature – extreme slow reaction
- Combined with a p-toluidine (example: dipropoxy-p-toluidine)
  - Addition 0.1-1%
  - Reaction possible down to 0°C

Why using Peroxide curing…

Curing is not dependent from layer thickness because no radiation source is involved

Well selected reactive (meth)acrylates as diluents.

- Depending on temperature and peroxide.
- Low temperature cure is possible

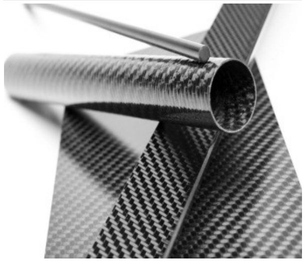


- Hardness - Flexibility
- Scratch resistant
- Chemical resistance
- Outdoor - Indoor
- …

Depending on type of peroxide (halflife at given temperature)

- Free of volatile monomers like styrene
- Most common solvents can be used

Peroxide Curing, Applications

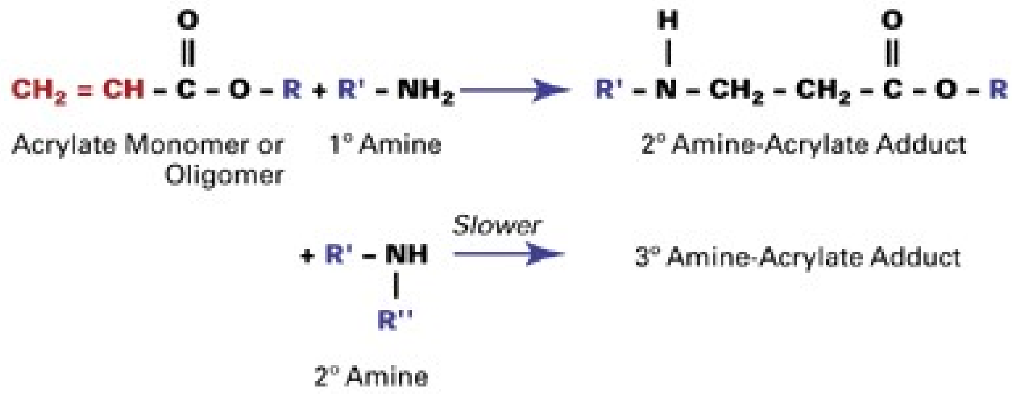
Adhesives	Composite Resin	Waterproofing Membranes	Chemical Anchoring	Rubber Vulcanization
				
Epoxy acrylate, Polyester acrylate, Urethane acrylates	Epoxy acrylate, Polyester acrylate, Urethane acrylate	Epoxy acrylate, Urethane acrylates	Epoxy acrylate, Urethane acrylates	Polyester acrylate, Urethane acrylates

- **What?**
  - Protection of surfaces to water ingress
- **Why using peroxide curing?**
  - High thickness layers
  - Good curing speed

Michaël Addition with (Meth)Acrylates

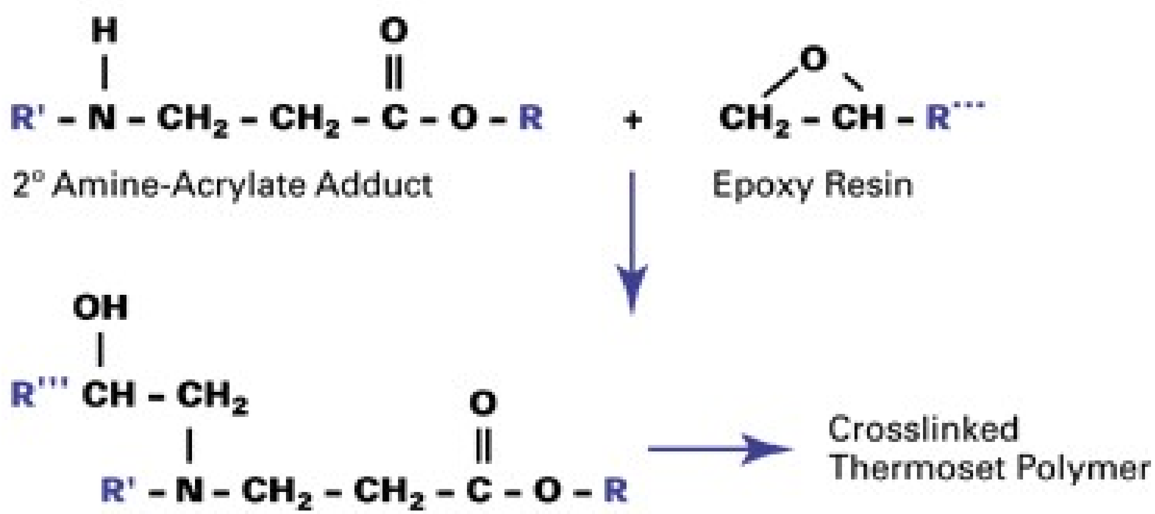
Ebecryl resin / Amine Formulation

- Michaël Addition reaction
  - Acrylate – amine reaction
  - Acrylate – Thiol reaction
  - Acrylate – Malonate
  - …
- Reaction speed is influenced by type of amine, thermal energy and higher pH
  - Aliphatic amine > Cycloaliphatic amine > polyether amine
- Stoichiometric ratio's are required
  - Epoxy + acrylate functions compared to amine functionality



Ebecryl monomer in Epoxy – Amine Formulation

- **Acrylate as x-linker in Epoxy – Amine 2k curing system**
  - Fast reaction (Michael addition) of acrylate double bond with primary amine and/or secondary amine. The created amine-acrylate adduct reacts further with the epoxy to create a more x-linked network
    - Aliphatic amine > Cycloaliphatic amine > polyether amine
  - Stoichiometry: Epoxy + acrylate functions compared to amine functionality



Advantages

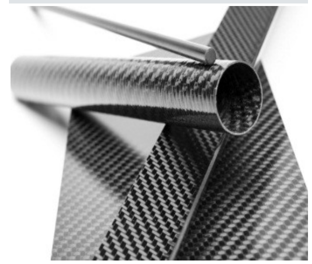
- Viscosity control without the loss of properties
- Property modification possibilities
  - Decreased time to gel point
  - Flexibilization
  - Increased X-linking
  - Increased solvent resistance
  - General performance increase
- Reduced amine blush
  - Whitish haze formed on the surface
  - Reaction of the amine with moisture and CO_2

Applications

Adhesives

Concrete Floor

Composite Resin



Chemical Anchoring

- General 2K epoxy coatings
  - Traffic paint
  - Concrete & Industrial flooring
  - Protection coatings
    - Tank linings
    - Corrosion resistant primers
- Fiber Composites
- Adhesives

- **What?**
  - Fixation of non-glass fiber composites
- **Why using Michael Addition?**
  - Easy viscosity modification without compromising the final properties
  - Reaction speed of amine – acrylate reaction
    - Reducing side reactions of primary amine functions

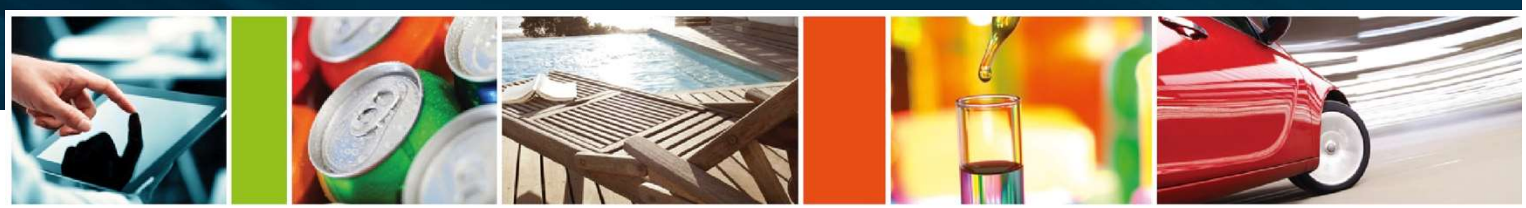
Summary

Key Facts…

- Using UV Waterbased, sufficiently ***low water content is required before curing***
- Alignment of ***UV Lamp and type of photoinitiators***
- ***Pigments can be competitors*** for photoinitiators to absorb the light
- UV curing is a ‘***in line of sight***’ curing technology
  - No curing in the shadow
- *O2 is an inhibitor* for radical reactions
- (meth) Acrylates can also be ***cured by peroxides***
- (meth) Acrylates can be used as property ***modifier in 2K epoxy/amine*** formulations

23 June 2020

Thank you



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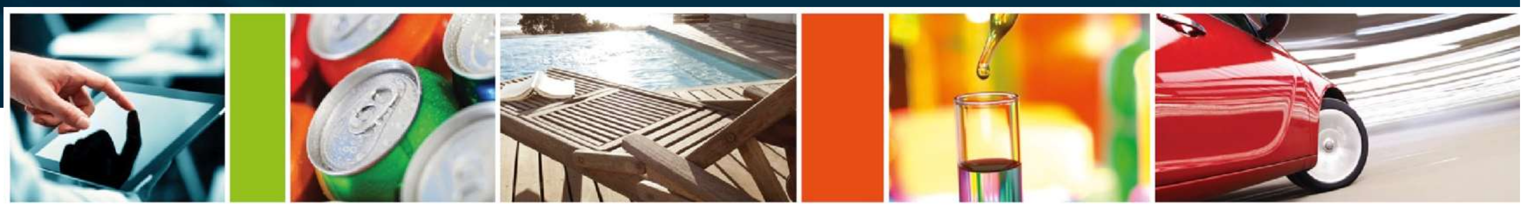

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