Advanced Polymer Strategies for Enhancing the Performance of Water-Based Exterior Coatings

Coatings Trends & Technologies Conference

September 2024

Agenda

- Performance needs for water-based Exterior Coatings
- Overview of Polymer Design Techniques
  - Multi-phase polymers
  - Nanoparticle size emulsions
  - Functionalization
  - Polymerizable Surfactant Technologies
- Leveraging polymer design to enhance coating performance

Water-based Exterior Coatings

- Water-based exterior coatings have come a long way in the last 30 years.
  - VOC regulations have accelerated change
  - With movement to lower VOC, emulsion polymer technology has modernized to improve performance with lower coalescent loading
- Key Performance Properties
  - Gloss and color retention
  - Dirt Pickup Resistance
  - Water resistance performance
  - Sufficient hardness yet flexible

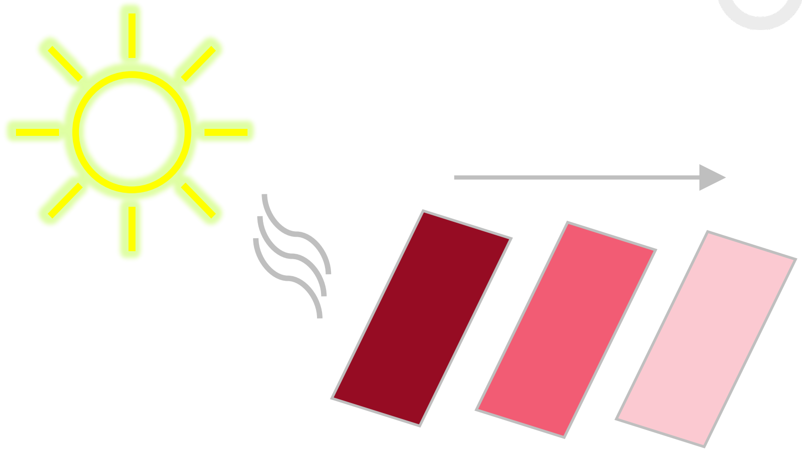
CARB Architectural Coatings VOC Suggested Control Measure Limits [g/L]

Year Adopted	Flat	Non-Flat	High Gloss	Imple-mented
1989	150	250		
2000	100	150	250	1/1/2003
2007	50	100	150	1/1/2010
2019	50	50		1/1/2022

Key Performance Properties for Water-Based Exterior Coatings

Gloss and Color Retention

- Interactions between binder and pigments play a significant role in determining gloss and appearance of a coating surface
- UV light and weather effects cause degradation over time
- Many thermoplastic acrylic polymers are generally UV resistant though coatings can vary in their performance
- Factors affecting gloss and color retention for an acrylic coating
  - Initial surface uniformity and roughness
  - Efficiency of coalescence and film formation
  - Degree of crosslinking

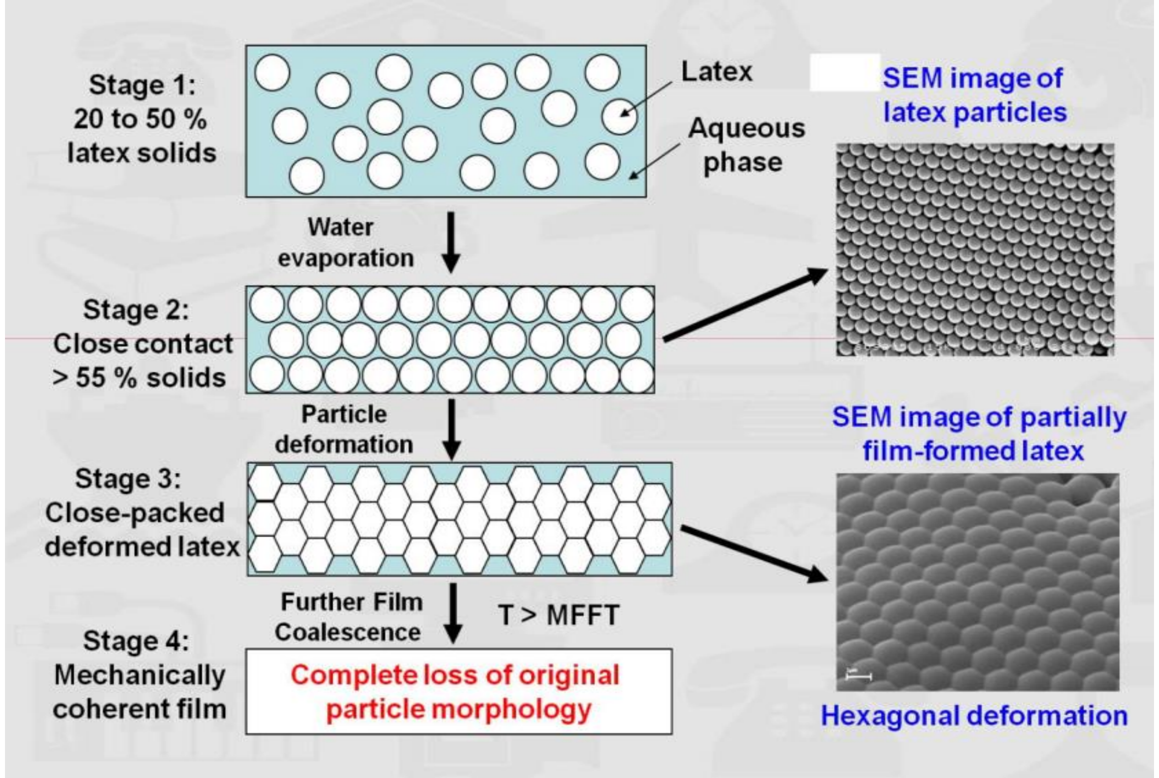


Gloss and Color Retention

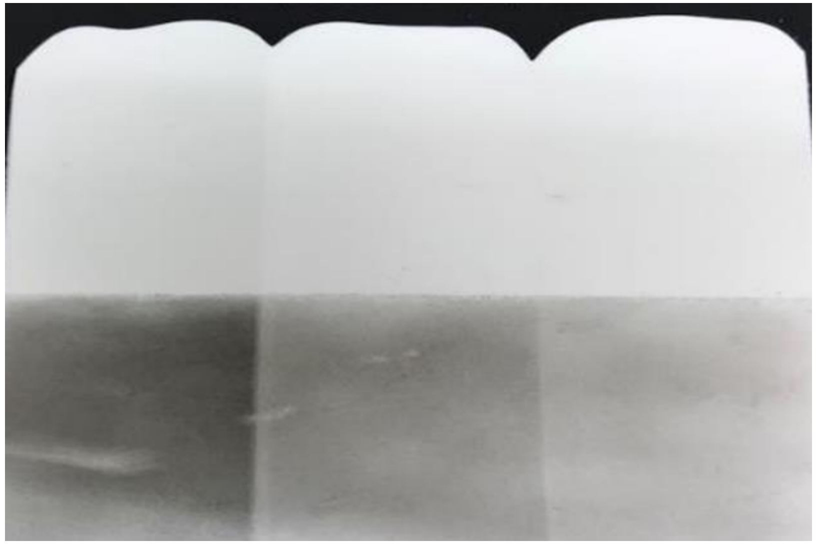
Latex polymer impacts on gloss and color retention:

- Efficient latex particle flow, wetting, and pigment interactions
  - Poor pigment coverage can lead to larger area of exposed colored pigments vulnerable to UV degradation
- Presence and speed of crosslink
  - Slow or limited crosslink could leave film vulnerable
  - Fast crosslink may lead to potential for cracking or other film defects to depress gloss

Film coalescence model of neat Latex



Dirt Pickup Resistance



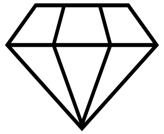
- Coatings surface variables that impact dirt pickup resistance
  - Surface film composition
  - Tackiness
  - Surface Hardness
  - Surface wettability
  - Porosity and Roughness
- Latex polymer contributes to quality of coating surface
  - Polymer composition
  - Tg
  - Morphology

Water Resistance Performance

- An exterior coating must resist water penetration for substrate protection and to maintain integrity of the coating itself
- Qualities of emulsion polymers used in exterior coatings
  - Hydrophobic monomer composition
  - Form low surface energy coating to prevent water wetting
  - Form a tight and uniform film

Hardness-Flexibility Balance

- Exterior coatings must be hard yet flexible
- Major challenge with low VOC deep color deco paints
  - Soft polymer with low coalescent demand is used to formulate low VOC paint
  - Plasticized further with high loading of colorant to make the dark colors
  - Results in undesirable soft and “cheesy” film feel



Hard
- General surface durability
- dirt pickup resistance
- Mar and abrasion resistance

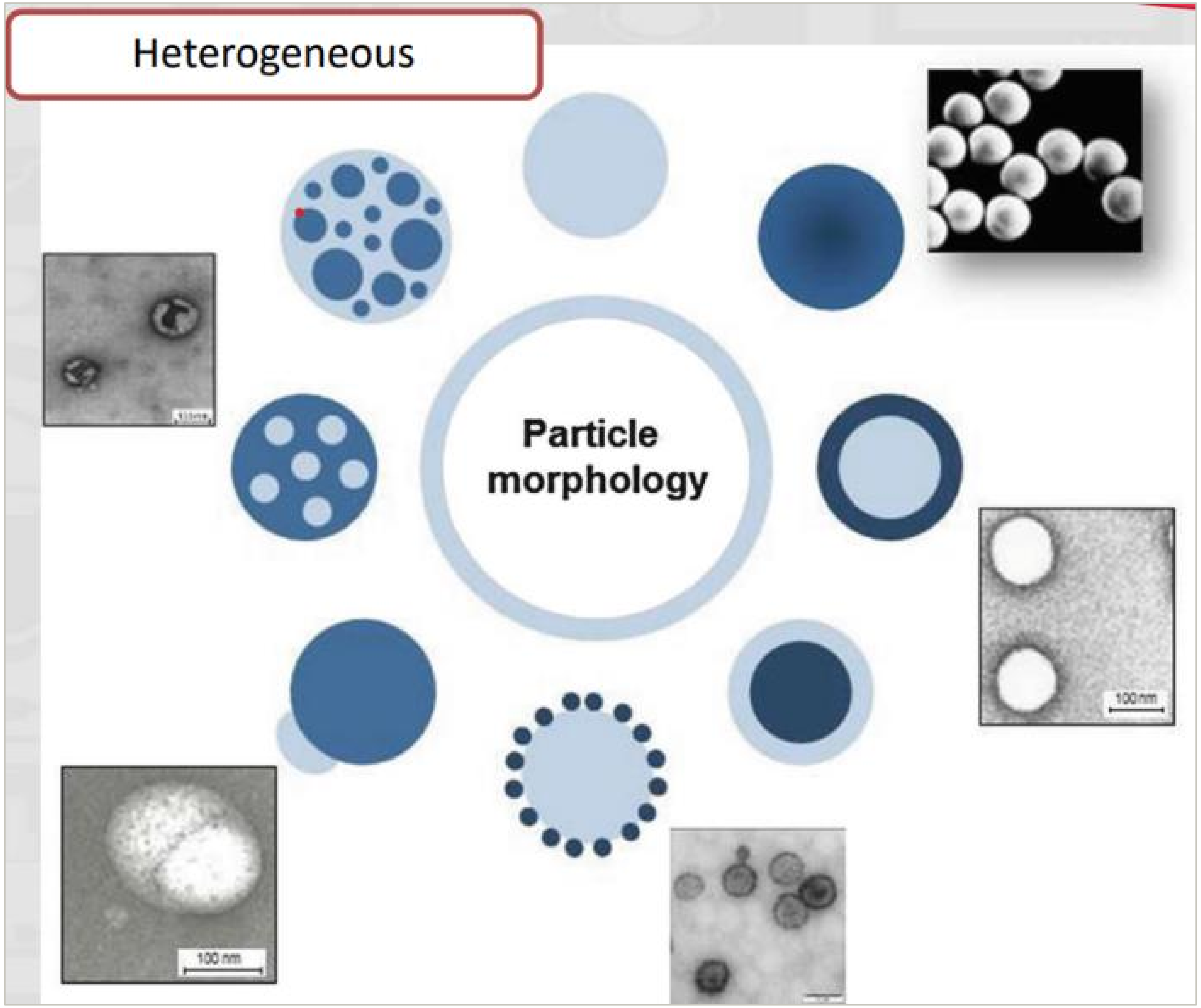
Flexible
- Dimensionally unstable surfaces like natural wood
- Able to bridge cracks
- Resist embrittlement
- Hot and cold temperature extremes

Polymer Design Techniques to give varying performance

Multi-Phase Polymers

- Use of multiple polymer phases incorporated in a single latex system
  - Hard vs soft polymer phases
  - Functional monomer placement
  - Distinct hard core / soft shell
  - Gradient polymer design
  - Lobed structure
- Deliver best of two polymer systems in a single hybrid system
  - Hardness of high Tg with flexibility of low Tg
  - Chemical resistance of epoxy with UV-durability of an acrylic
  - Weathering resistance of silicone with paintability of polyurethane or acrylic

Multi-Phase Polymers

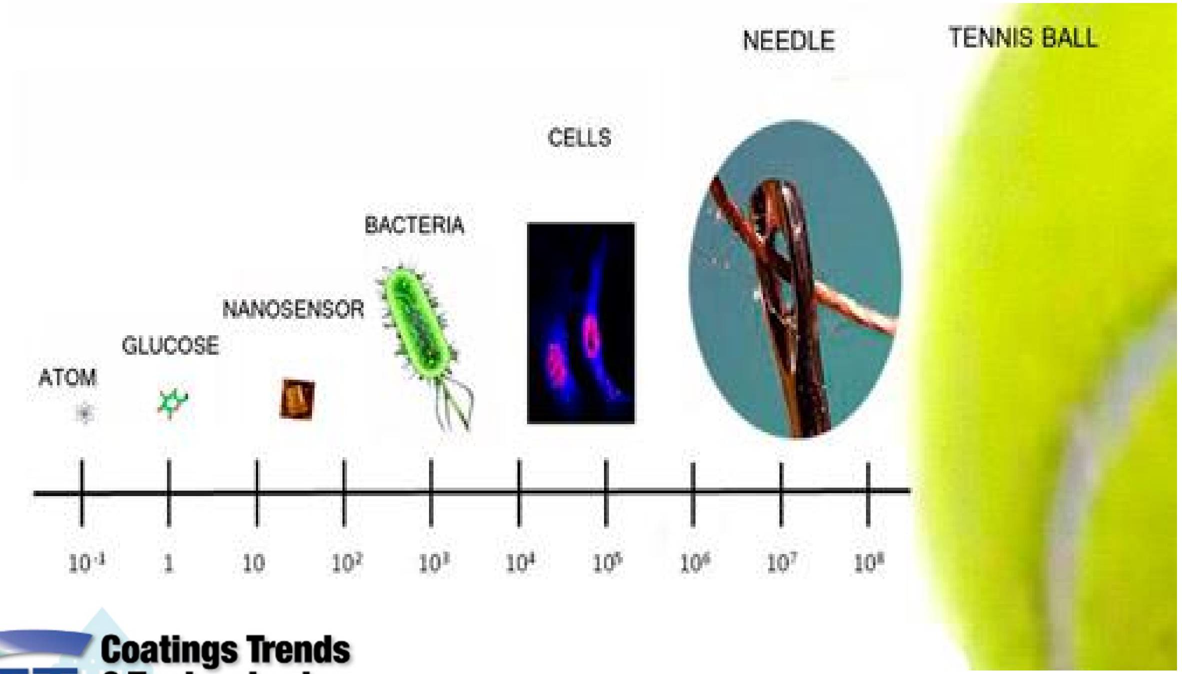


Nanoparticle Size Emulsions

NANOTECHNOLOGY

- 1nm=10^{-9}m in practice the relationship between a nanometer and a meter corresponds, roughly, to the ratio of magnitude that exists between the diameter of a tennis ball and the diameter of the earth

Nano Scale

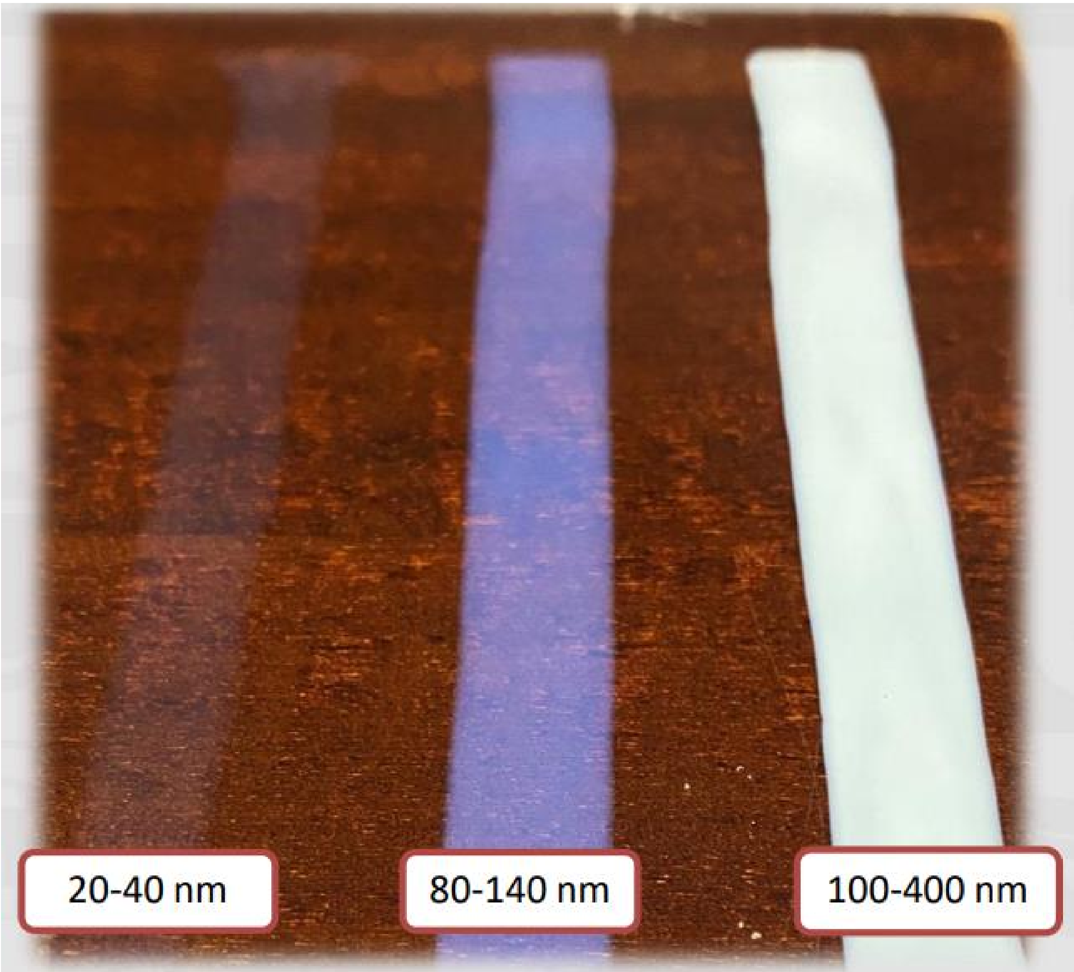


Nano Technology in modern Age

- Optical engineering
- Bio Technology
- Medicine and Bio Science
- Defense
- Energy
- Nano fabrics - textile
- Coating

Act on these dimensions means intervening on matter at atom level to create new functional materials, tools and systems with extraordinary properties derived from their structure and improve the quality and characteristics existing process.

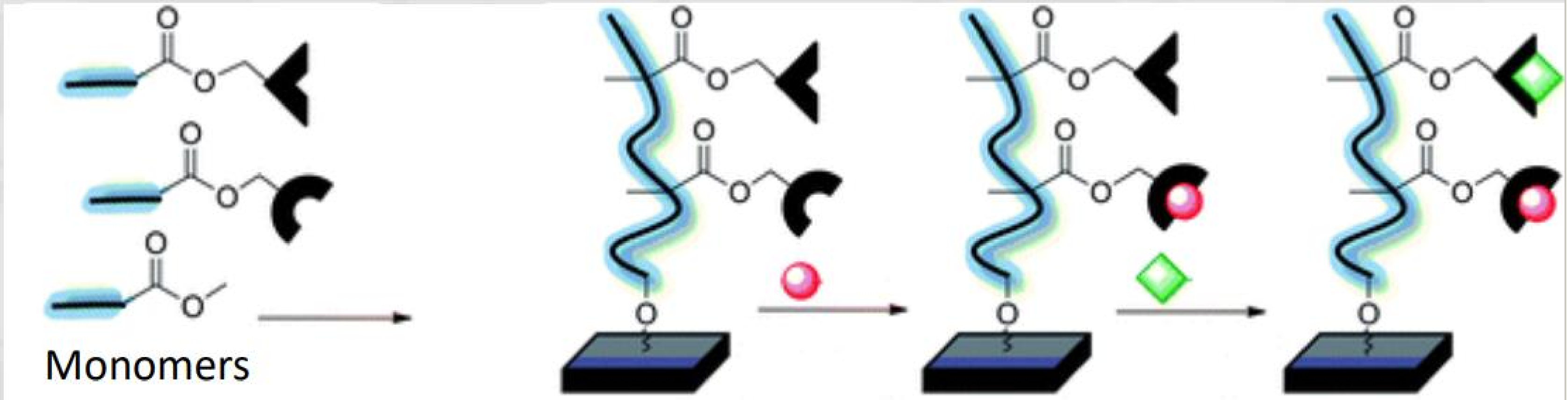
Nanoparticle Size Emulsions



- Features of nanoparticle size emulsions
  - Average Particle size < 100nm
  - More transparent
  - Easier film formation
  - Higher penetration capacity
  - High surface specific area
  - High surface functionality

Functionalization

- Functionalization allows to give special properties to the polymer
  - Adhesion on metallic surfaces
  - Hydrophobicity or hydrophilicity
  - Reactivity to specific substances
  - Crosslinking
- Special properties may be achieved by using at least one monomer with two or more functional groups

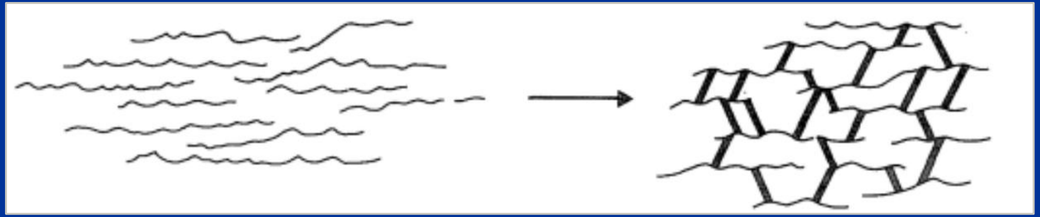


Example of interaction with different substrates/molecules

Functionalization

- Crosslinking is the formation of a polymer network, based on the reaction of functionality present on the polymer chain, catalyzed by pH variations, UV light, heat or solvent/water evaporation.
- Crosslinking enhances mechanical properties, heat and water/solvent resistance etc.

Polymer chains → Crosslinked structure



- Crosslinking mechanisms used in acrylic emulsions for water-based coatings
  - Metal complexes – chelation of polyvalent metal ions with carboxyl groups
  - Keto-dihydrazide / diamine reaction
  - Embedded UV-crosslinker activated by natural sunlight

Polymerizable Surfactants

Polymerizable surfactants provide emulsion stability and are bound directly to the polymer backbone

- Conventional surfactants – 0% bound to polymer
- Polymerizable surfactants could have 40% or more bound to polymer

Exterior coating properties benefit from latex stabilized with polymerizable surfactants

- Improved water repellency
- Enhanced surface properties such as blister resistance
- Reduction in aqueous phase migration – improved surfactant staining resistance

Exterior Coating Examples with varying Latex Design Techniques

Polymer 1: Multi-Phase, Nanoparticle Size

- Polymer 1 Characteristics
  - 100% acrylic
  - Gradient polymer morphology
  - Tg Hard Phase +130°C
  - Tg Soft Phase -5°C
  - MFFT +10°C
  - Average Particle Size of 50nm

- Key application areas
  - Exterior wood coatings – stain or topcoat
  - Composite panel coatings
  - Low VOC metal coatings

Polymer 1: Multi-Phase, Nanoparticle Size

Sample formula, Exterior Clear Wood Finish

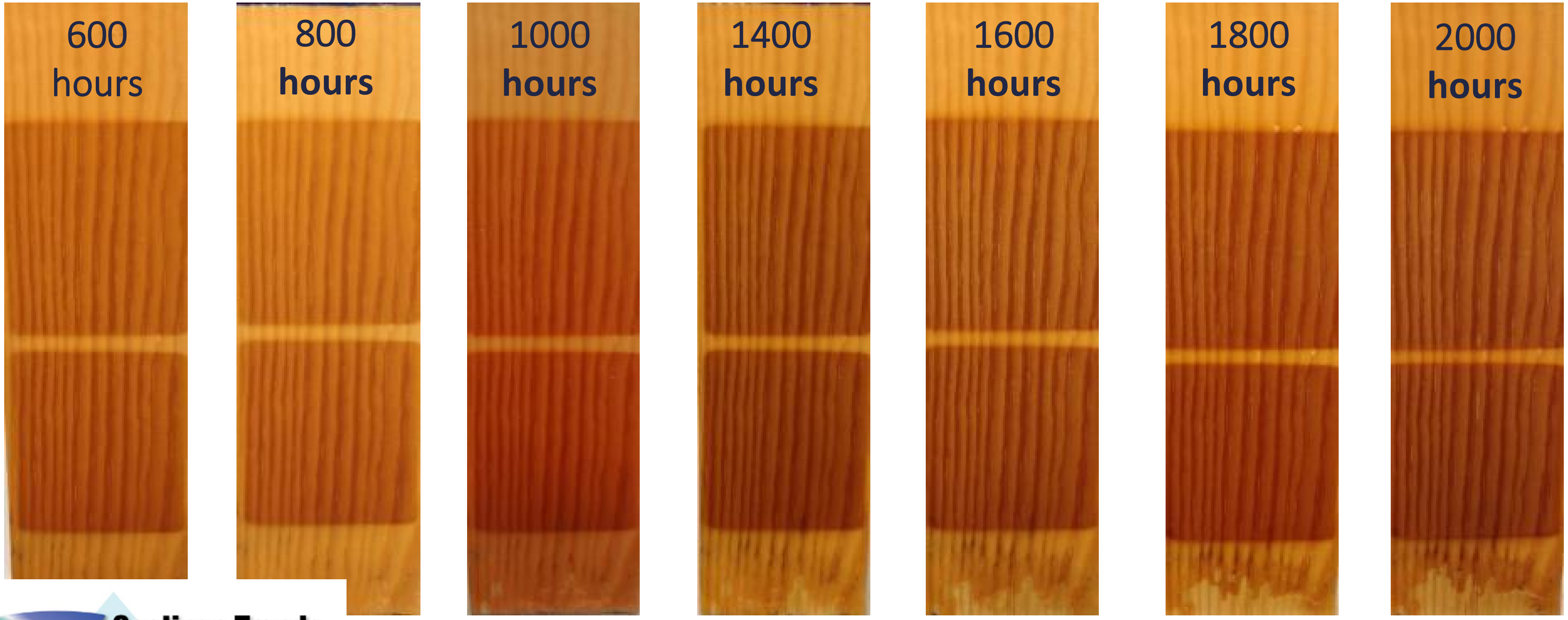
Material	wt %	Function
Polymer 1	90.0	Binder
Polyether Siloxane	1.0	Defoamer
Water	3.2	
Butyl diglycol	2.0	Coalescent
HEUR thickener	0.2	Thickener
Wetting Surfactant	0.5	Wetting Agent
Acrylic thickener	0.7	Thickener
Ammonia (28%)	0.2	pH regulator
Modified Siloxane	2.0	Defoamer
Trans Red dispersion	0.1	Pigment
Trans Yellow dispersion	0.1	Pigment
TOTAL	**100.0**	

- T&E, 500μm film
  - Tensile Strength at break: 6.8 N/mm^2
  - Elongation at break: 300%
- Block Resistance
  - 400μm film
  - 0-5 scale 0=excellent no block, 5=extremely poor block
  - 25°C, 1kg/cm^2, 8 hours = 1
  - 50°C, 0.3kg/cm^2, 8 hours = 2
- Persoz Hardness, 150μm film
  - 130 seconds

Strike the balance of Hard yet Flexible

Polymer 1: Multi-Phase, Nanoparticle Size

- 2000 hours UV-Condensation with spray
  - UVA 340 nm
  - Method UNI E 927/6



No film deterioration or loss of adhesion over 2000 hrs UV-Condensation testing

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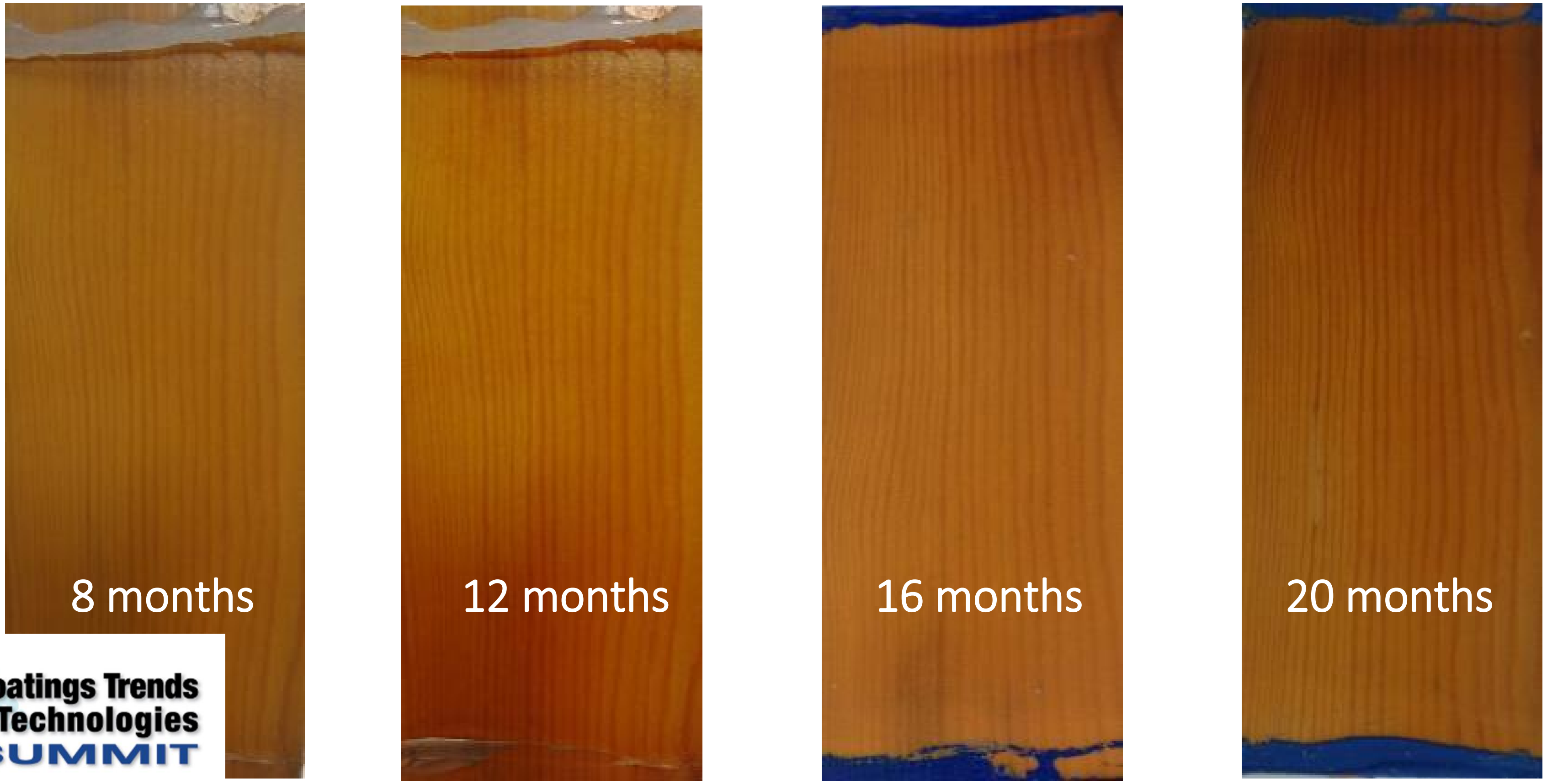
Polymer 1: Multi-Phase, Nanoparticle Size

- Natural weathering in Italy, South 45° Exposure
- No significant deterioration noted over 20 months



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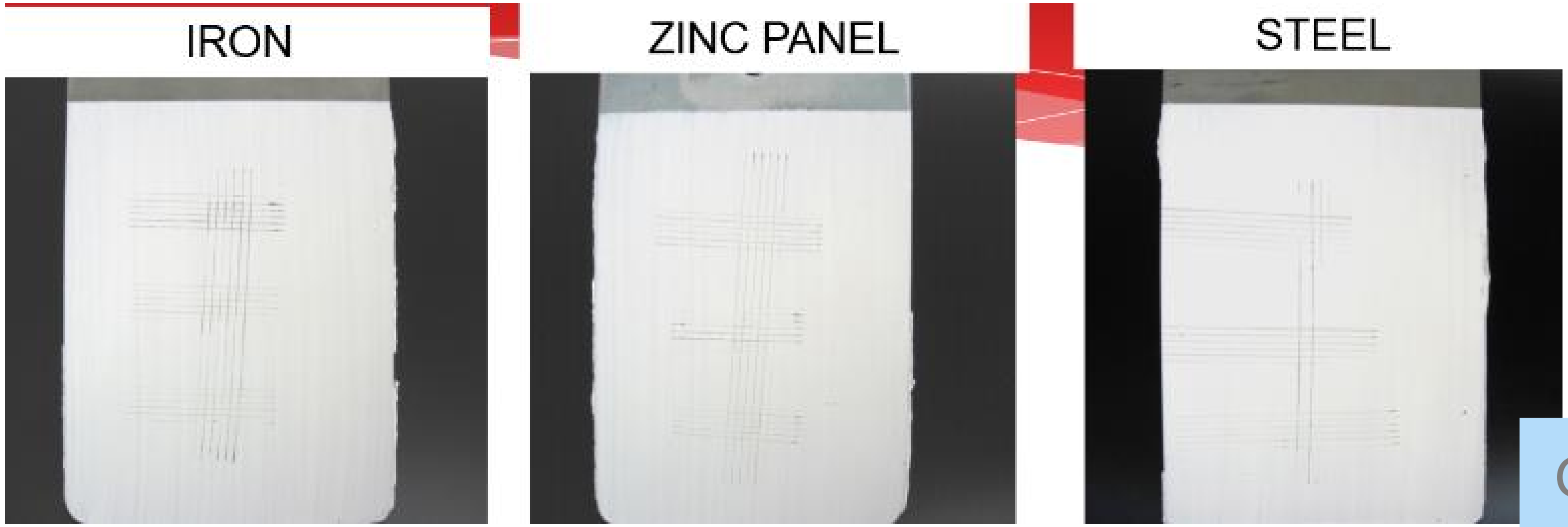
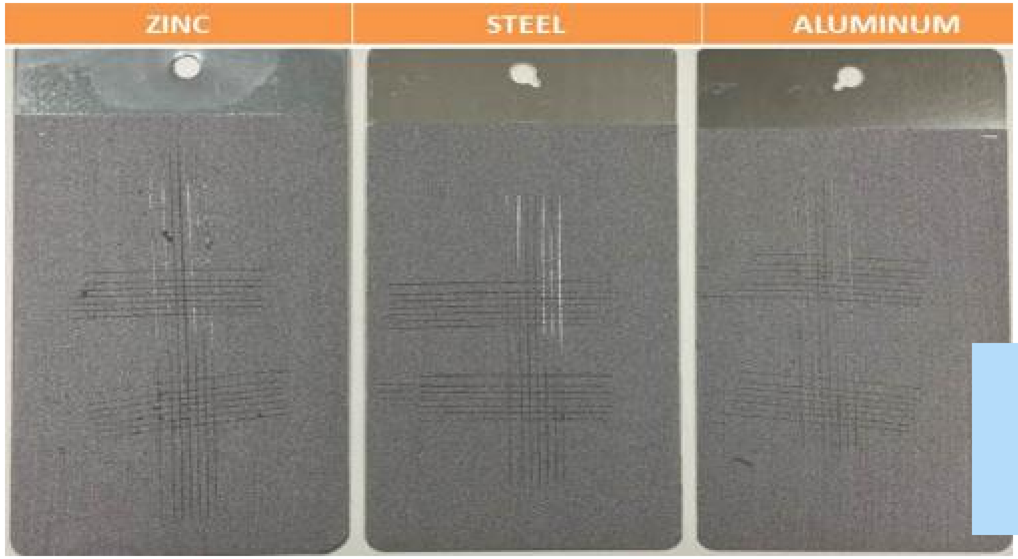
Polymer 1: Multi-Phase, Nanoparticle Size



- Versatile polymer for multiple uses
- Adhesion profile over metal substrates

Gloss enamel formula



Micaceous iron oxide formula

Polymer 2: Nanoparticle Size Emulsion

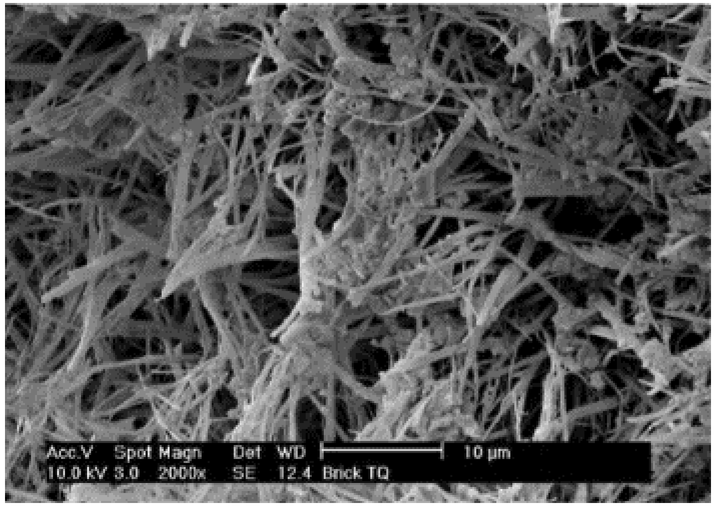
- Polymer 2 Characteristics
  - 100% acrylic
  - Homogeneous particle morphology
  - Average particle size of 25-40 nm
  - Tg +15°C

- Key benefits
  - High penetration capacity
  - Consolidation effect
  - Promote adhesion
  - Barrier effect to efflorescence

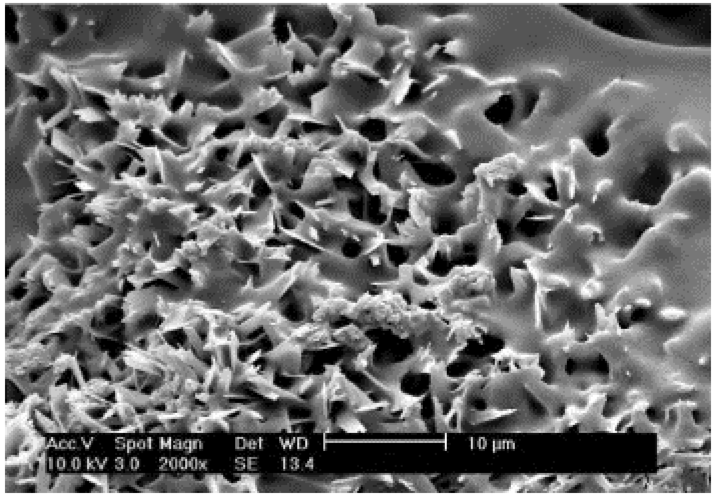
Polymer 2: Nanoparticle Size Emulsion

- Consolidating primer formulation

Material	Wt %
Water	49.5
Defoamer	0.3
Polymer 2 (31% solid)	50.0
Biocide	0.2
Total	100.0



Untreated mineral substrate

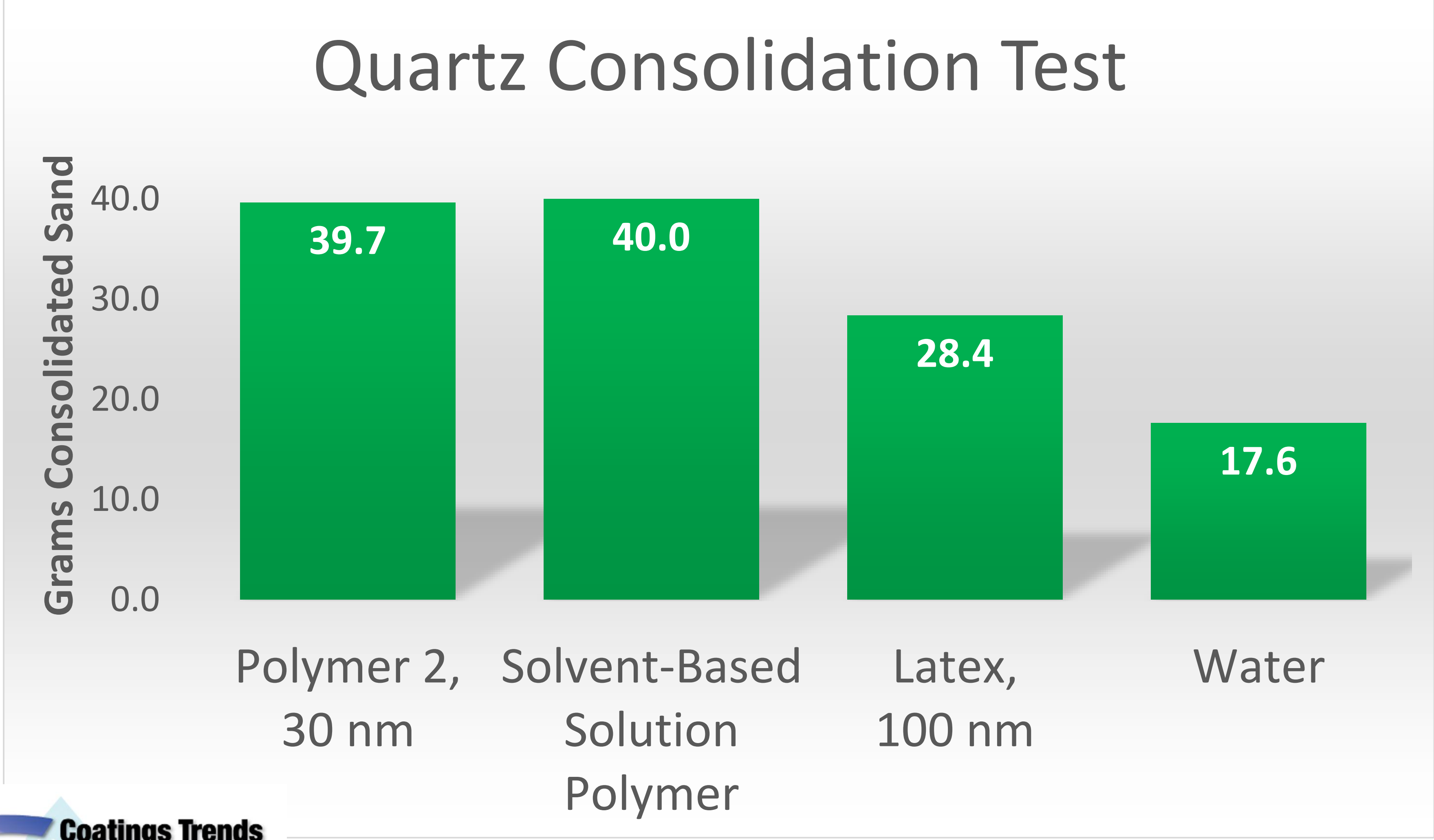


Treated substrate: covers and protects but breathability is maintained

Polymer 2: Nanoparticle Size Emulsion

- Quartz consolidation test
  - Liquid material dropped onto quartz sand
  - Scoop out the consolidated material and weigh to determine effectiveness

Polymer 2: Nanoparticle Size Emulsion



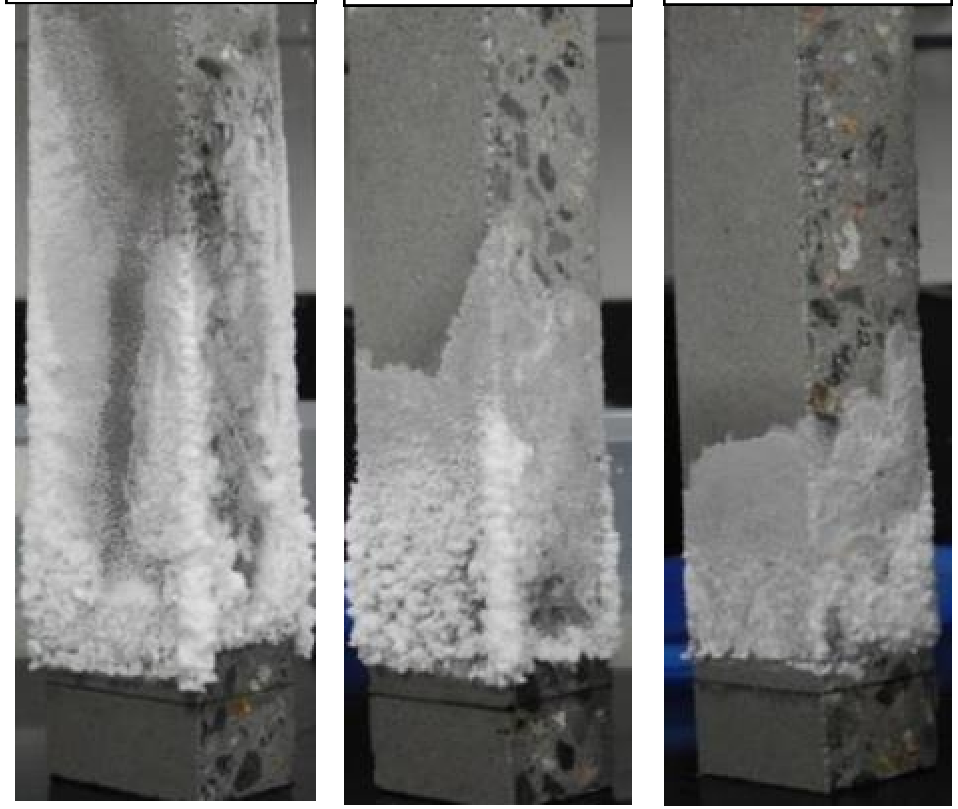
Polymer 2 emulsion penetrates and consolidates comparably to solvent-based solution polymer

Polymer 2: Nanoparticle Size Emulsion

- Particle size affects penetration
- Demonstrated by relative efflorescence performance
  - Acrylic emulsion, M_v 150 nm
  - Nanotechnology acrylic, M_v 30 nm
  - Solvent-based solution polymer
- Coated masonry blocks with bottom portion placed in saturated salt solution and allowed to stand for 7 days

Polymer 2 based primer penetrates pores blocking salt migration

Particle size 150 nm	Polymer 2, 30 nm	Solution Polymer



Polymer 3: Core-Shell Self-Crosslinking

- Polymer 3 characteristics
  - 100% acrylic
  - Core-shell morphology
  - Self-crosslinking acrylic
  - Tg Hard Phase +70°C
  - Tg Soft Phase +15°C
  - MFFT +10°C
  - Average Particle Size of 90nm

- Key Benefits
  - Low VOC capability
  - Block resistance
  - Weatherability

Polymer 3: Core-Shell Self-Crosslinking

Sample formula, Gloss Enamel

Material	wt %	Function
Water	7.5	
Polyether Siloxane	0.3	Defoamer
Propylene Glycol	3	
Acrylic dispersing	0.4	Dispersant
Amino alcohol	0.4	Neutralizing agent
TiO_2	22	Pigment
Polymer 3	60	Binder
Texanol	2.5	Coalescent
Polyether Siloxane	0.3	Defoamer
Zn compound	0.6	Corrosion Inhibitor
MIT/BIT	0.2	Biocide
HDPE Emulsion	1.2	Wax Emulsion
Silicone Surfactant	0.4	Wetting Agent
HEUR Thickener	1.2	Thickener
TOTAL	**100**	

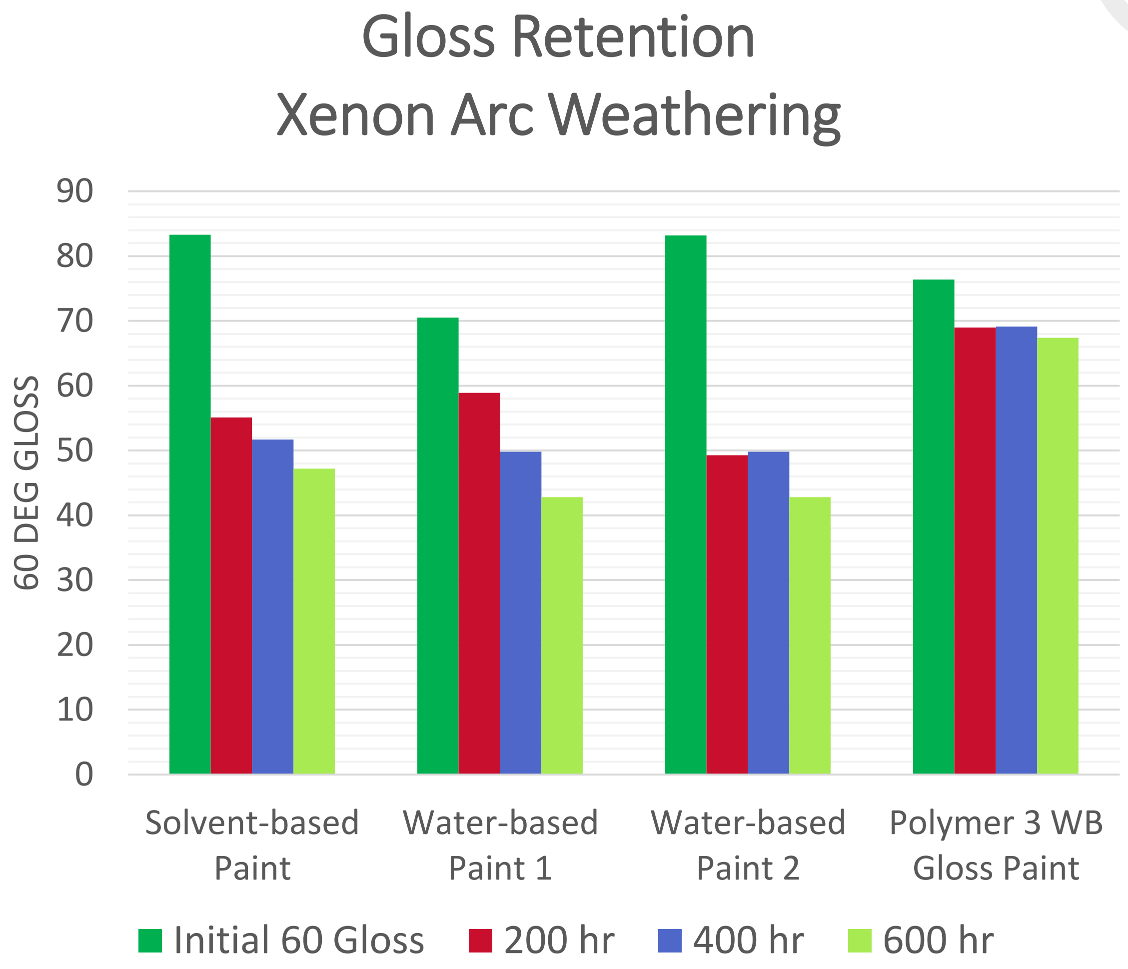
- Gloss @ 20°/60°
  - 53 / 78
- Persoz Hardness, 24 hrs dry, 70 seconds
- Cross-hatch Adhesion
  - Wood, Aged Alkyd, Steel, Zinc – all 5B
- Block Resistance, excellent

Self-crosslinking polymer delivers strong performance at low VOC

Polymer 3: Core-Shell Self-Crosslinking

- Xenon Arc Weatherometer test, ASTM G155

Polymer 3 paint yields excellent gloss retention of 88% over the 600-hr accelerated weathering test



Polymer 4: Special Monomer Incorporation

- Polymer 4 characteristics
  - Homogeneous morphology
  - Vinyl versatic acid ester copolymer
  - Tg +24°C
  - MFFT +13°C

- Benefits
  - Hydrophobicity
  - Alkali Resistant
  - Pigment compatibility and high binding power
  - Low Surface tension

Polymer 4: Special Monomer Incorporation

GRIND

Material	Use	Polymer 4 Masonry Paint
Water	Water	125
HMHEC Cellulosic	Thickener	1.5
Ammonia (28% aq)	pH Stabilizer	2
Mineral Oil/silica defoamer	Defoaming	3
Anionic Pigment Dispersant	Dispersant	12
Surfactant	Wetting	2
Attapulgite Clay	Stabilizing Agent	2
Titanium Dioxide	Primary Pigment	200
Nepheline Syenite	Extender	100
Calcium Carbonate	Extender	50
Talc	Extender	75
Water	Water	189

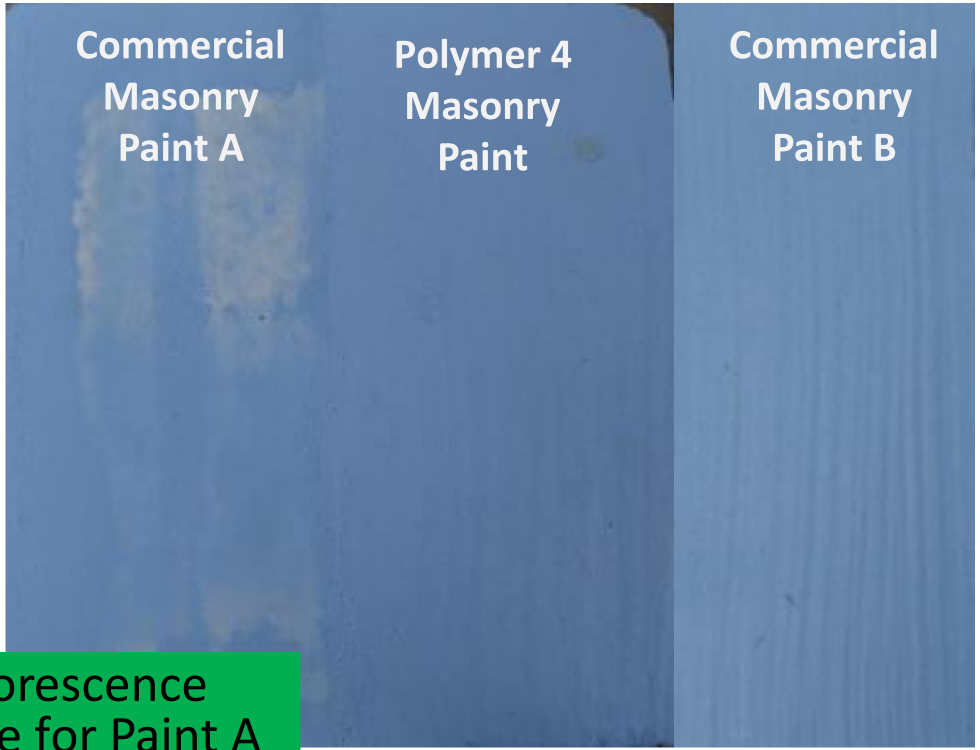
LETDOWN

Material	Use	Polymer 4 Masonry Paint
Polymer 4	Binder	353.8
Mineral Oil/silica defoamer	Defoaming	2
Texanol	Coalescing	9.0
Non-VOC Coalescent	Coalescing	12.5
In-Can Preservative	In-Can Preservative	4
Mildewcide	Film Protection	4.0
PU High Shear Modifier	Associative Thickener	7
PU Low Shear Modifier A	Associative Thickener	1.8
Total Weight (Pounds/101 Gal)		1156

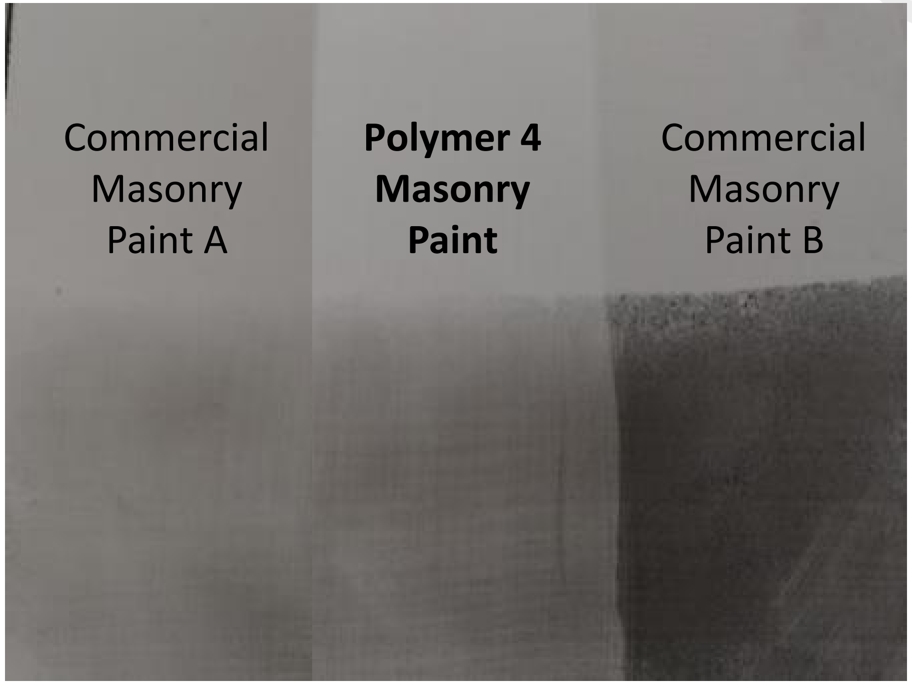
Formula is 43 PVC, 39% Volume Solids, VOC of 30 g/L

Polymer 4: Special Monomer Incorporation

- Polymer 4 gives both strong dirt pickup resistance and strong alkali/efflorescence resistance

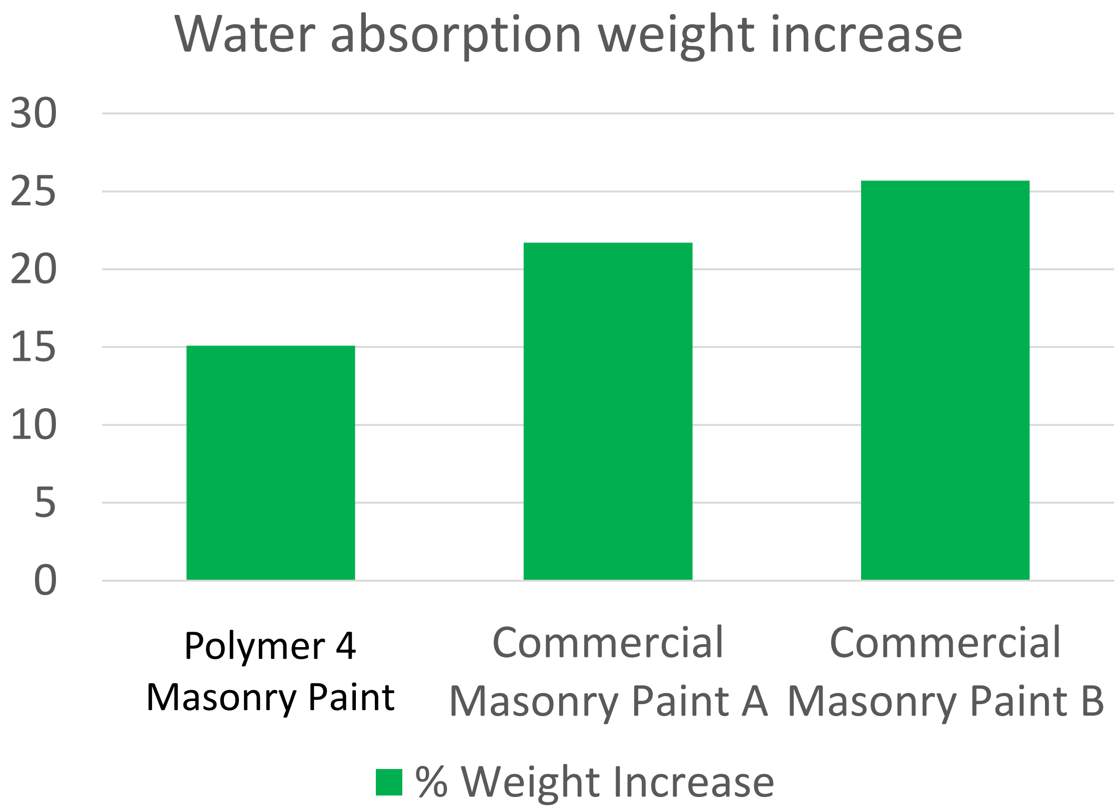


Poor efflorescence resistance for Paint A



Very poor dirt pickup for Paint B

Polymer 4: Special Monomer Incorporation



- **Water Absorption Resistance**
  - Samples fully dried in oven at 50°C and weighed
  - Immersed in water for 7 days and weighed
- **Polymer 4 shows best water resistance resulting from hydrophobic character of versatic acid ester copolymer**

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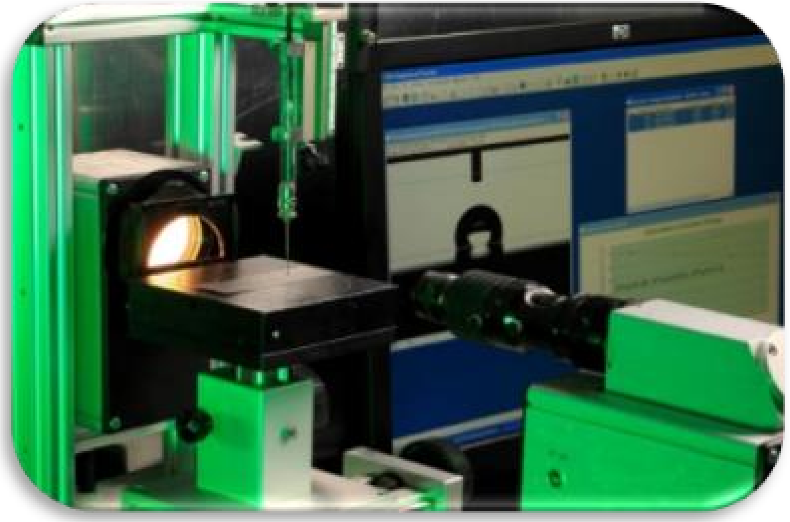
Polymer 5: Polymerizable Surfactant

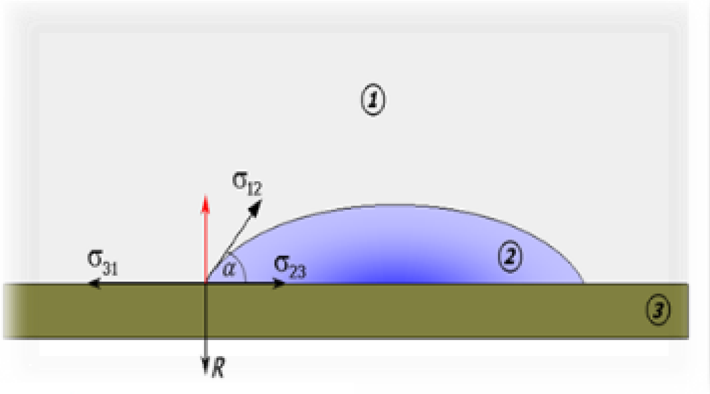
- Polymer 5 characteristics
  - 100% Acrylic
  - Homogeneous morphology
  - Tg +21°C
  - MFFT +10°C

- Key benefits
  - Low total surface energy for water resistant benefits
  - Strong pigment binding
  - Excellent weathering capability

Polymer 5: Polymerizable Surfactant



Surface tension or surface free energy is the work required to form more surface (for liquid): to bring molecules from the interior of the phase into the surface region. Force acting along unit length in the surface (for solid).
Surface tension (solid and liquid) can be expressed as sum of surface tension fractions each due to a particular type of intermolecular forces.
Dispersive fraction: Van der Waals,…
Polar fraction: Hydrogen bonding; dipole- dipole,…



	Polymer 5	Acrylic A
Total Surface Energy [mN/m]	**32.57**	68.92
Polar Part [mN/m]	5.46	57.44
Disperse Part [mN/m]	27.10	11.48

$W_{sl} = \gamma_{lv} (1- \cos \theta)$ Young-Duprè equation

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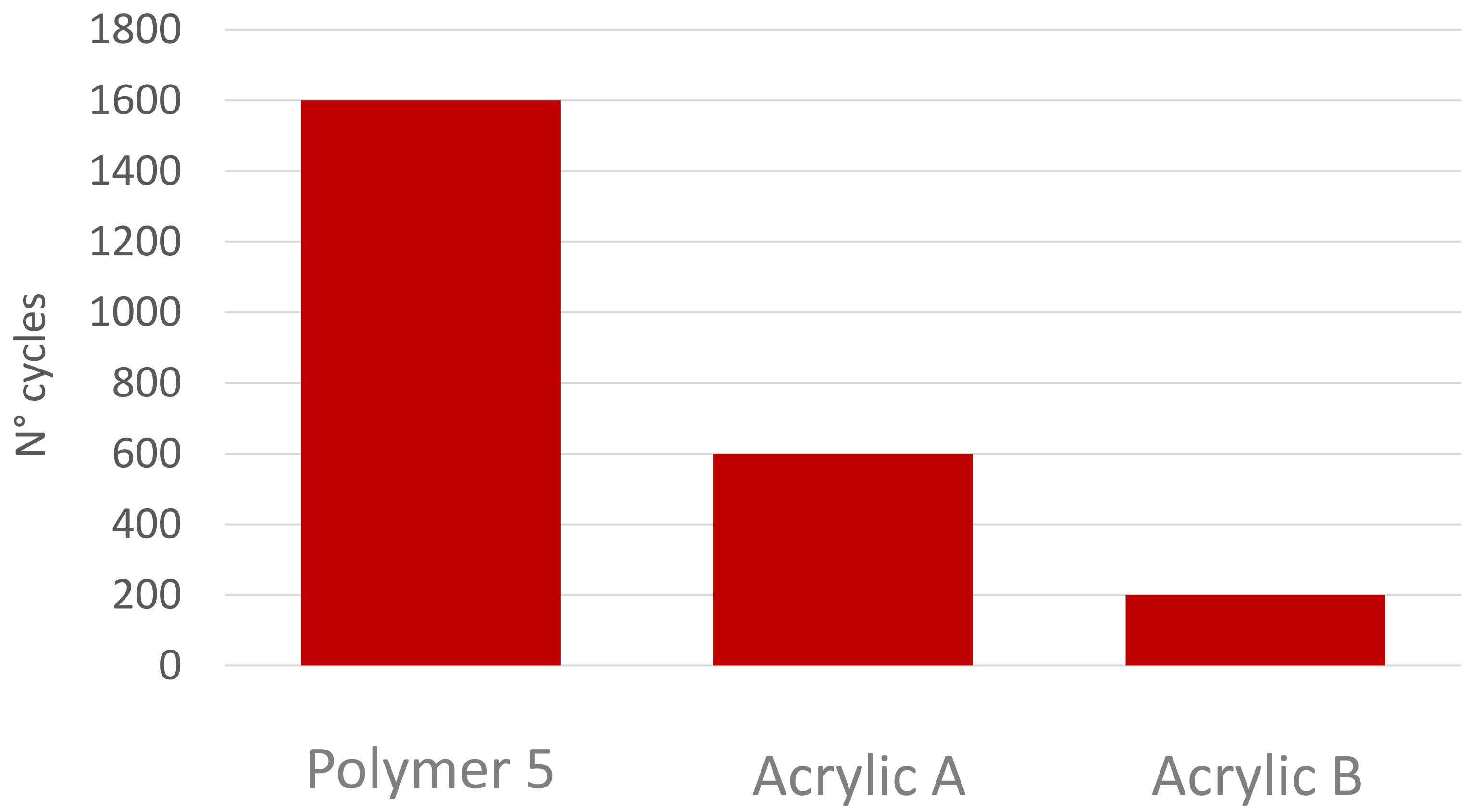
Polymer 5: Polymerizable Surfactant

Wet scrub resistance for 80% PVC paint in accordance with DIN 53778



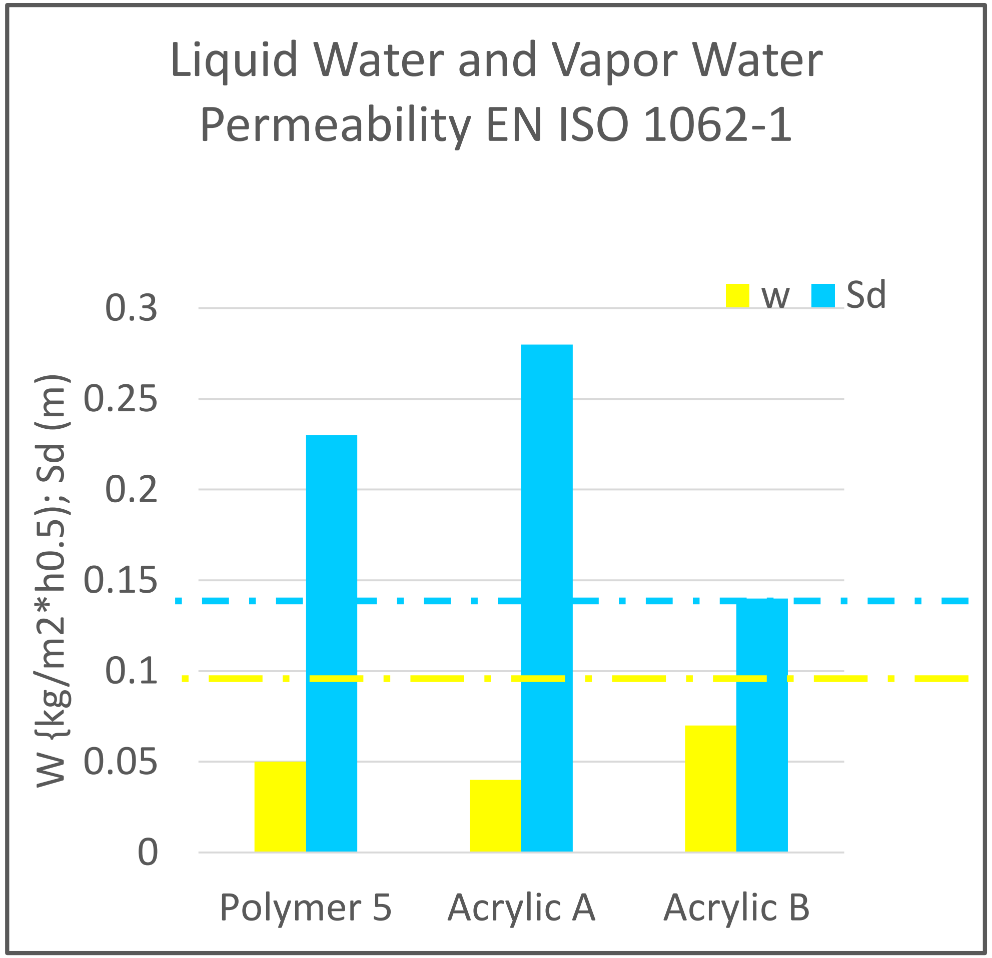
Polymer 5 gives excellent pigment binding effect and scrub result

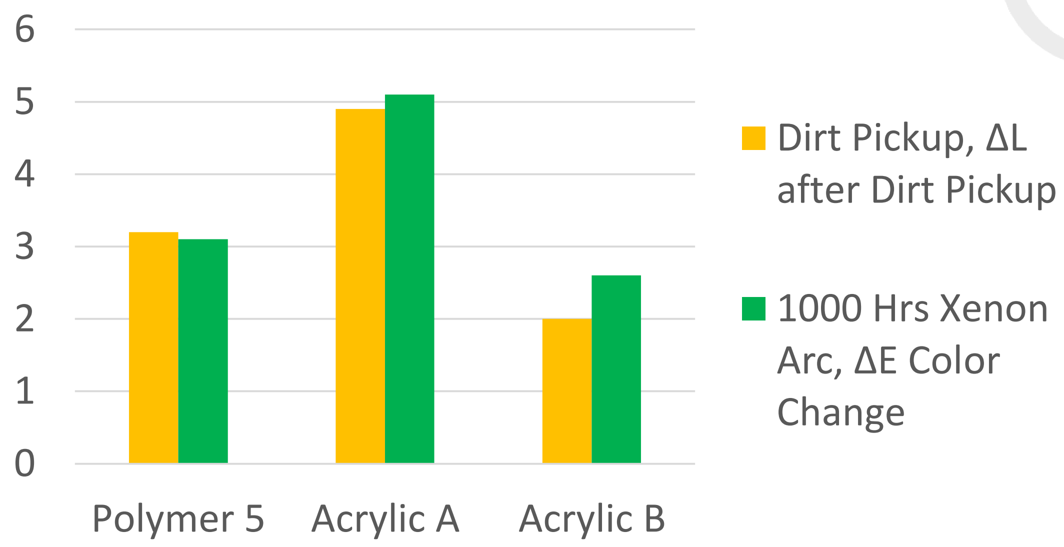
Polymer 5: Polymerizable Surfactant

Components	w. %	Function
Water	15,40	
Polysiloxane	0,30	Defoamer
HEC Cellulosic	0,40	Thickener
Amino alcohol	0,10	pH regulator
Sodium exametaphosphate (sol. 10%)	1,00	Dispersant
Acrylic dispersing	0,60	Dispersant
BIT Isothiazolin	0,30	Biocide
Texanol	1,20	Coalescent
Propylene glycol	0,80	Co-solvent
TiO_2	16,00	Pigment
$CaCO_3$ 5μm type	4,50	Filler
Quartz (100 μm)	25,00	Filler
Calcined Kaolin	6,00	Filler
Paraffin wax emulsion	1,50	Hydrophobic wax
Amino alcohol	0,20	pH regulator
Polysiloxane	0,20	Defoamer
Binder (50% solid)	**25,00**	
Water	1,50	
Total	100,00	

Model Exterior paint formulation used to evaluate polymer 5 and 2 comparison acrylic resins

Polymer 5: Polymerizable Surfactant





- Use of polymerizable surfactant in Polymer 5 enables unique combination of performance
  - Excellent pigment binding and scrub
  - Liquid water barrier with high water vapor permeability
  - Strong Dirt pickup and color retention performance

Advanced polymer design strategies enhance coating performance

- Polymer design strategies include
  - Multi-phase polymer morphology
  - Nano-particle size latex
  - Incorporation of functional monomers and self-crosslinking
  - Use of polymerizable surfactants
- Use and combination of these polymer designs create high performance polymer solutions for exterior coatings

CONCLUSION

- Modern emulsion polymerization design is essential to produce resins that enhance performance of exterior water-based coatings
- Selecting a polymer supplier experienced with many advanced polymer strategies can elevate exterior coating formulations to a higher performance level

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