FREE RADICAL SYSTEMS (UV/EB) FOR COIL
RADTECH 2024

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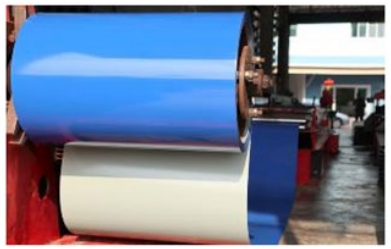

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Agenda

Introduction

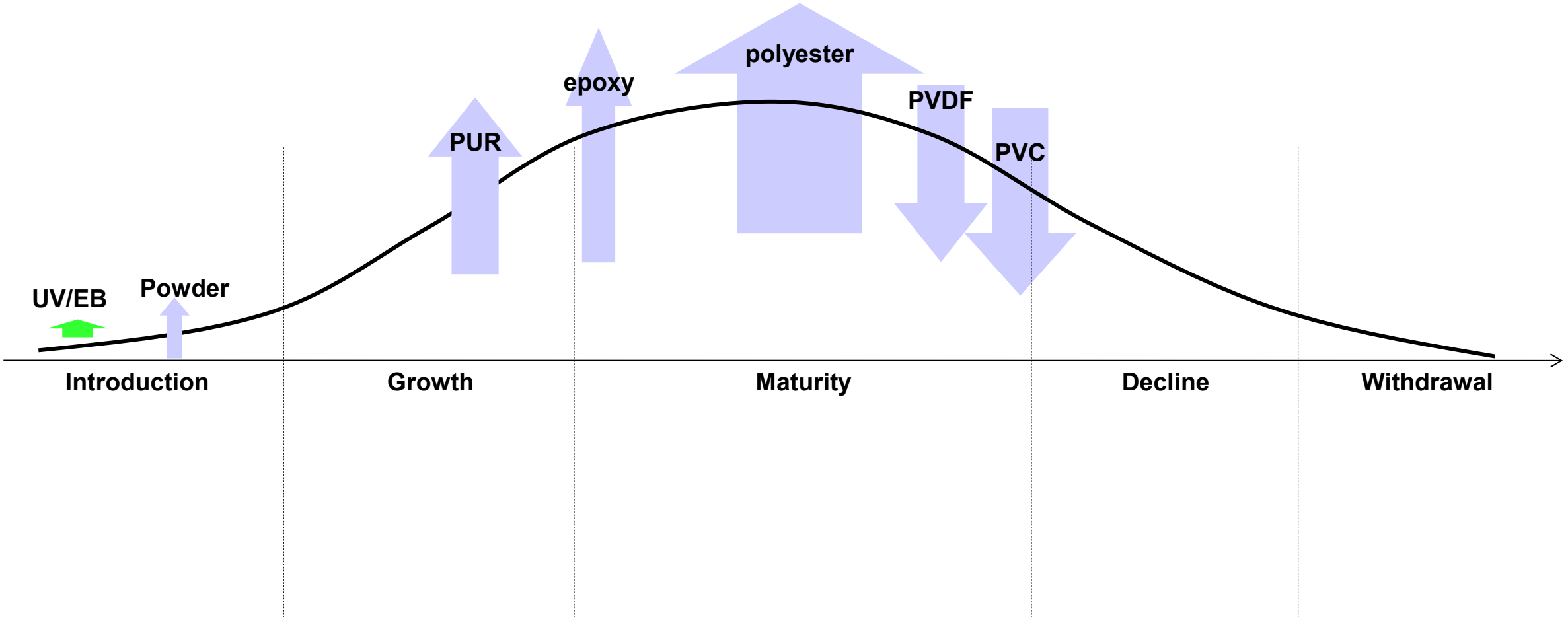
Introduction to free radical technology

Early developments of energy-curable systems for coil

Technical advancement leading to Gen II products for coil

Conclusion

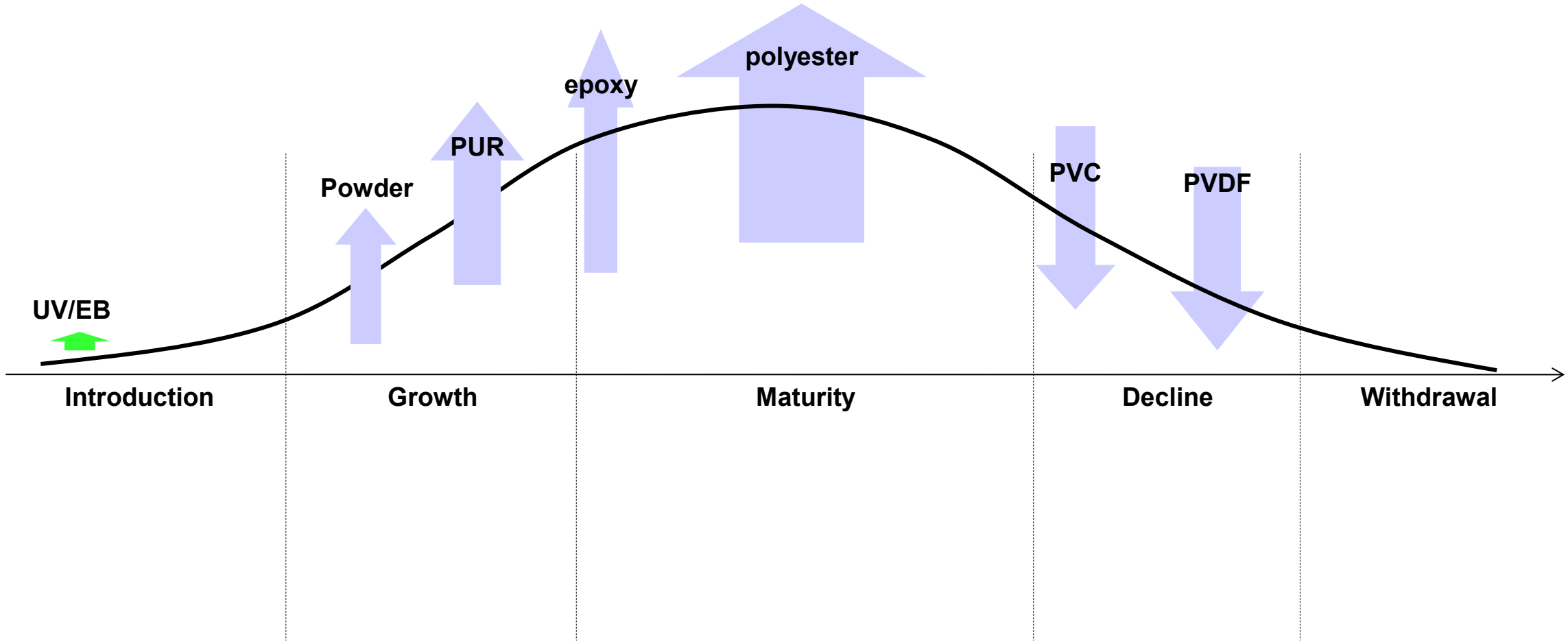
Coil coating product life-cycle 2005



Value Proposition of free radical Resins

- Lower utility cost/smaller carbon footprint
- Improve throughput and performance
- Improved efficiencies

Coil coating product life-cycle 2023



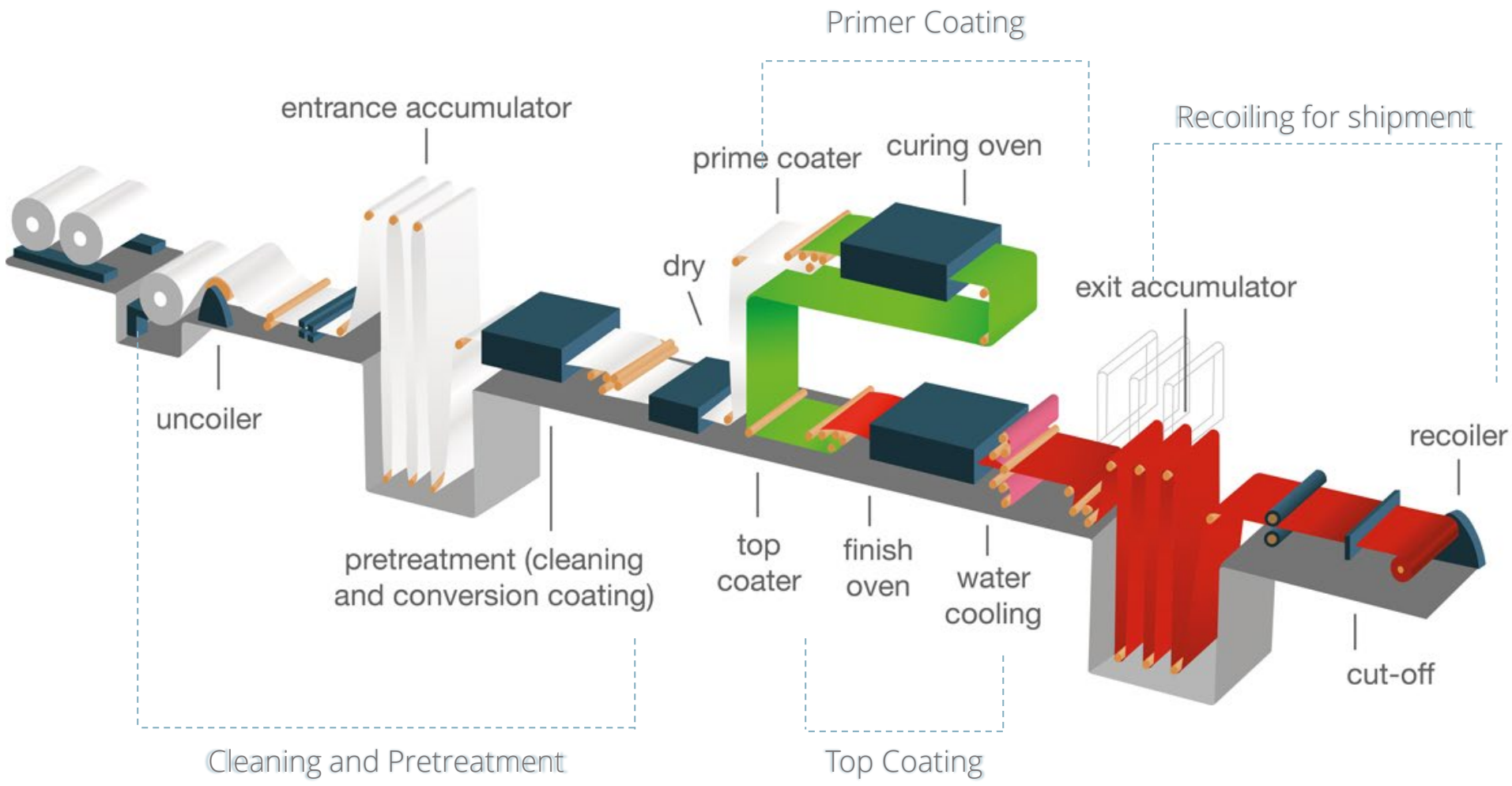
What is different in 2023 versus 2005 for UV/EB Resin in Coil Coatings

- Environmental changes
- Brand owners' market pull through for free radical Resins
- Improved throughput
- Environmental Friendly

Introduction

COATING TECHNOLOGY	LAYER	CROSSLINKER	ADVANTAGE	DISADVANTAGE
Polyester	Topcoat	amino	• versatile system interior and exterior • good to excellent formability	• well-balanced profile, no particular disadvantages
1C PUR	Topcoat and Primer (PES systems)	blocked polyNCO	• high flexibility, meet special forming requirements. • advantage vs amino – weather resistance and max achievable thickness (35 µm)	• low surface hardness
Epoxy	Primer Backcoats	amino	• excellent metal adhesion • excellent corrosion protection • Excellent hardness	• disappointing flexibility • bad weather resistance
Acrylics	Carrier PVC plastisol	polymer dispersions	• Used in automotive as Top coat	• limited adhesion to metal, therefore formulated with PER or epoxy resins.
PVDF	Topcoat high performance	dissolved in acrylic resins (70:30)	• extremely good weathering resistance • top-quality high UV durability • excellent formability • low dirt pick-up, high chem. resist.	• Fluorine emissions arising from the scrapping of PVDF-coated metal sheets have attracted criticism
PVC Plastisol	Top coat		• used where corrosion protection is paramount (marine applicaitons)	• halogen emissions
UV/EB	Primer Top coat	free radical	• no solvent, good flexibility • fast cure, efficiency,	• still some limitation in viscosity • not many products outdoor resistance

How UV/EB can fit within the coil process



Cleaning and Pretreatment

- Bare metal is uncoiled
- Coil splicing
- Accumulator stack (entry)
- Metal degreasing, cleaning rinsing & chemical pretreatment
- Drying oven

Primer coating

- Primer unit – one or both sides
- Curing oven

Top coating

- Coating unit-top coat applied on one or both sides
- Curing oven

Laminating or embossing

- Laminating – one or both sides or embossing

Recoiling for shipment

- Accumulator stack (exit)
- Recoiling finished metal

Introduction to UV/EB curing

- Energy savings
- Space limitation
- Productivity increase
- Environment compliance
- Performance level
- Appearance quality
- Heat-sensitive substrate

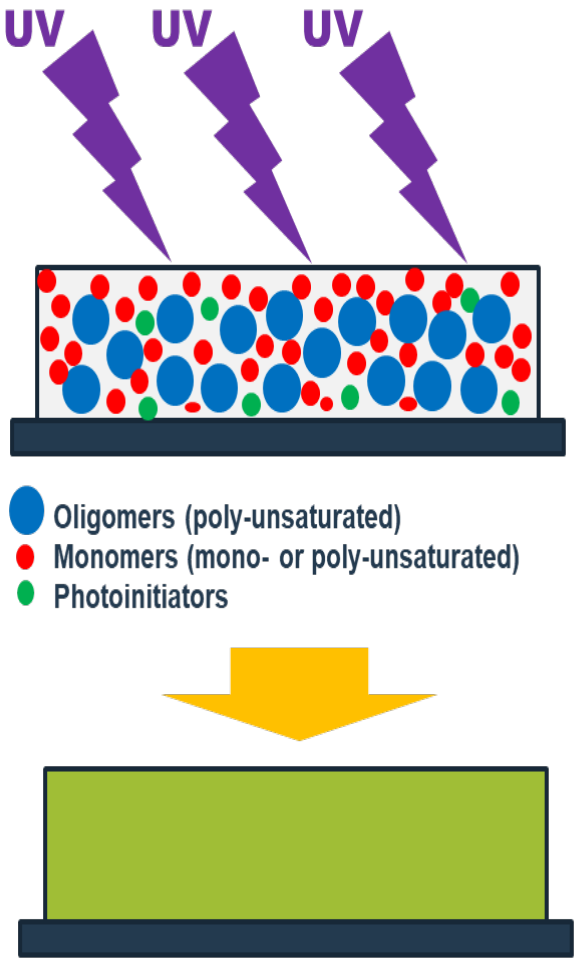
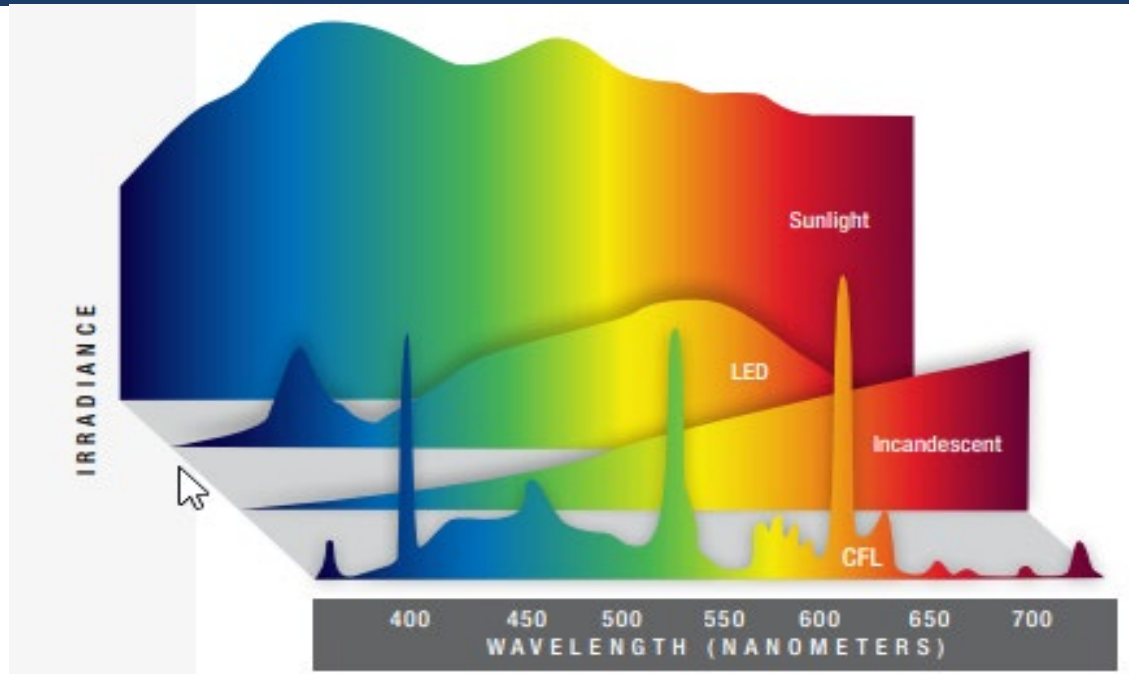
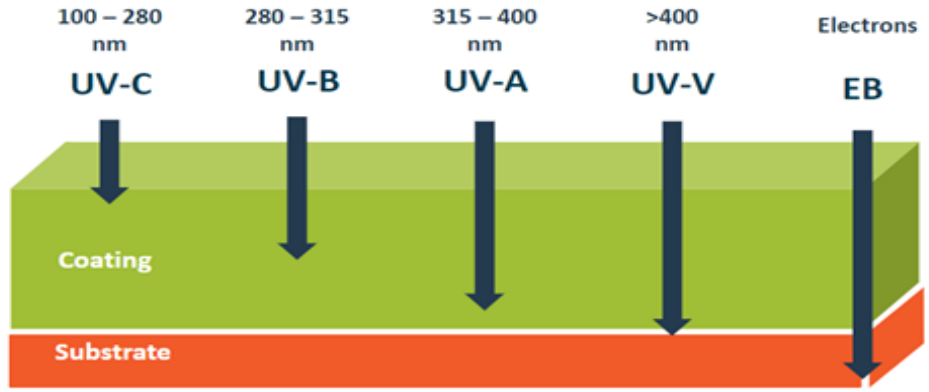


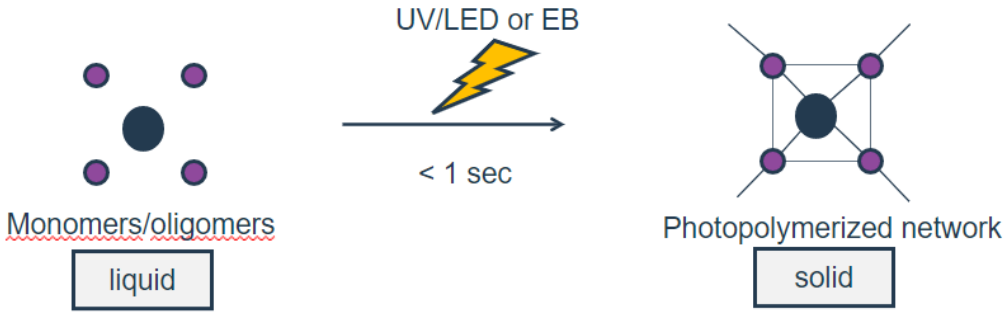
Figure: formation of a high crosslinking density hardcoat by energy-induced radical polymerization of acrylated monomers and oligomers in the presence of a photo-initiator (UV-light) or not (Electron beam)





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

Introduction to UV/EB curing



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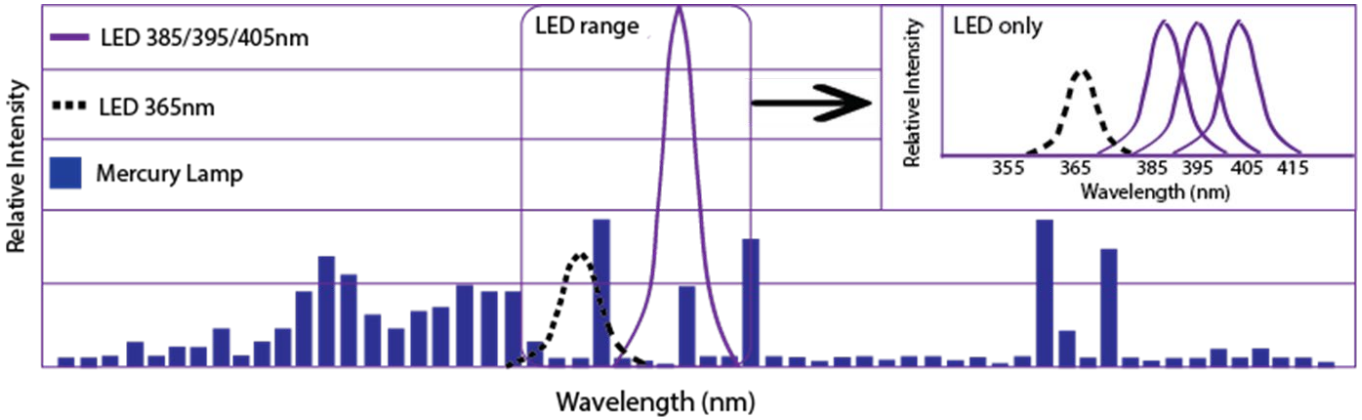
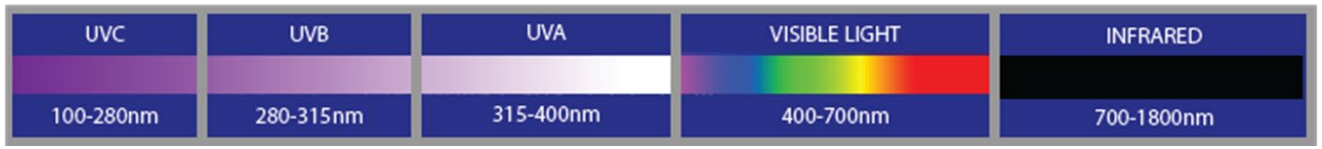




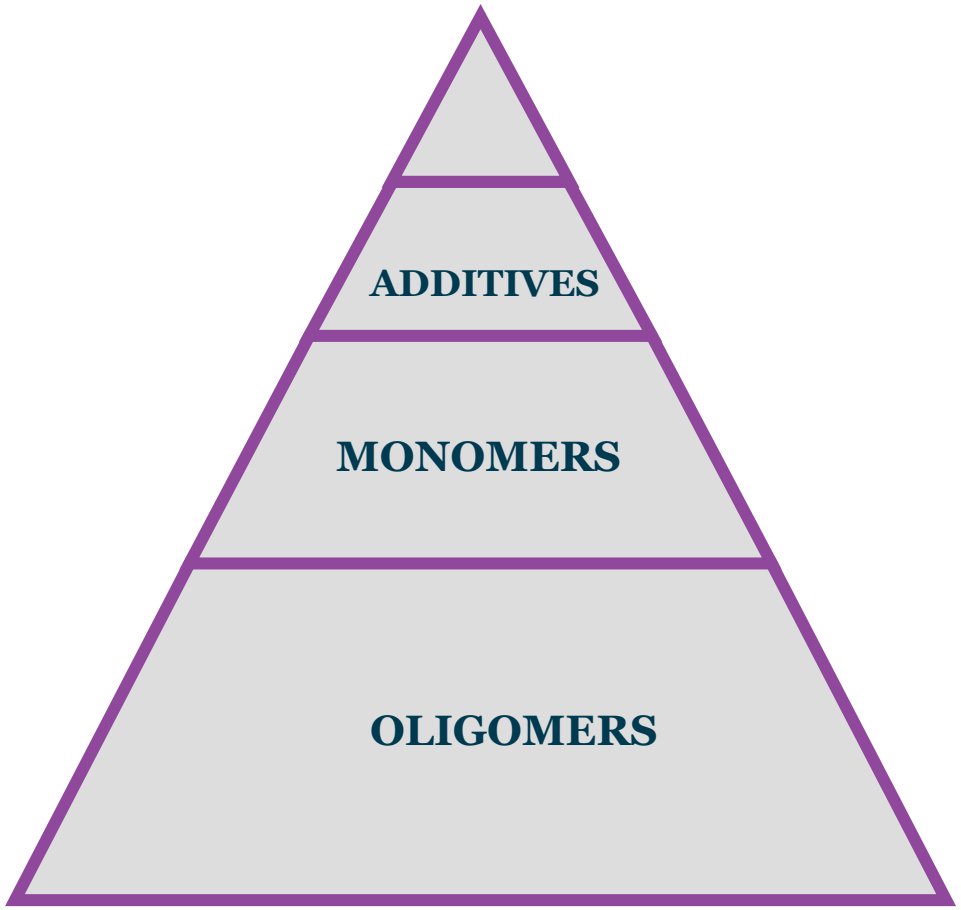
	UV	Electron Beam
Investment	Medium	High
Nitrogen	Optional	Necessary
Photoinitator	Yes	No
Matting	"Easy"	Difficult
Cure 1 mm clear	Possible	Limited
Cure 200 µ pigmented	No	Yes

	UV	LED
Lifetime (h)	1000-2,000	> 20,000
Environmental	Mercury Waste Ozone Generation	Mercury Free Ozone Free
Input Power	Large	Small (~ half)
On / Off	Minutes	Instant
Heat generation (substrate)	High	Low

E-beam cure offers the highest double bond conversion rate

com allnex The Coating Resins Company

Introduction to UV/EB curing



ALL COMPONENTS INFLUENCE FINAL PROPERTIES

Oligomer
- Type
- Molecular Weight
- Functionality

Monomer
- Reactive Diluent
- Functionality

Photoinitiator (UV Cure)
- Type
- Concentration

Other Components
- Additives
- Pigments
- Formulator Expertise
- Formulator Specific

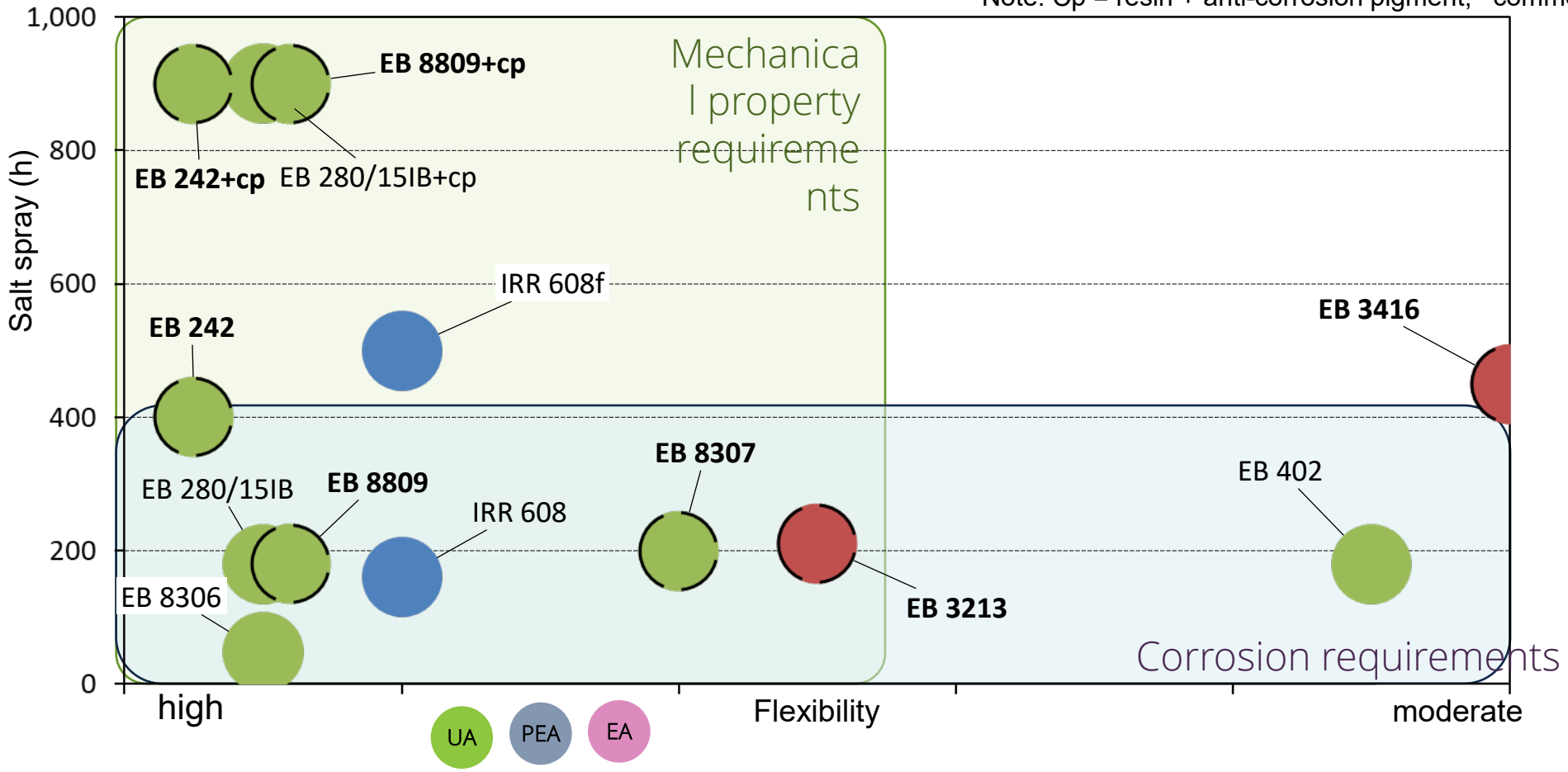
(Meth)Acrylated	Characteristics
Epoxies	Economical, fast curing, hard, solvent resistance; BPA issue
Aliphatic Urethanes	Flexible, tough, non-yellowing, best weathering properties
Aromatic Urethanes	Flexible, tough, lower cost than aliphatic urethanes
Polyesters	Good pigment wetting properties, lower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

Gen I free radical for coil

Allnex resins developed for Coil coatings

Commercial – no longer commercial

Note: Cp = resin + anti-corrosion pigment; commercial grades

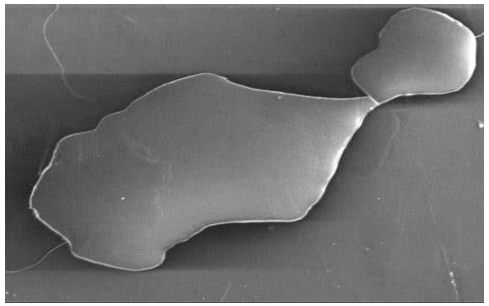


- Outstanding flexibility but limited adhesion due to poor surface treatment
- Good corrosion resistance but with Cp
- Poor durability results due to low cross link density
- Limited products in the toolbox

Gen I Challenges for free radical for coil

Adhesion

- Direct to metal
  - Cleaning of the process oils
- **Primer**
  - Chemistry not robust to adhesion to multiple primer types



Corrosion Resistance

- Lack of data
- Limited resistance

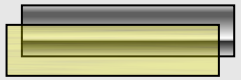
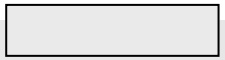
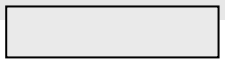
Viscosity

- Resin performance
  - Performance properties diminished after dilution

Performance

- Weatherability
  - Best weathering tends to be softer materials
- **Flexibility**
  - High flexibility systems tend to be high mw or low crosslink density

Coating layers and their function

	LAYER	TECHNOLOGY	THICKNESS	FUNCTION
	bare metal	Steel or Al	0.4 - 2 mm	substrate
	metallic coating	HDG (Zn/Fe), EZ	5 - 25 µm	corrosion resistance
	temporary protection	mineral oil	n.a.	temporary protection from oxidation
	conversion layer (pre-treatment)	chromatation or phosphatation (Galvanite)	< 1 µm	corrosion resistance adhesion of coating
	primer/base coat	PES, Epoxy	5 - 15 µm	corrosion resistance base coat
	top coat	PES, PU, Epoxy PVC plastisol, PVDF	20 - 200 µm	protection decoration
	backcoat	PES	10 µm	
	lamination	PET film foil	120 µm	protection, gloss (home appliances)
	embossing	patterned steel roll	n.a.	decoration, finish

Next-gen free radical systems for coil

What makes the free radical system feasible now

Cleaning protocol improvements coil

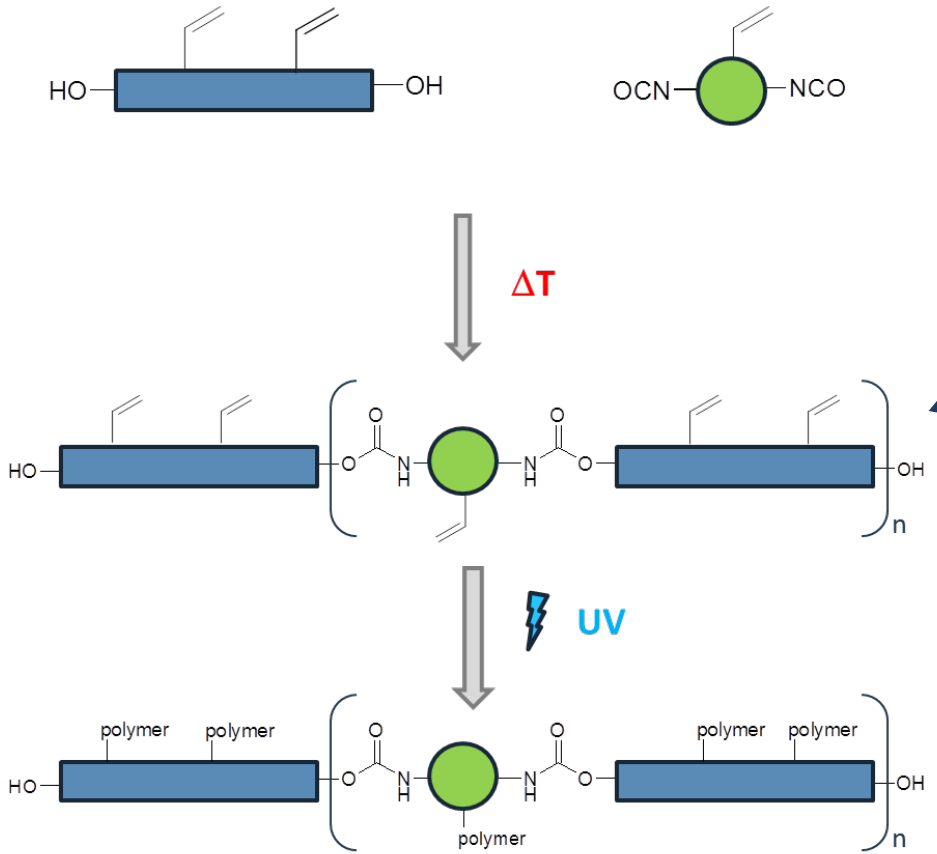
Lower equipment cost for e-beam

Chemistry advancements over the past 18 years

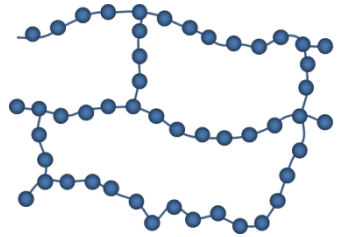
- High functionality and flexibility
- Dual cure technology marrying conventional and free radical chemistries
- Waterborne UV that offers water release that can be on par with solventborne

Dual cure free radical for coils

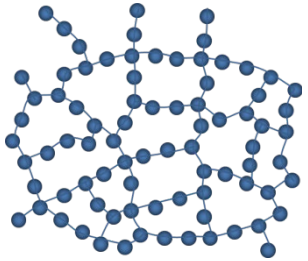
The coating system consists of a conventional NCO/OH thermal curing followed by UV/EB curing of acrylate groups after the thermoforming step



ELASTOMERIC BEHAVIOUR –
LOW CROSSLINKING DENSITY



THERMOSET BEHAVIOUR –
HIGH CROSSLINKING DENSITY



free radical for dual cure

Free radical dual cure advantages

Can be combined with conventional 2k offering formul

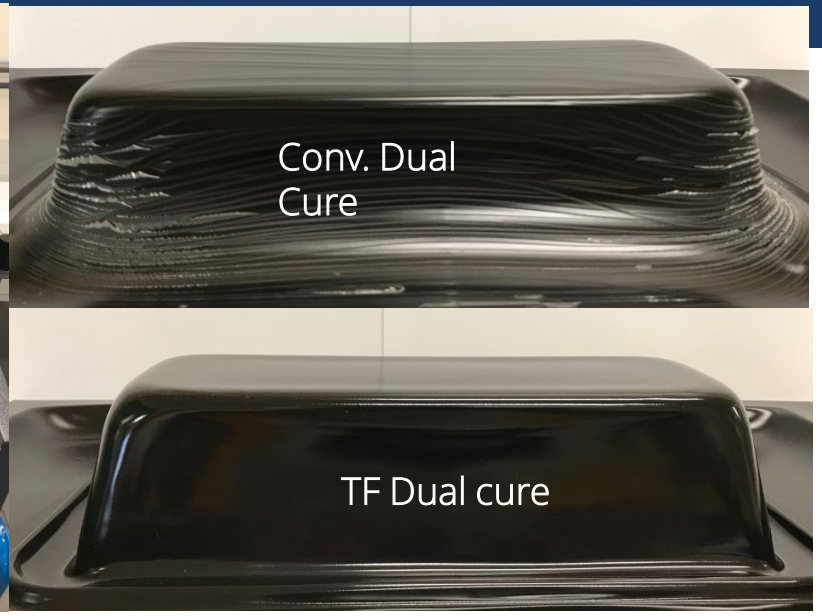
Thermal cure typically completed by solvent evaporatio

Elongation after thermal >300% and after cure 10%

Substrate can be rolled up, taken offline, abrasion and

Pot life can be 8 hours

Acrylic and urethane-based chemistries offering outsta



20 µm dry on Veralite 200 (PETG) substrate

	Free radical	Conv. Dual Cure	Free radical 2k
Touch dry after oven tack free : fingerprint (5 : no mark)	5 (UV cure)	5	5
Thermoformability			
Cylinder 1 cm (50 % elongation)	pass	fail	pass
Cylinder 3 cm (150 % elongation)	fail	fail	pass
Cylinder 5 cm (200 % elongation)	fail	fail	pass
Cylinder 8 cm (300 % elongation)	fail	fail	pass

free radical waterbase for coil

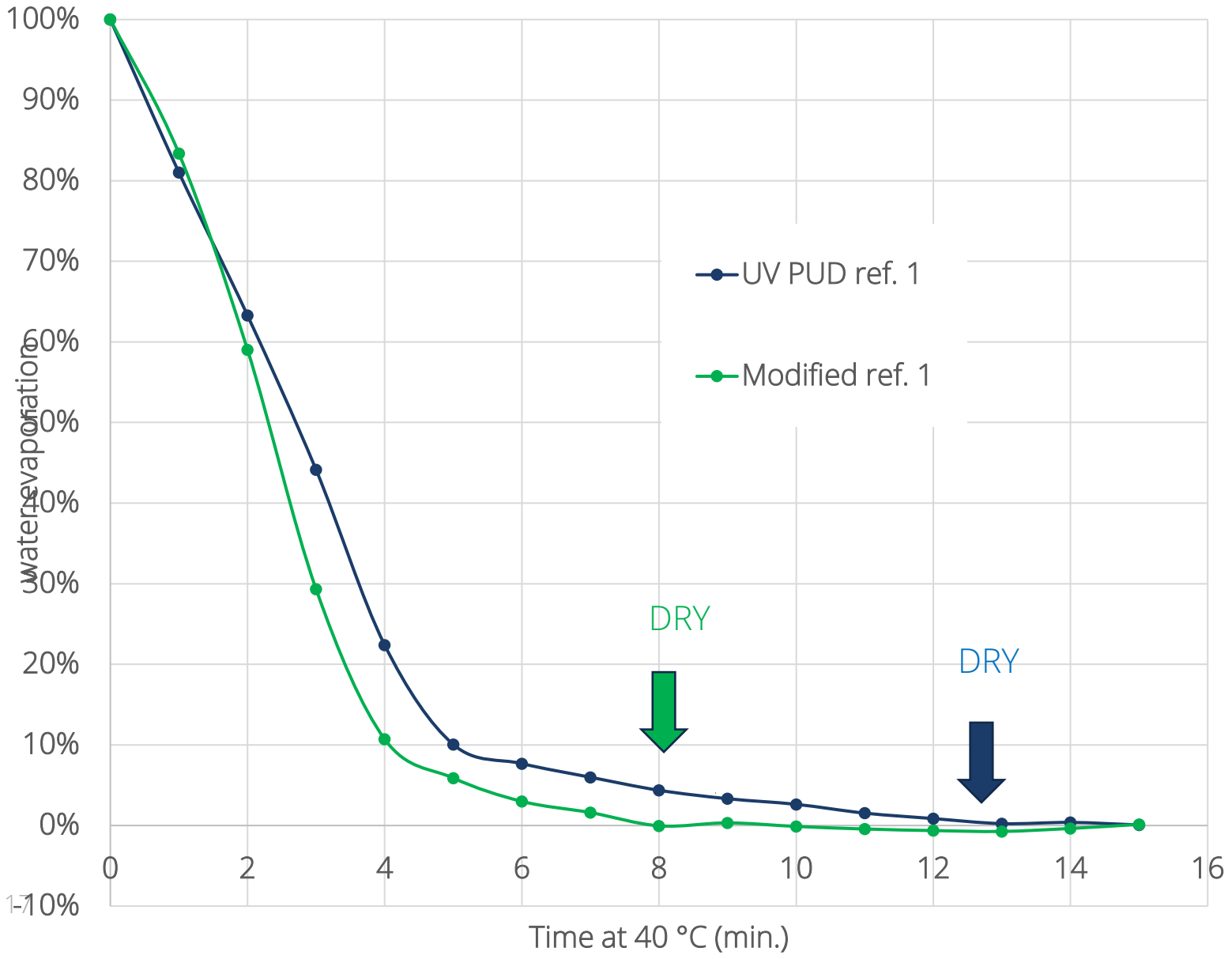
High DOI and gloss can now be achieved in clears

Improve outdoor durability

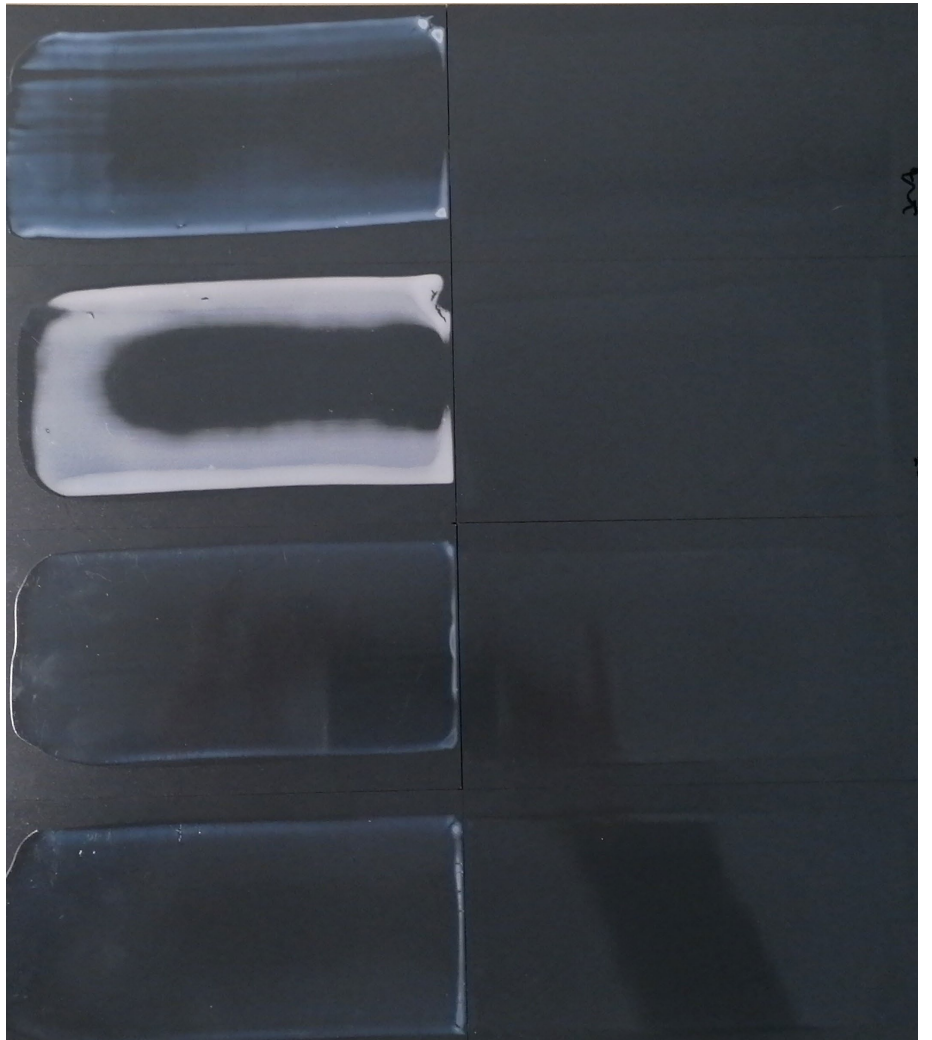
Improved water release that makes it possible on much shorter lines

Water release similar to solventborne

free radical waterbase – Faster water release

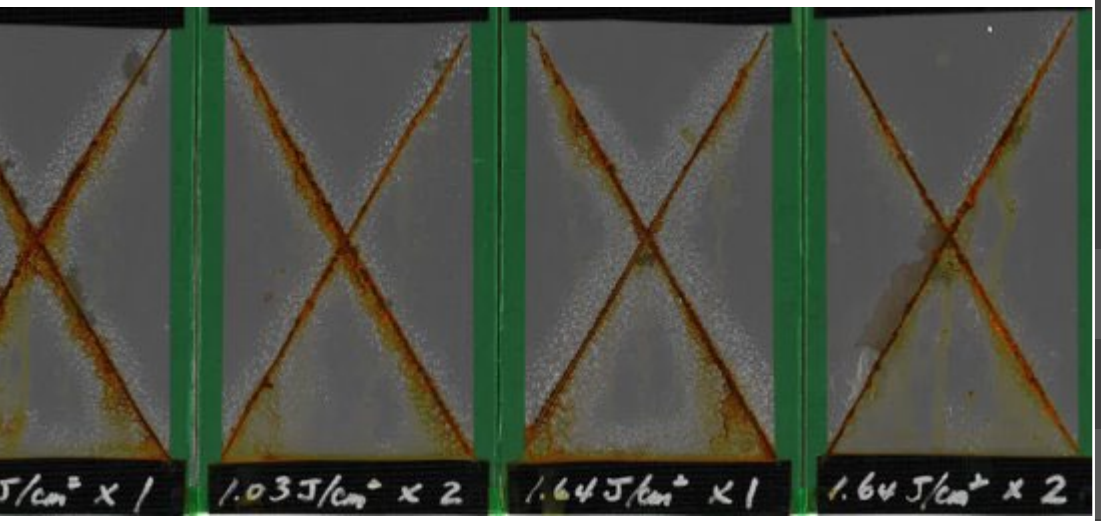


One-third less time to obtain non-detectable water by NIR



free radical waterbase for metal

7 Days Salt Spray Test- ASTM B-117
DFT – 1 mil



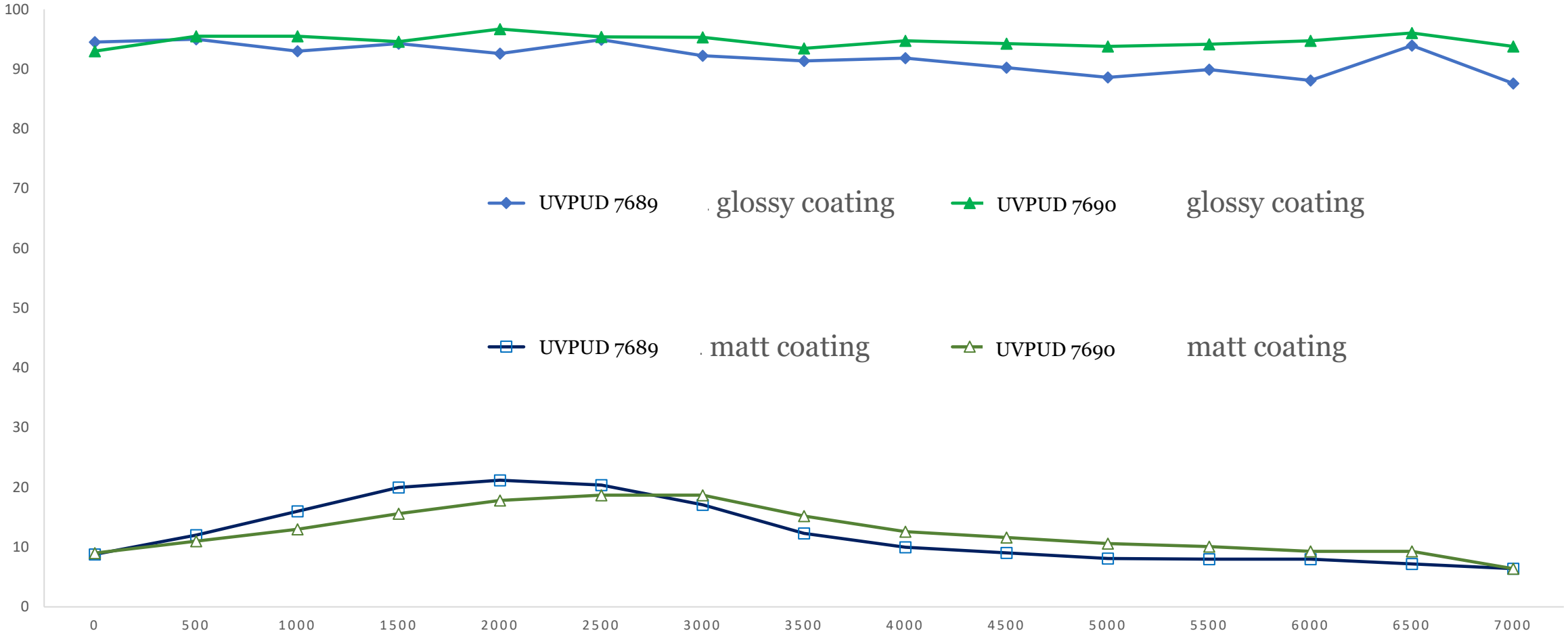
Waterborne PUD can be designed to offer excellent adhesion to a variety of metals and salt spray resistance analogous to conventional water-based alkyds and polyurethanes with increased chemical resistance and hardness

- Persoz hardness: 280 seconds
- MEK double rubs: >100 (1kg)

UVA 2807	**45.6%**
UVA 7655	45.6%
White corrosion inhibiting pigment	1.20%
TiO_2	1.00%
Iron oxide black pigment	0.50%
Fumed silica	0.35%
PI	1.37%
PI 2 (longer wavelength)	0.46%
Pigment dispersant	3.00%
Thickener	0.90%

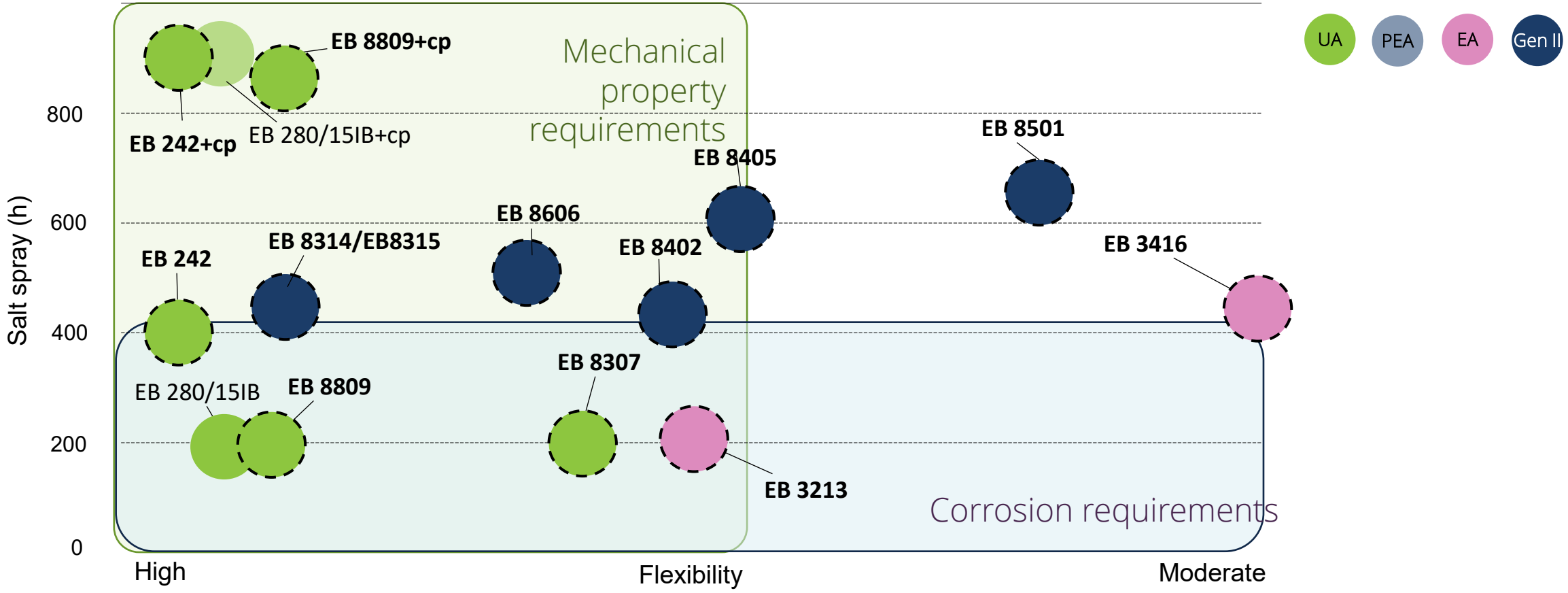
Direct Impact test, 20 inch-lb, 1/2" diameter ball, then 3M #600/610 tape applied	OK
Reverse Impact test, 20 inch-lb, 1/2" diameter ball, then 3M #600/610 tape applied	small removal
Crosshatch adhesion (Scotch 600 tape)	0% removal

free radical waterbase for exterior



No film defects after 7000 hrs of Xenon
No difference in evolution of gloss for the two versions

Gen II free free radical systems for Coil



GEN II Resins focus on exterior durability and bridging the gap between hardness and flexibility

EB 8314 and **EB 8315** are moderate viscosity *(<10k cps at 25°C)* aliphatic urethane acrylates that offer a combination of flexibility (>100%) and acrylate functionality (3)

EB 8501 is a tetra-functional aliphatic urethane that offers excellent adhesion to metal and excellent pigment loading for a urethane acrylate

EB 8606 and **EB 8405** are tetra-functional urethane acrylates that offer an excellent combination of flexibility (>40%) and acrylate functionality plus outstanding outdoor durability

Gen II free radical developments for coil

	Acrylate Functionality	Elongation, %	Tensile, psi	Xenon Weathering, hrs	Viscosity at 25°C
EB 8314	4	110	6000	7000	14000
EB 8315	4	115	5000	7000	9200
EB 8402	2	50	3300	6000	14000
EB 8405	4	30	4000	10000	85000
EB 8501	4	28	4200	5000	36000
EB 8606	4	70	5000	8000	90000
EB 242N	2	186	4000	1000	2000
EB 8809	2	24	5000	6000	187000

- **Gen II represents a new free radical chemistry platform**
  - **Unique backbones that reduce volume metric shrinkage upon cure through lower chain entanglement**
  - **Higher glass transition temperature to improve outdoor durability**
  - **Lower hydrogen bonding for lower intrinsic viscosities**

Conclusion

Free radical chemistry is now ready to meet today's challenges in coil

Lower carbon footprint

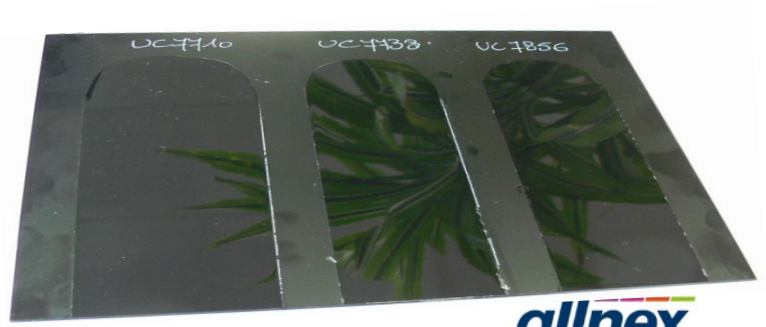
Increased productivity

Chemistry advancements that offer

Dual cure creating the best of both worlds

High-performance free radical waterbased that can offer fast water release, high DOI/gloss, and excellent weatherability

Free radical system can be designed to meet some of the most challenging exterior and durability needs



Thank You

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