THE USE OF REACTIVE NONIONIC SURFACTANTS IN EMULSION POLYMERIZATION TO IMPROVE RESIN WATER RESISTANCE

AGENDA

1. Emulsion Polymerization Challange
2. Project’s Goals
3. Development of Reactive Surfactant
4. Properties of Reactive Surfactant
5. Emulsion Polymers and Characterization
6. Wrap up
7. Questions

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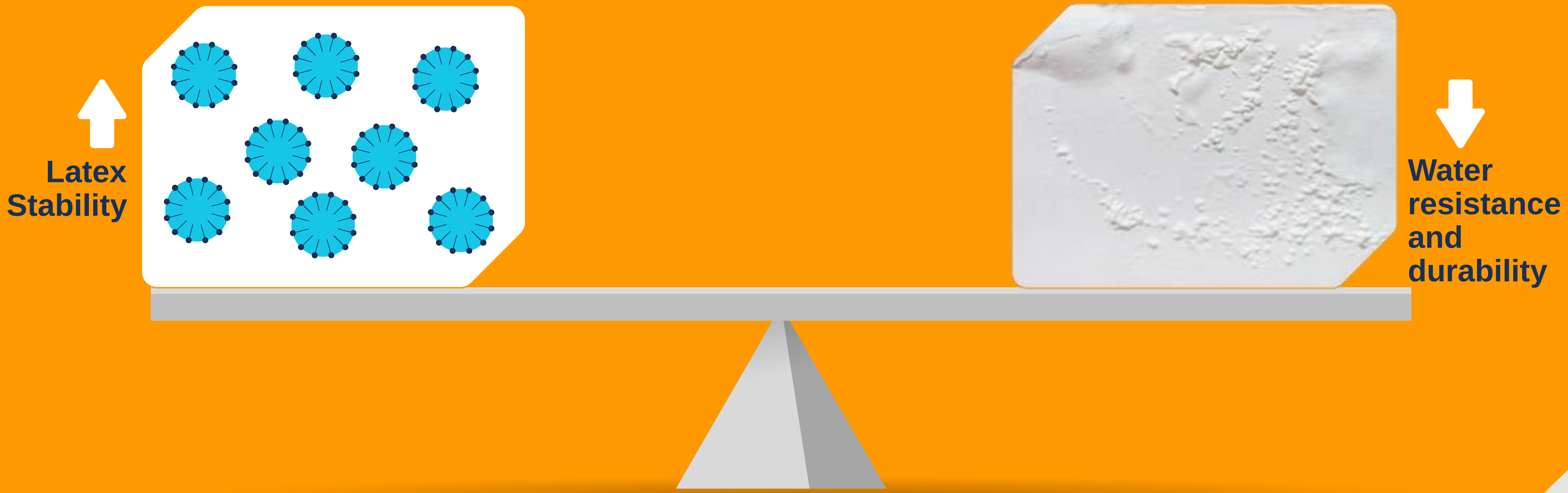
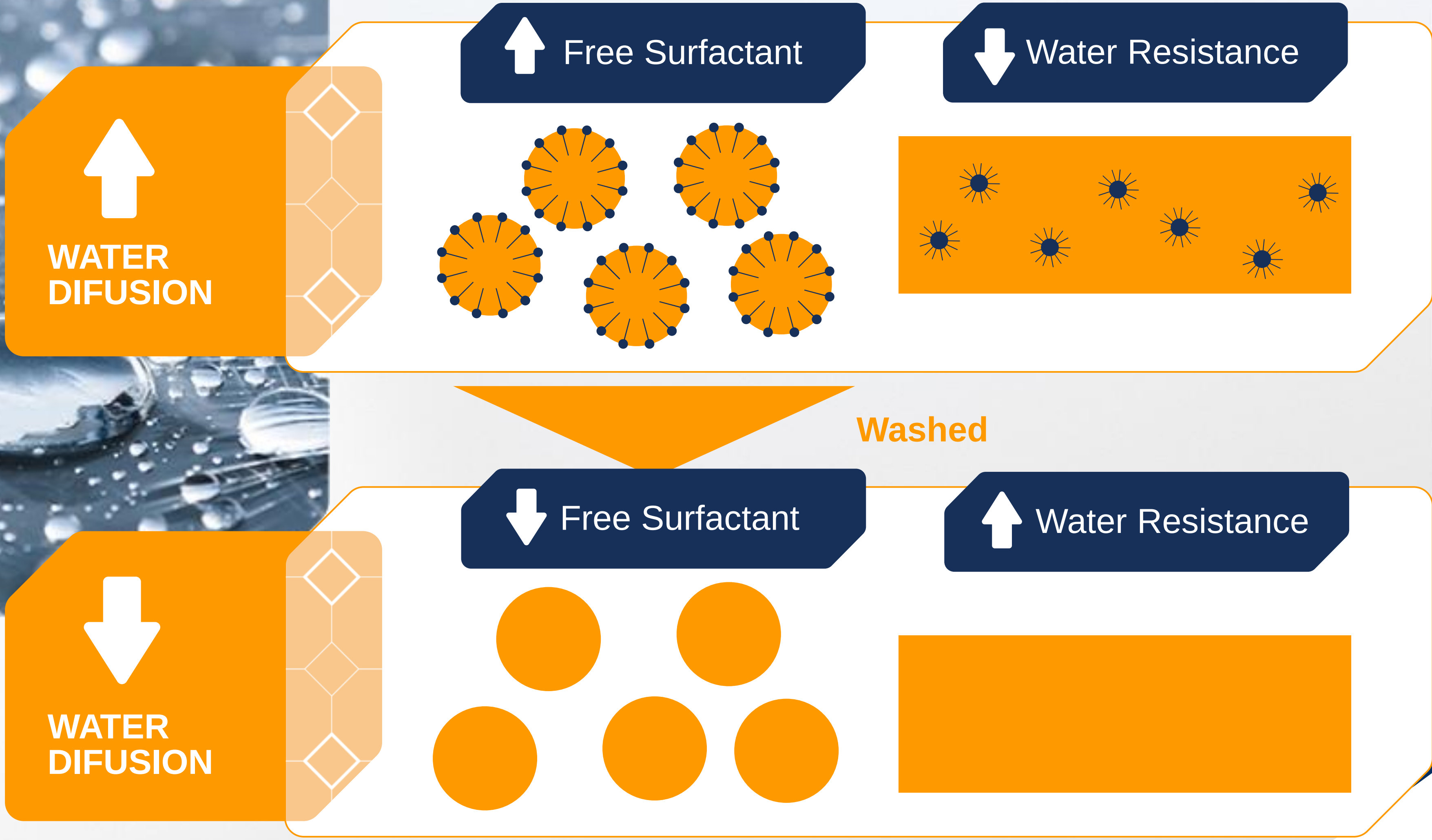
EMULSION POLYMERIZATION CHALLENGE

Balancing stability and performance with surfactants





How to improve water resistance?

Vanderhoff et. Al., J. Pol. Sci. **1973**, 41, 155-174.

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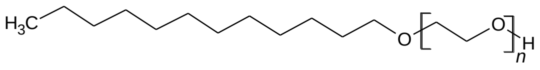
STRATEGY

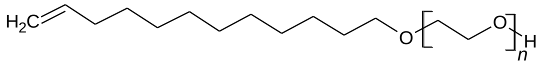
↓ Surfactant Migration ▶ ↑ Water Resistance

Conventional Surfactants
(no reactive)



▶

Reactive Surfactants



GOALS

Develop a Reactive Surfactant for Emulsion Polymerization

Analyze the effect of different processes in the incorporation of the reactive surfactant

Evaluate the performance of the emulsions in architectural paint formulation

Choosing a starting point

TO MINIMIZE SURFACTANT MIGRATION

Which surfactant is more incompatible with the matrix?

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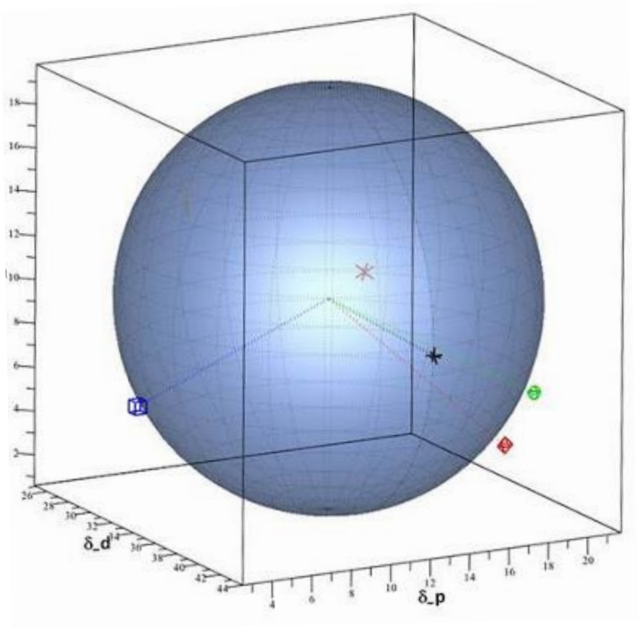
SURFACTANT COMPATIBILITY

Choosing a starting point to minimize surfactant migration

HANSEN SOLUBILITY PARAMETERS

$$Ra = \sqrt{4(\delta_{D\ Surfactant} - \delta_{D\ Latex})^2 + (\delta_{P\ Surfactant} - \delta_{P\ Latex})^2 + (\delta_{H\ Surfactant} - \delta_{H\ Latex})^2}$$



R_0: Radius of polymer's solubility sphere

RED: R_a/R_0

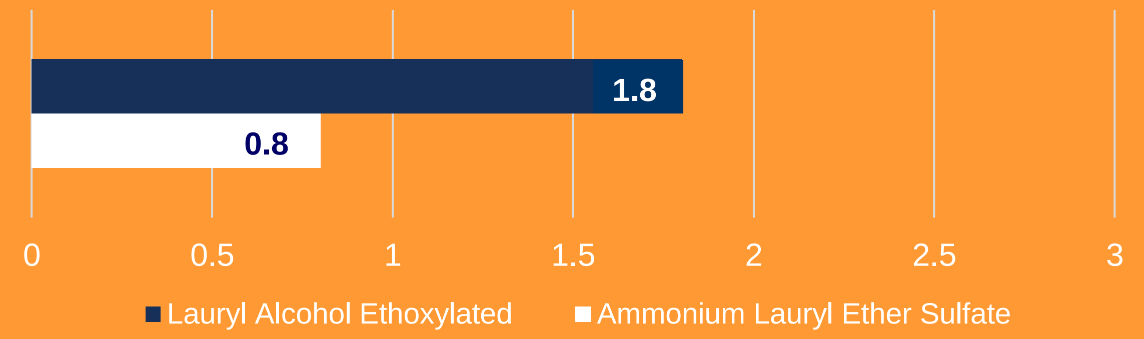
RED: ***R****elative* ***E****nergy* ***D****ifference*

RED < 1

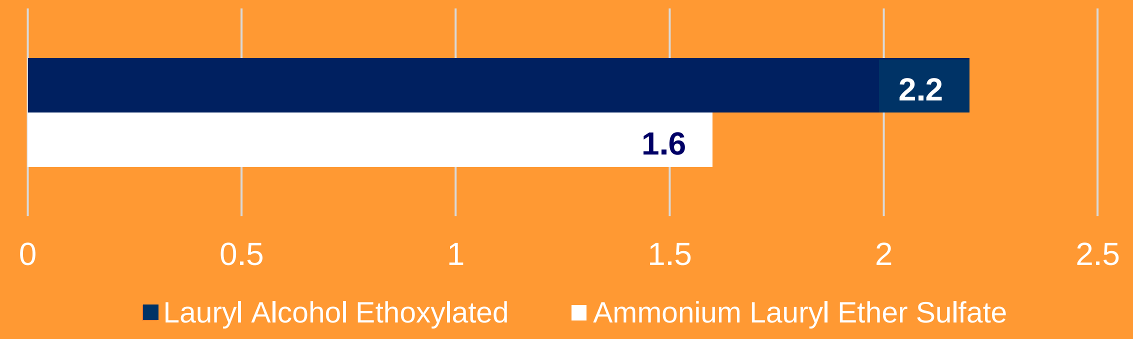
SURFACTANT COMPATIBILITY

Relative Energy Difference (RED)

Vinyl-Acrylic Emulsion



Styrene-Acrylic Emulsion



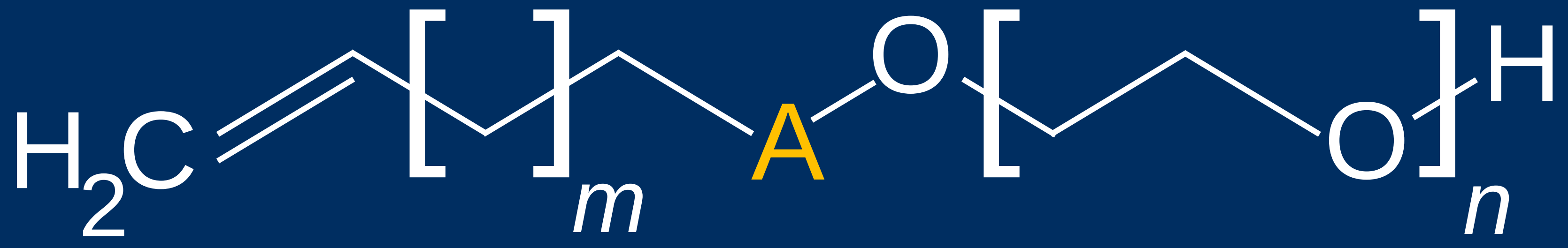
SURFACTANT REACT N1

APE-free

Renewable

VOC ≤ 5 g/L

Concentrated
Solids > 99 wt%



Liquid

HLB = **15**

Compatible with all common Emulsion Chemistry's

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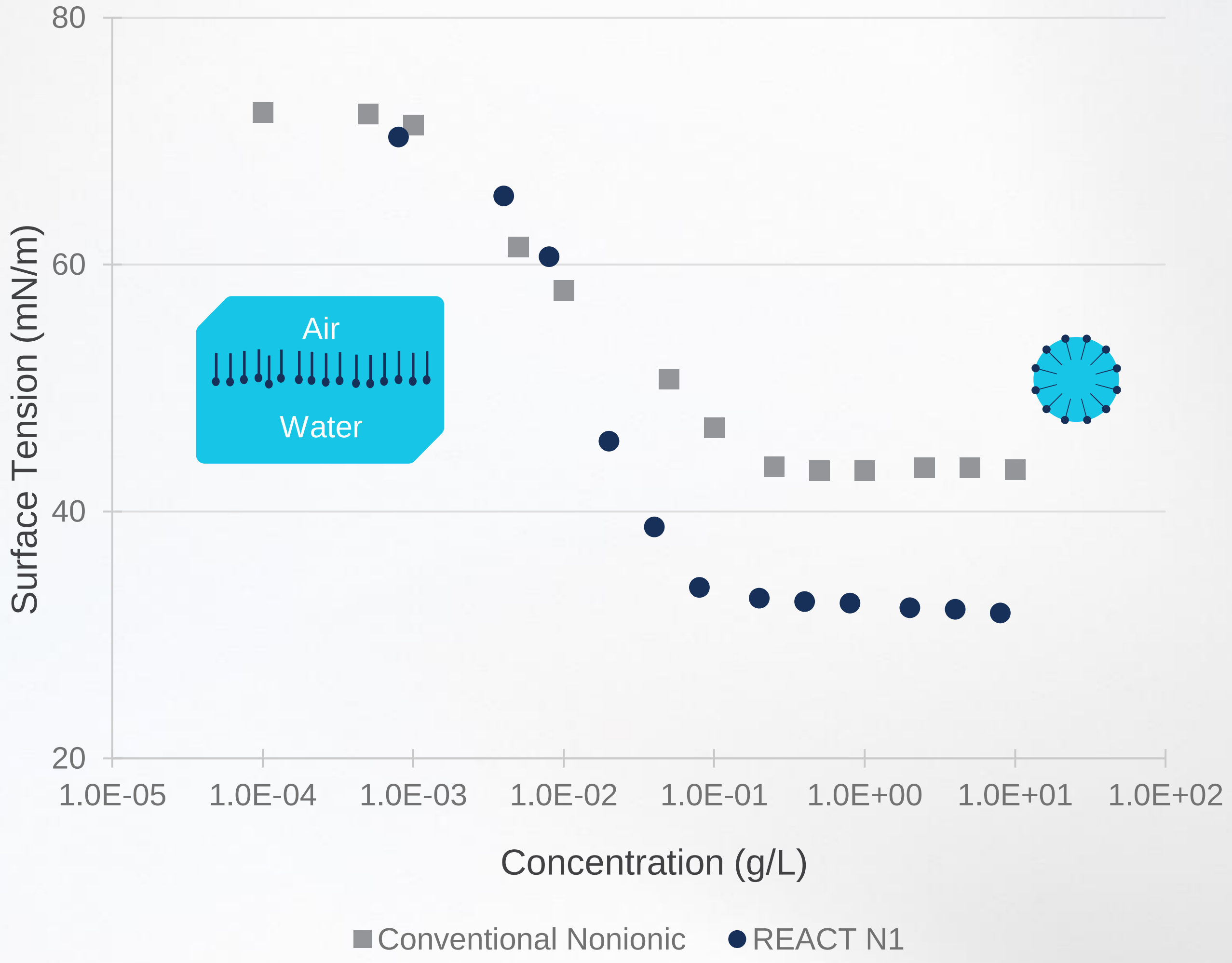
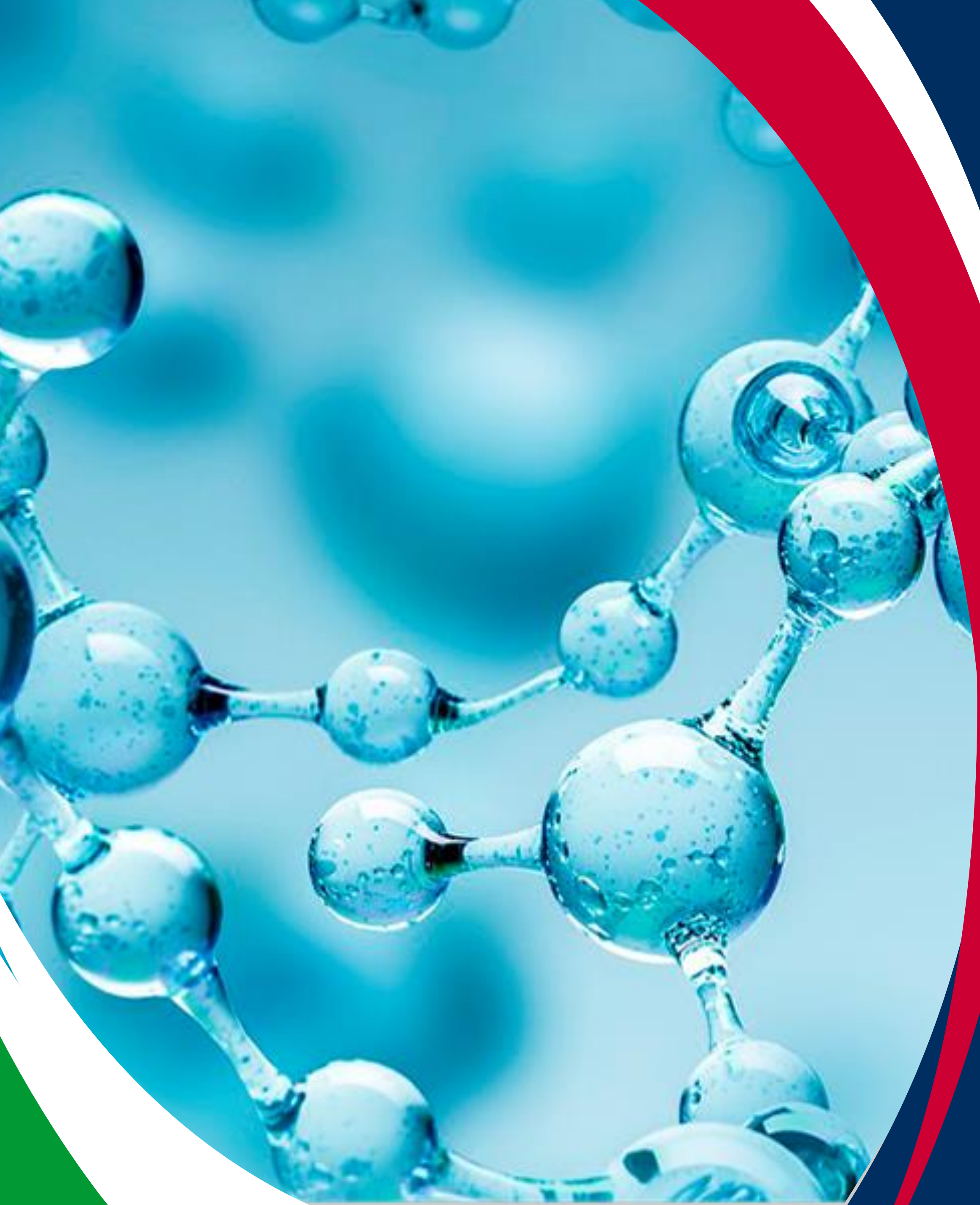
SURFACE ACTIVITY

SURFACE ACTIVITY OF REACT N1



	REACT N1	Conventional Nonionic
Surfactant Concentration to Reduce the Surface Tension in 20 mN/m (mg/L)	13	50
Critical Micelle Concentration (CMC) (mg/L)	59	230
Surface Tension at CMC (mN/m)	34	43

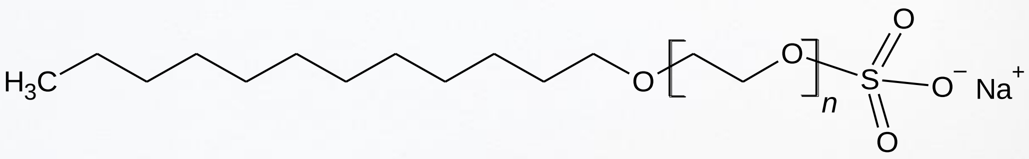


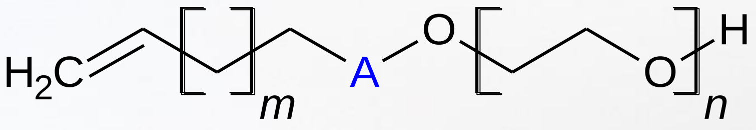
EMULSION POLYMERIZATION

Process I

EMULSION POLYMERIZATION

Process I





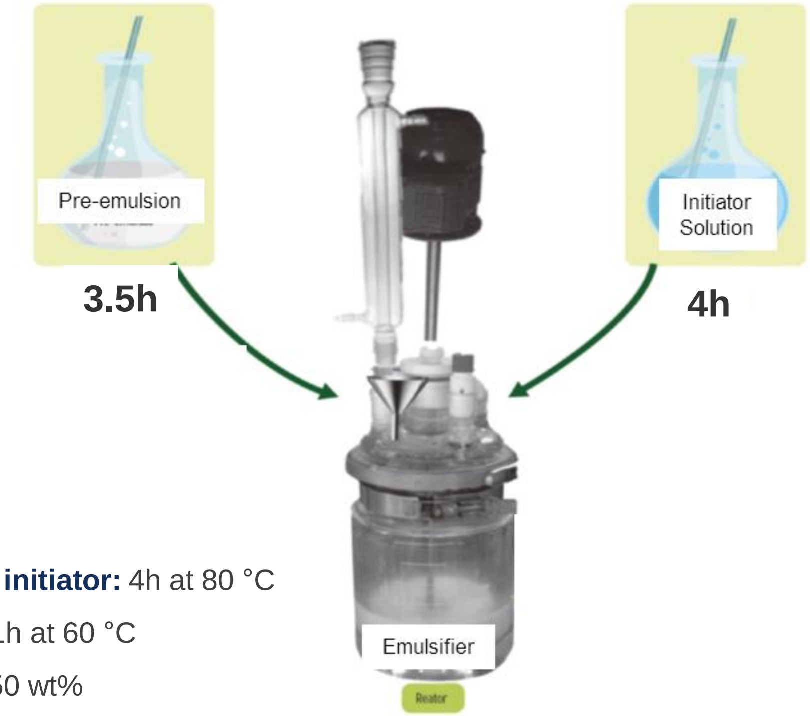
- Typical **semi-batch polymerization**
- **Seeds generated** *in situ*
- **Growing seeds stabilized** by anionic and nonionic surfactants

EMULSION POLYMERIZATION

Process I – Formulation

Components (phm)	Formulation 1
Styrene	53
Butyl Acrylate	45
Acrylic Acid	2
Anionic Surfactant*	1
REACT N1	**3**
Potassium Persulfate	0.3
Oxidizing Agent	0.04
Reducing Agent	0.04

PROCESS I



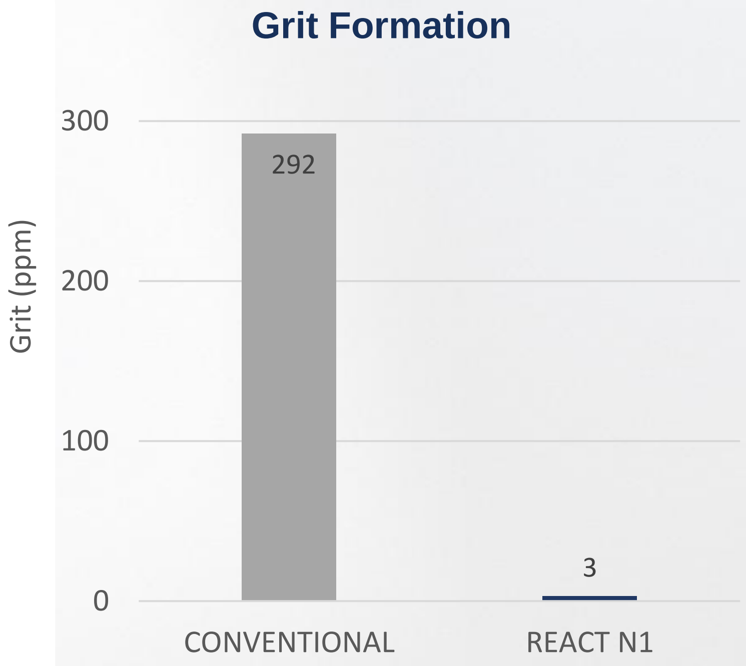
- **Thermal initiator:** 4h at 80 °C
- **Redox:** 1h at 60 °C
- **Solids:** 50 wt%
- **Neutralizer:** MEA

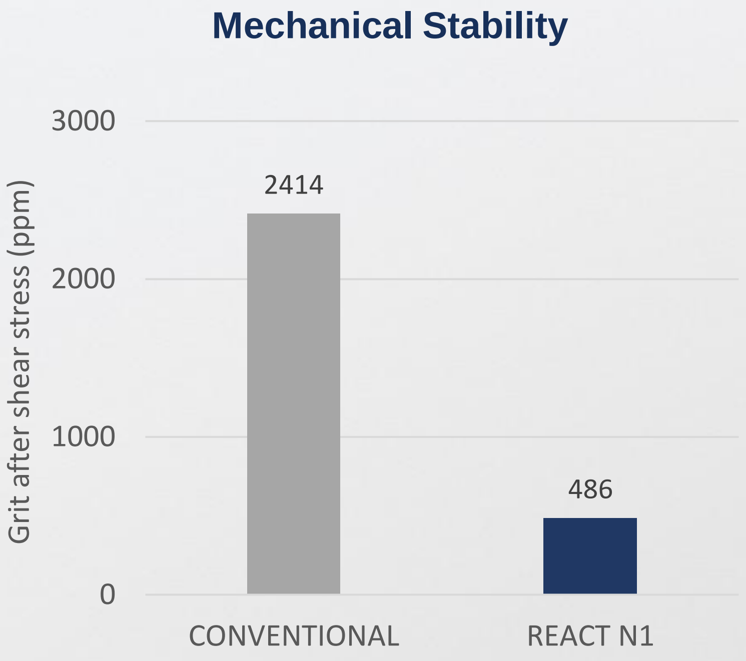
* Lauryl ether sulfate sodium salt

PROCESS I

Emulsion properties and stability

Properties	Formulation 1
pH	8.5
Solids (wt%)	50
Particle Size (nm)	128
Viscosity (cP, 25 °C)	280
Surface Tension (mN/m, 25 °C)	37



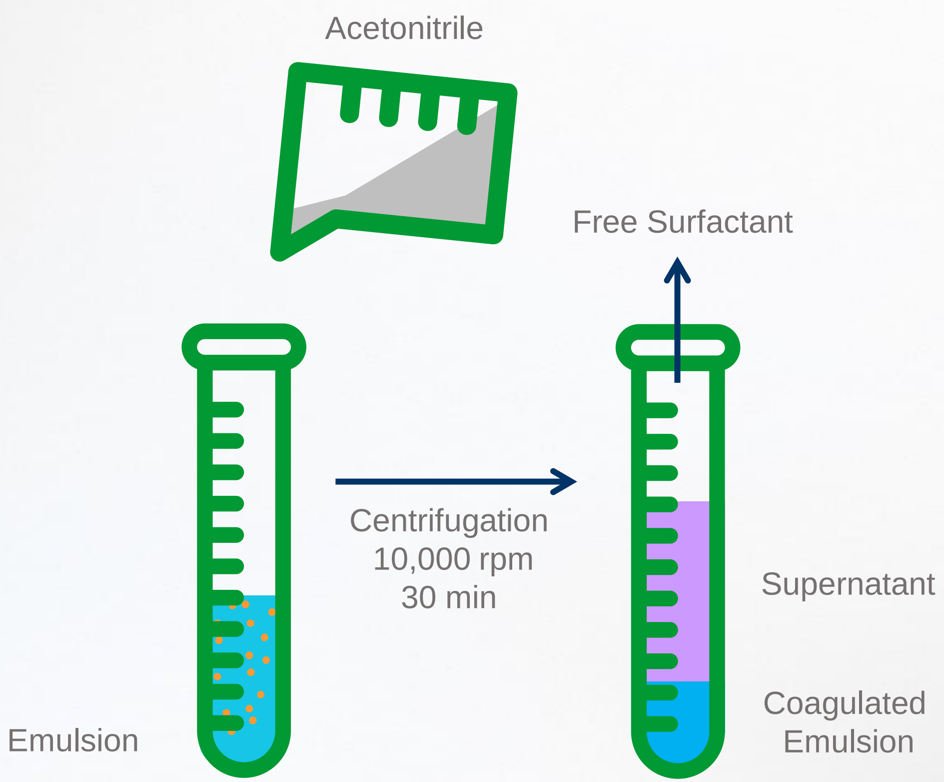


Conventional nonionic surfactant: Fatty Alcohol 23 EO

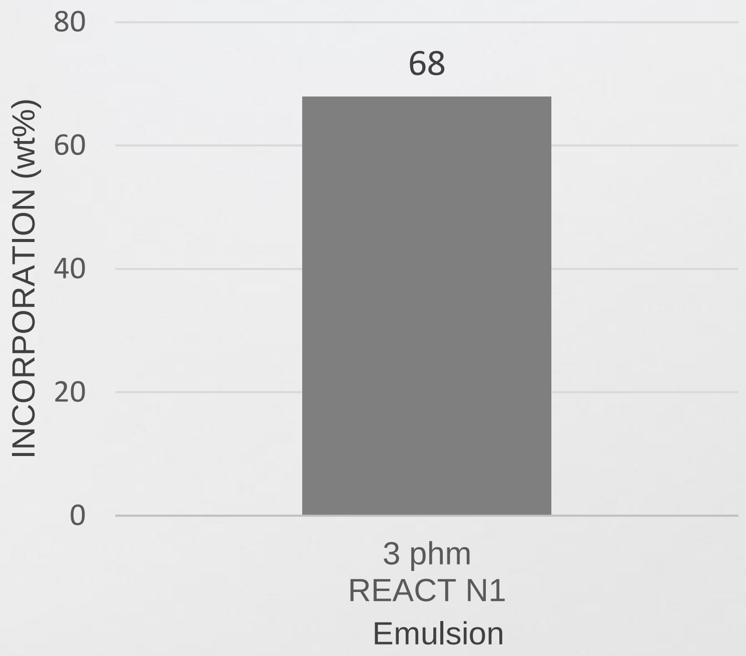
Formulation 1: 3 phm of REACT N1

EMULSION POLYMERIZATION

Incorporation of Reactive Surfactant



Surfactant Incorporation = Added Surfactant – Free Surfactant

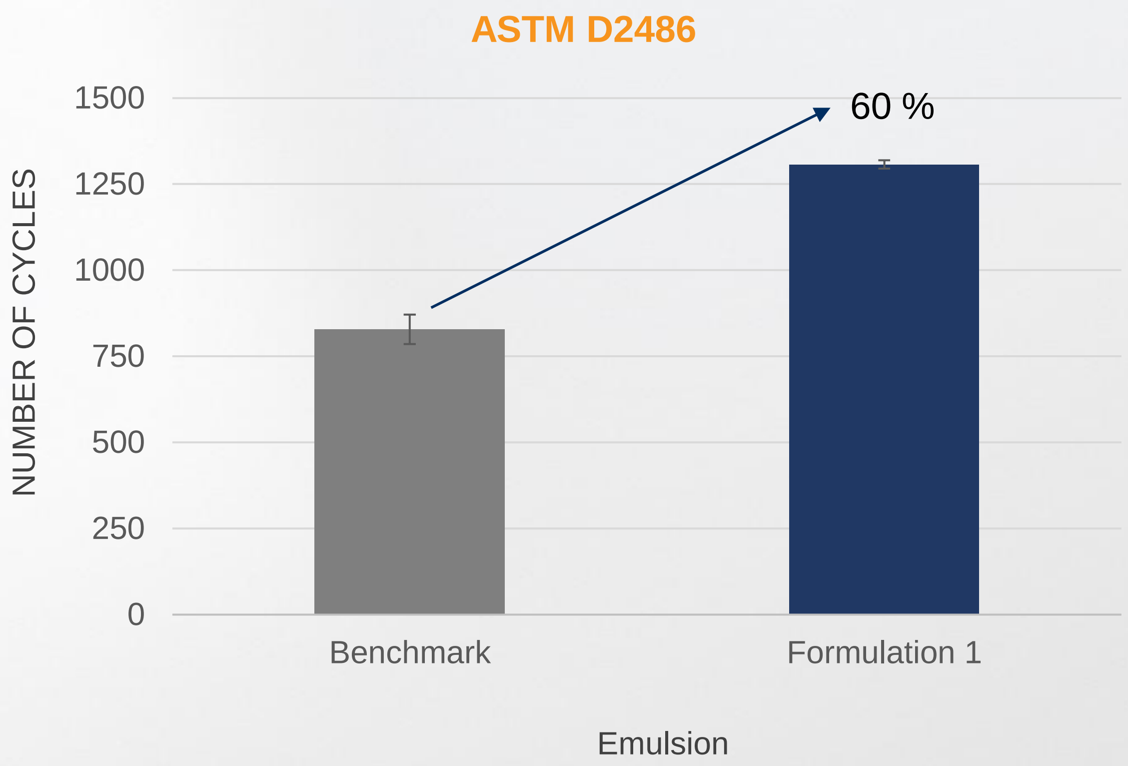


PAINT EVALUATION

Scrub resistance in semigloss formulation

FORMULATION

PVC	~ 26 %
Emulsion	~ 43 %
Coalescent	~ 2 %
Viscosity	105 +/- 5 KU
pH	9.0 – 9.5



Benchmark: Commercial Styrene-Acrylic Emulsion
Formulation 1: Emulsion made with 3 phm of REACT N1

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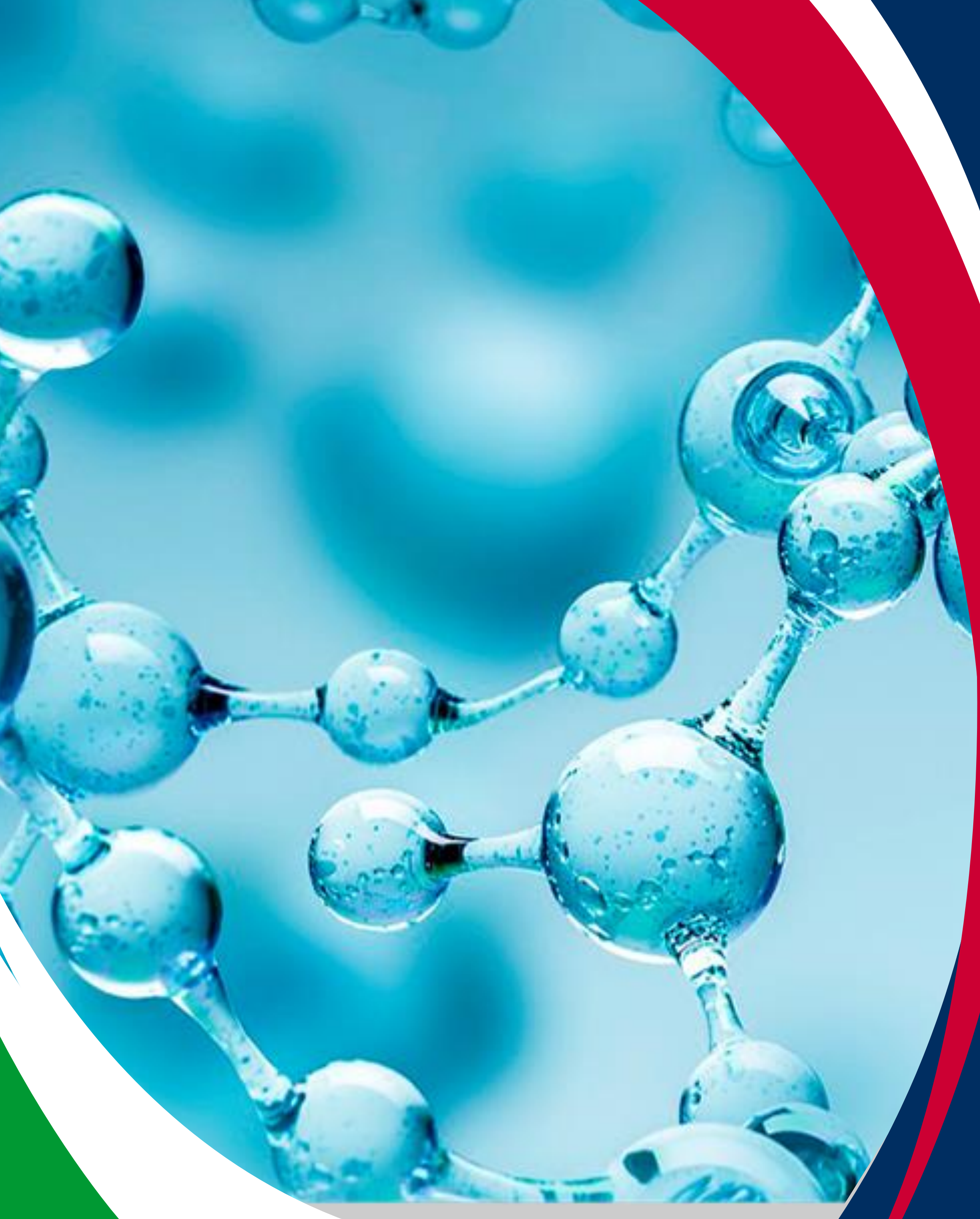

EMULSION POLYMERIZATION

Process II – Optimization of incorporation

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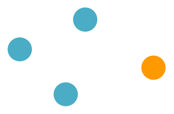
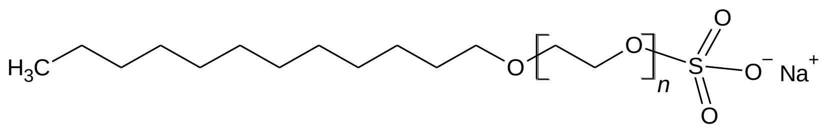
EMULSION POLYMERIZATION

Process II

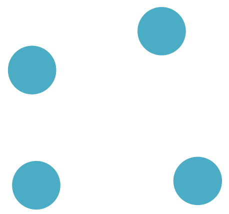
STEP 1: Seeds generation



EMULSIFIED MONOMERS

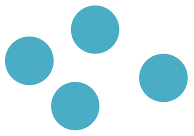


25 phm



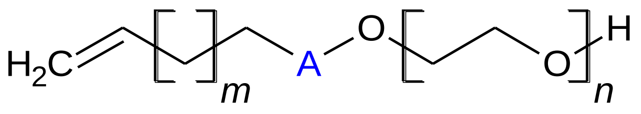
40-50 nm
SC ~ 10 wt%

STEP 2: Seeds growth

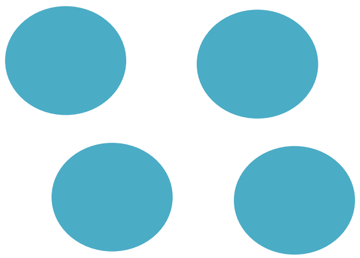


10^{18} seeds/L

MONOMERS + REACTIVE SURFACTANT



Total surfactant concentration:
Anionic = 0.8 phm
Nonionic = 2.0 phm



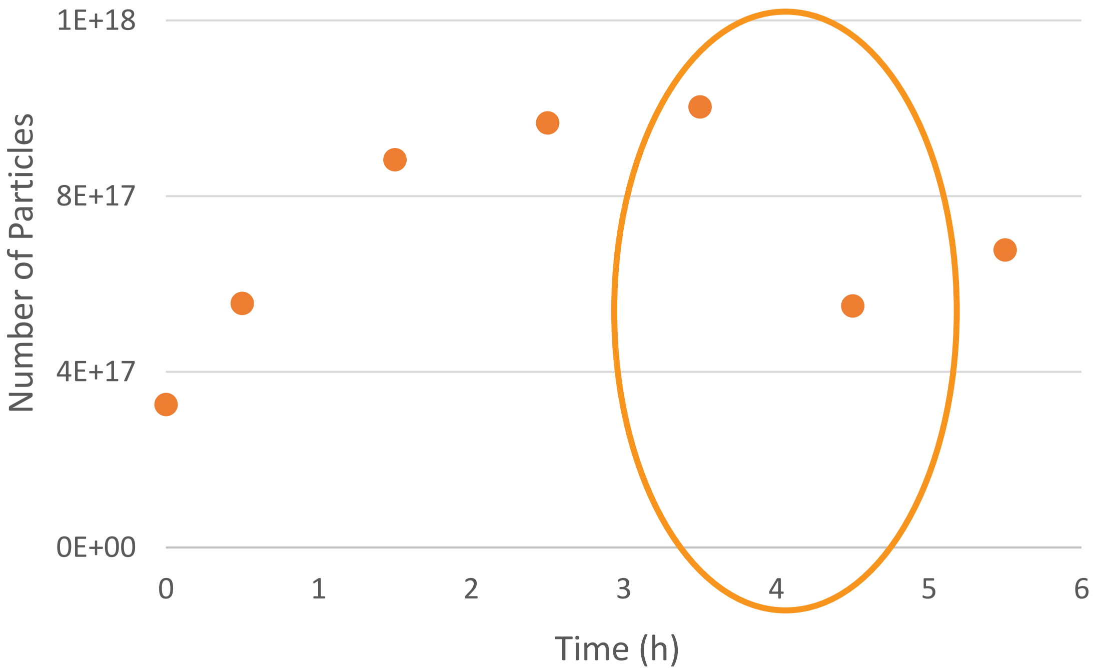
80-110 nm
SC ~ 45 wt%

E. Aramendia et. *Al.*; *Langmuir* **2003**, 19, 3212 - 3221.

PROCESS II

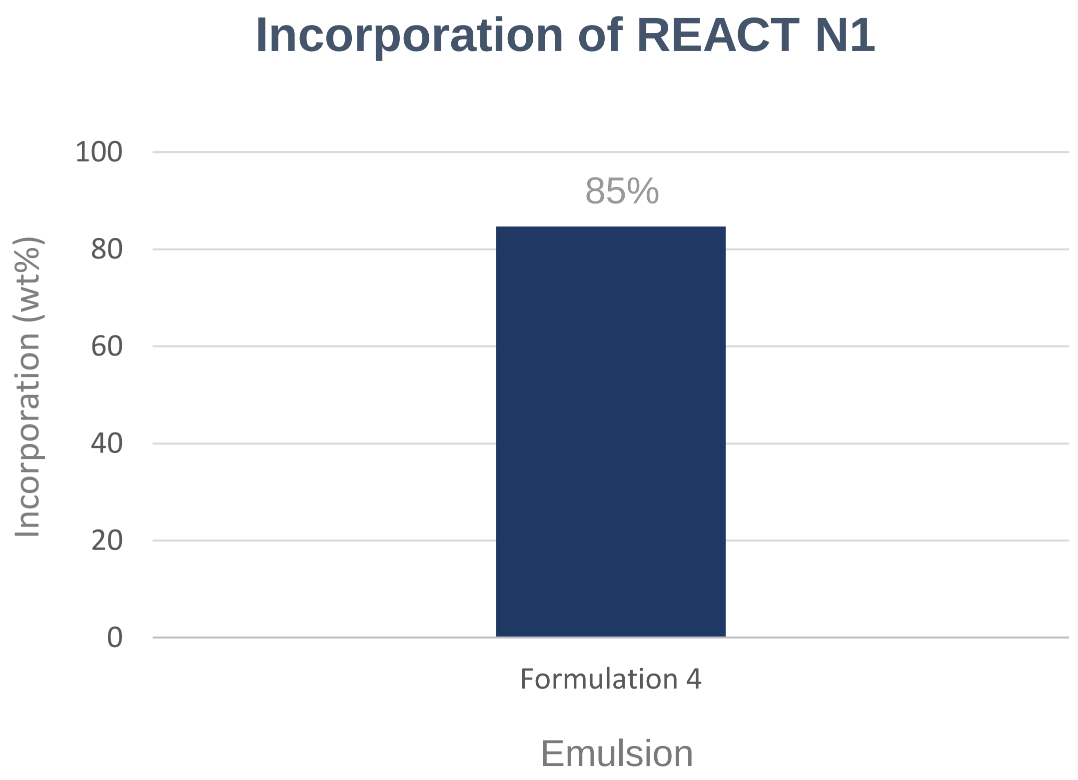
Emulsion properties and stability

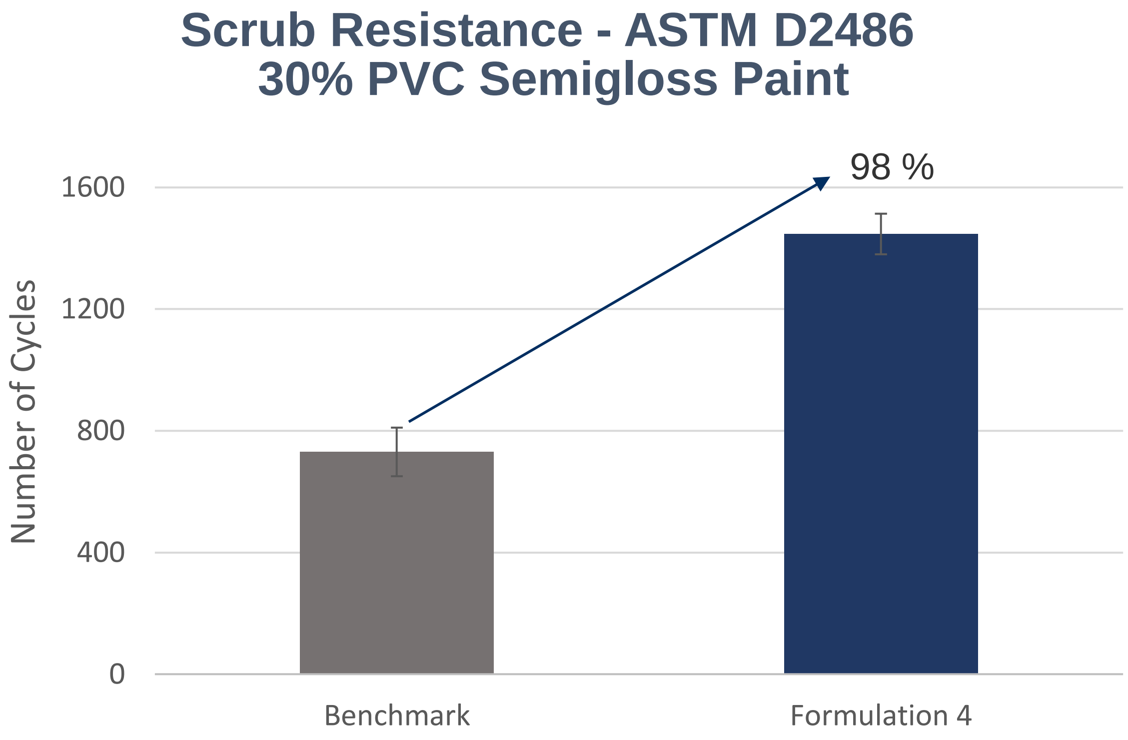
Formulation	4
pH	8
Grit (wt%)	**1.4**
Solids (wt%)	47
Particle Size (nm)	101
Viscosity (cP, 25°C)	27
Surface Tension (mN/m, 25 °C)	37



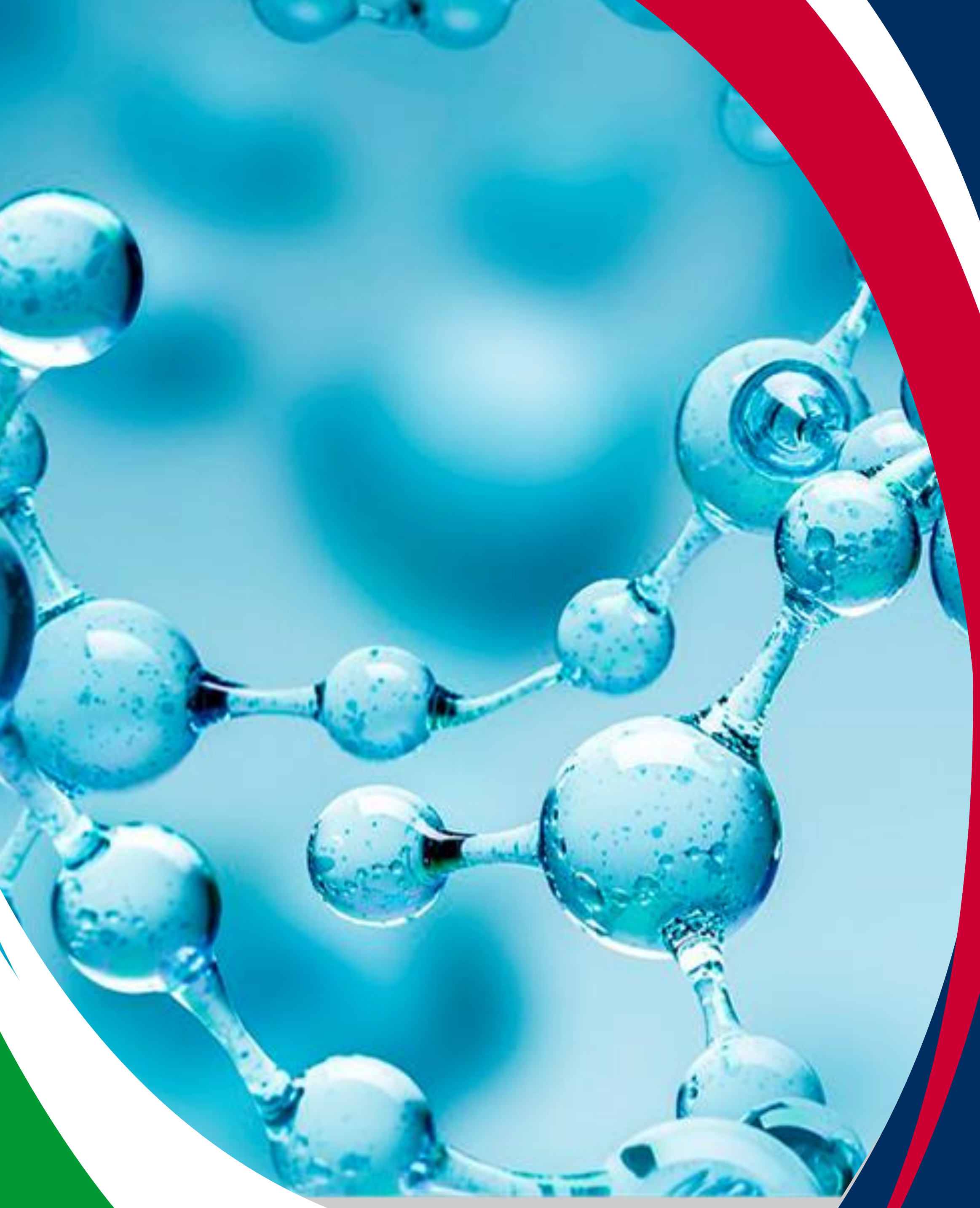
PAINT EVALUATION

Scrub resistance in semigloss formulation





Benchmark: Commercial Styrene-Acrylic Emulsion
Formulation 4: Emulsion made with 2 phm of REACT N1 under process II



EMULSION POLYMERIZATION

Process III – Optimization of stability

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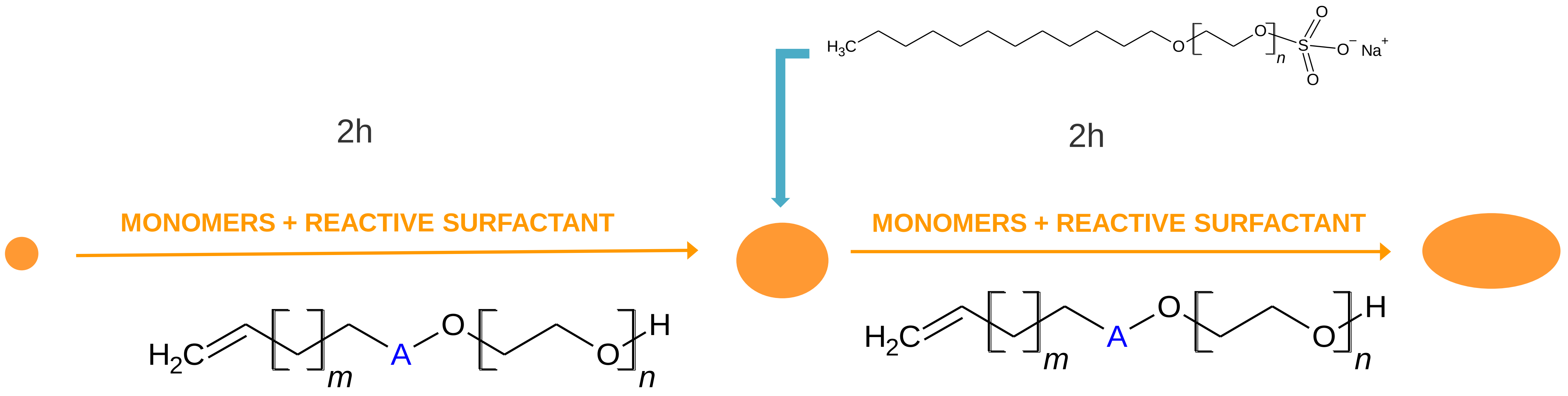
EMULSION POLYMERIZATION

Process III – shot addition of anionic surfactant after 2h

STEP 2: Seeds growth



Seeds ~ 2.5 wt%
40 nm

Conversion ~ 60 wt%
65 nm

Conversion ~ 100 wt%
80-90 nm

Total surfactant concentration:
Anionic = 1.2 phm
Nonionic = 2.0 phm

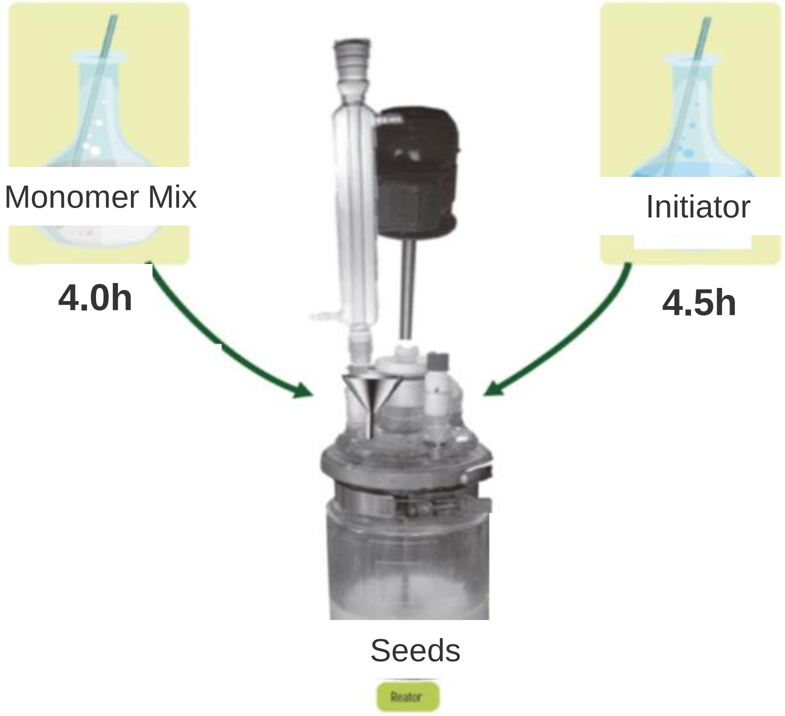
EMULSION POLYMERIZATION

Process III

Formulations 6 - 8

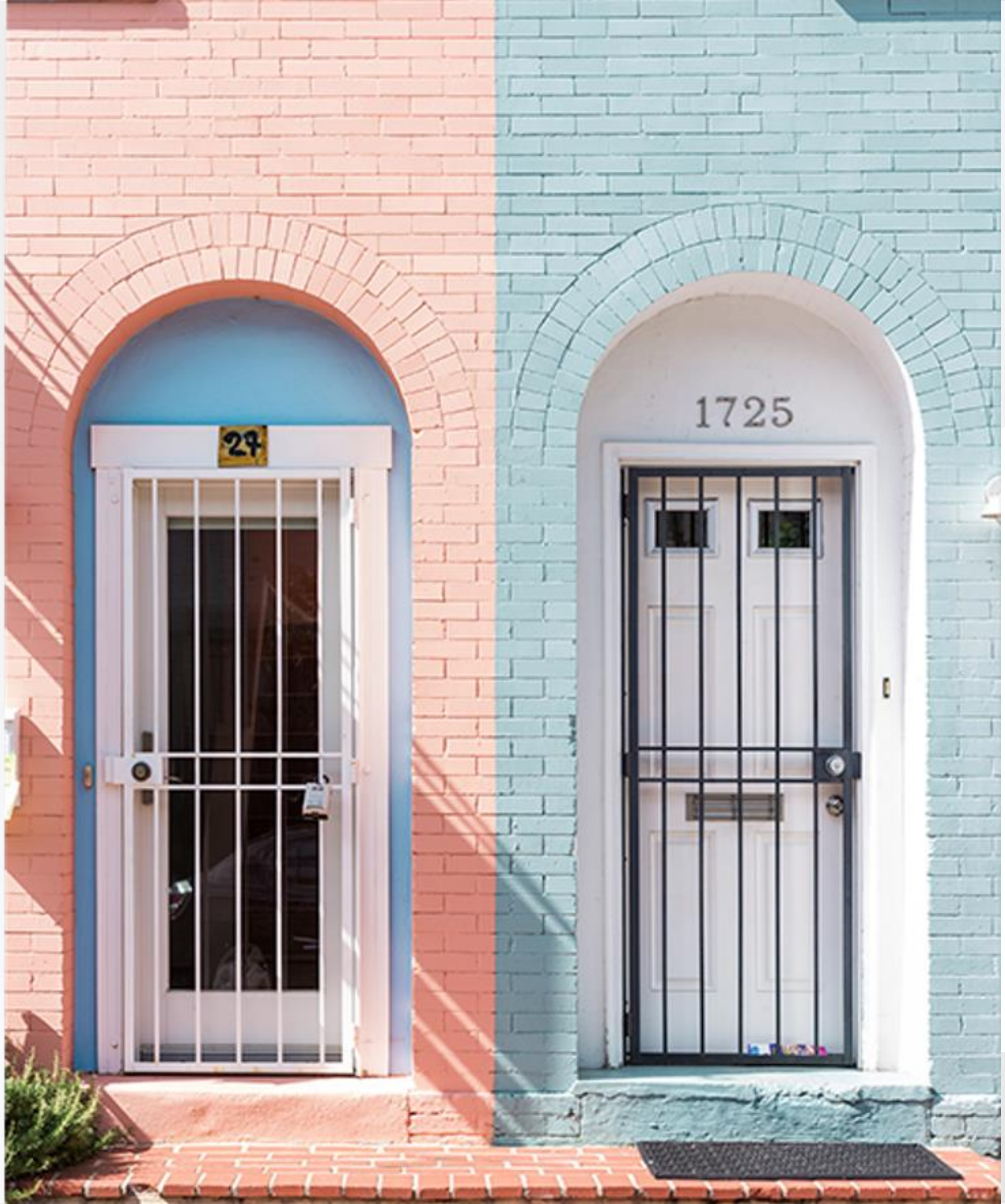
Components	Content (phm)
Styrene	53
Butyl Acrylate	45
Methacrylic Acid	2
REACT N1	2
Initiator	0.3

PROCESS III



Variables

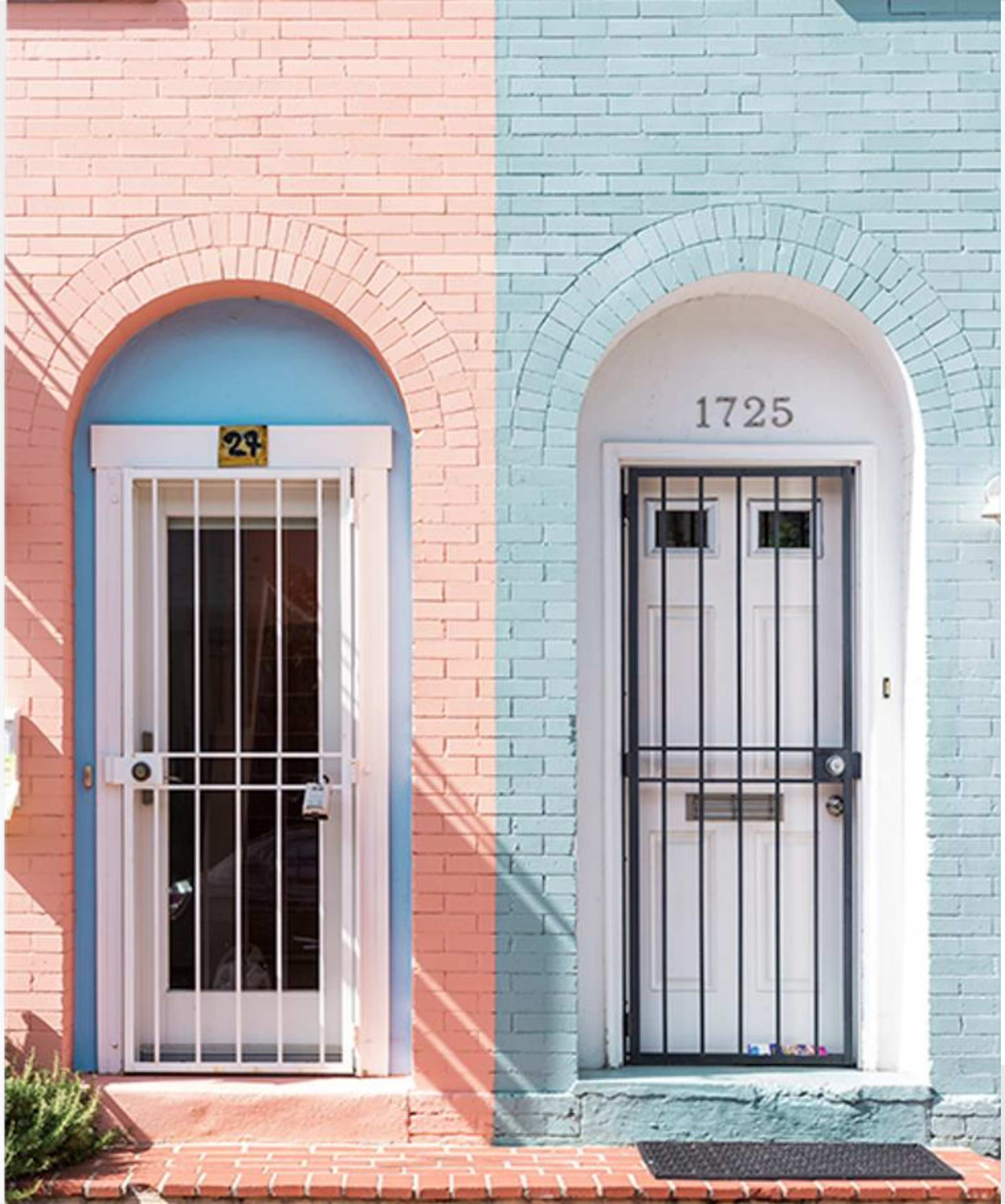
Formulation	T (°C)	Initiator
6	4 h/ 80°C	Thermal
7	2 h/80°C 2 h/60°C	Thermal Redox
8	4 h/ 60 °C	Redox



PROCESS III

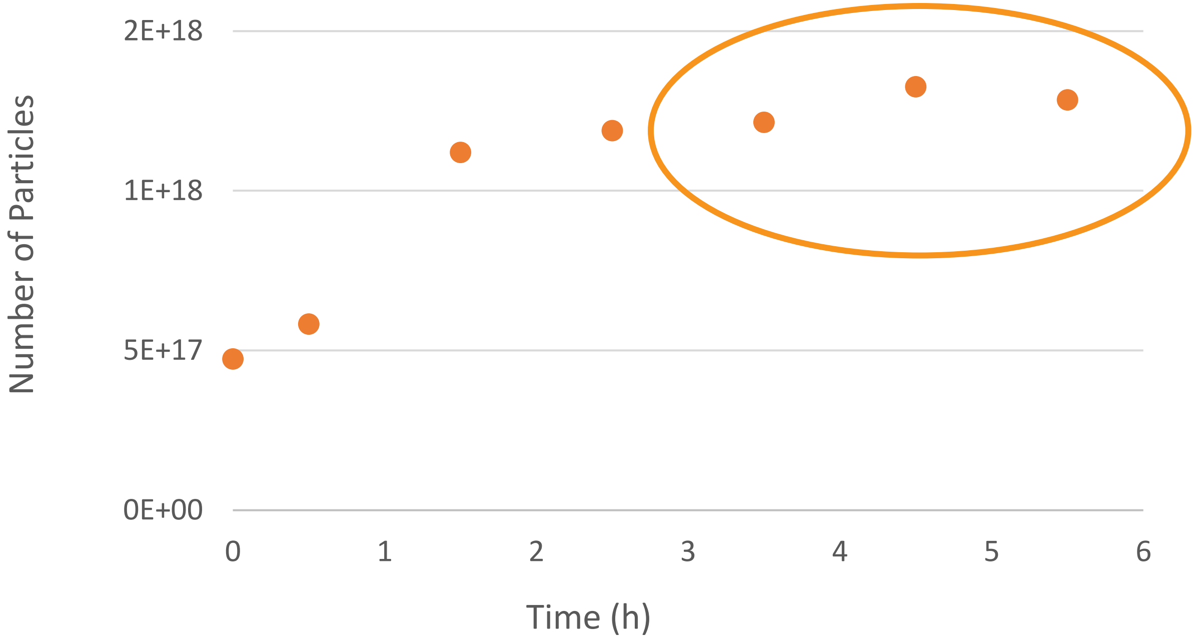
Emulsions properties

	4h/80°C – Thermal	2h/80°C – Thermal 2h/60°C – Redox	4h/60°C – Redox
Formulation	**6**	**7**	**8**
pH	8	8	8
Grit (wt%)	**0.4**	**0.8**	**0.3**
Solids wt%)	47	44	44
Particle Size (nm)	82	86	81



PROCESS III

Emulsion Properties



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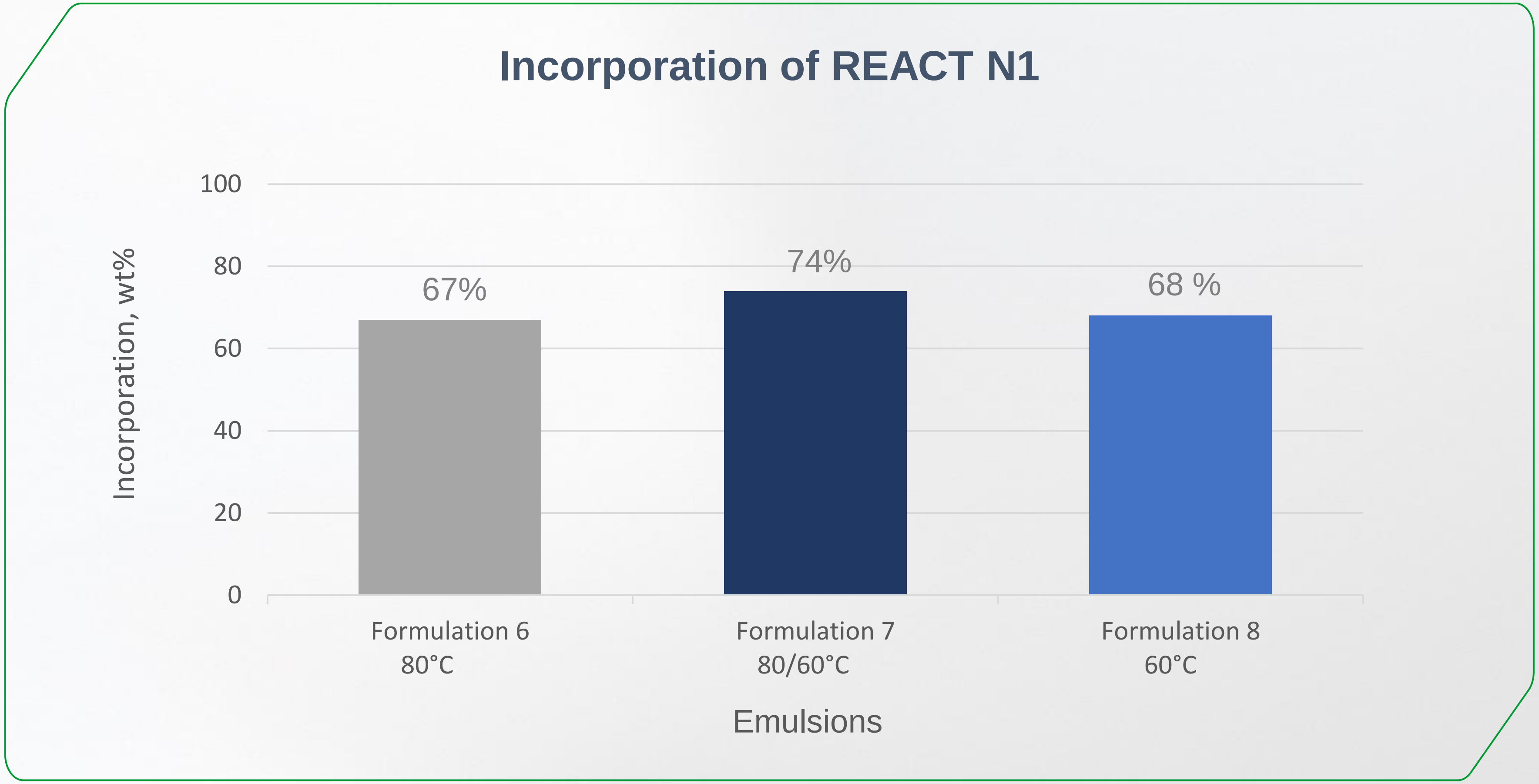
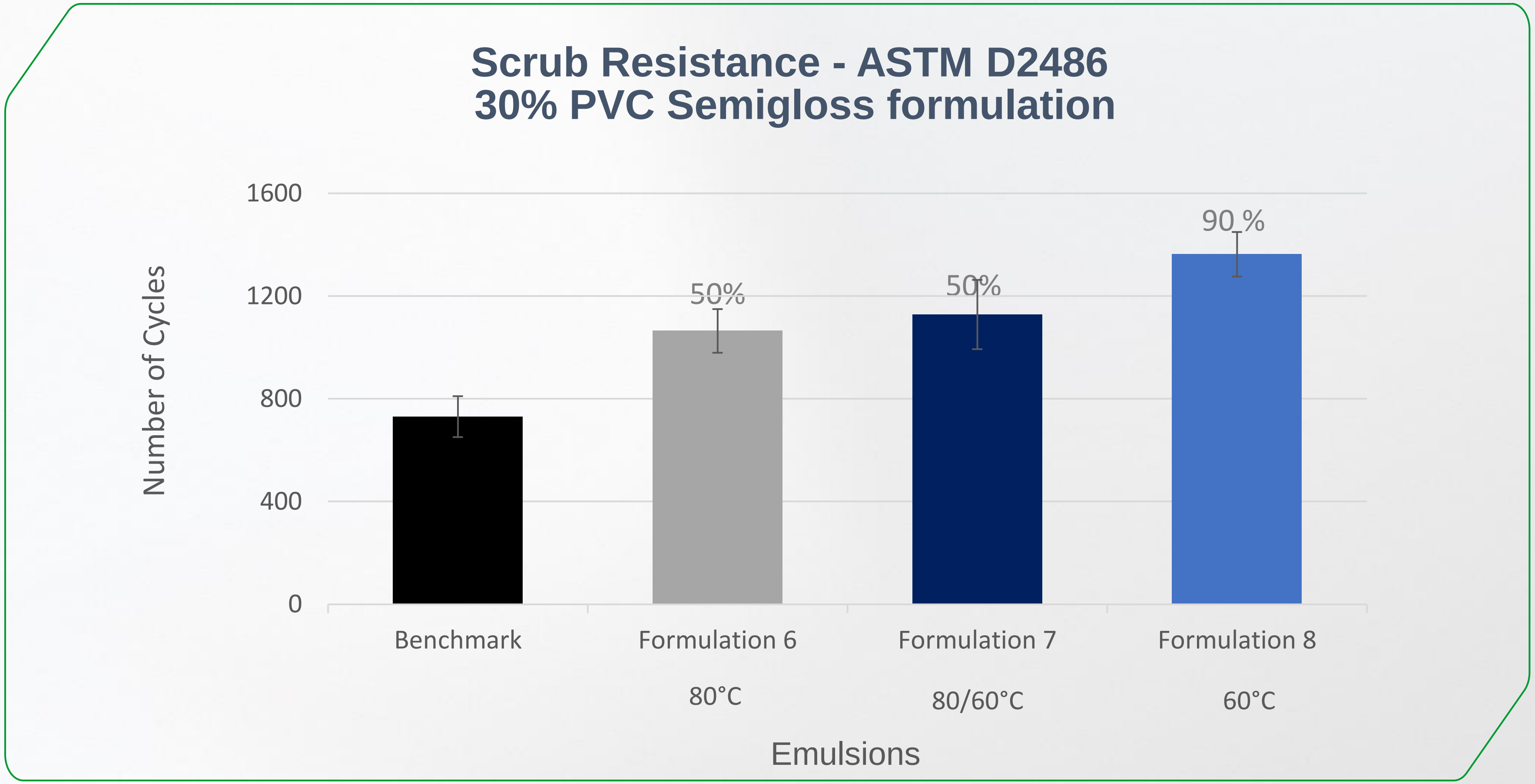
PROCESS III

Effect of temperature and initiator in the incorporation of reactive surfactant



PAINT EVALUATION

Scrub resistance of semigloss formulation



Benchmark: Commercial Styrene-Acrylic Emulsion

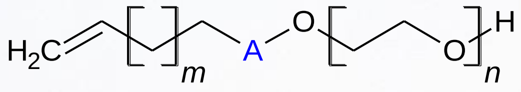
EMULSION POLYMERIZATION

Wrap up

REACT N1 unsaturation

in the hydrophobic portion presents surface activity similar to conventional surfactants

PROCESS I REACT N1 3.0 phm Anionic 1.0 phm	PROCESS II REACT N1 2.0 phm Anionic 0.8 phm	PROCESS III REACT N1 2.0 phm Anionic 1.2 phm
Stable Emulsion	↑ Free Surface Area	Stable Emulsion
Particle Size **100-140nm**	↑ Incorporation **85wt%**	Particle Size **80nm**
Incorporation **70wt%**	↑ Grit Formation	↑ Incorporation **70wt%**
↑ Wet Scrub Resistance **60%**	↑ Wet Scrub Resistance **98%**	↑ Wet Scrub Resistance **50-90%**



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THANK YOU VERY MUCH FOR YOUR ATTENTION!

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