Effect of different surfactants on emulsion polymerization of vinyl-acrylic latex

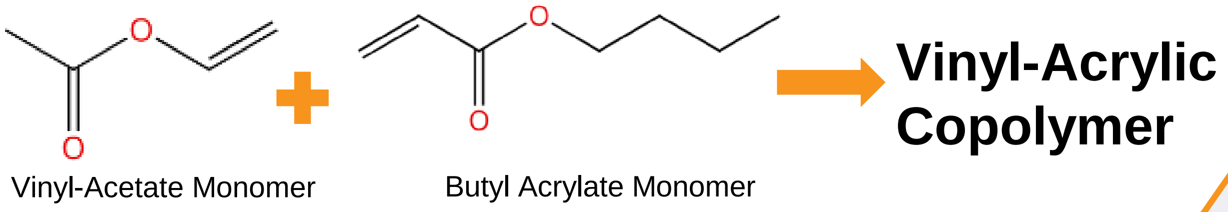
CTT 2023

Integrated Oxides and Derivatives

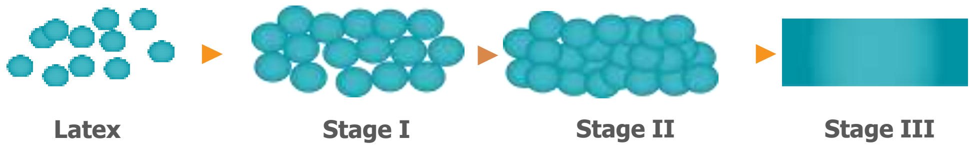
AGENDA

1. Why Vinyl-Acrylic?
2. Surfactants under study
3. Effect of Nonionic to Anionic Ratio
4. Effect of EO chain length in Anionic Surfactant
5. Effect of EO chain length in Nonionic Surfactant
6. Paint evaluation
7. Conclusion

VINYL-ACRYLIC POLYMER: ADVANTAGES AND CHALLENGES

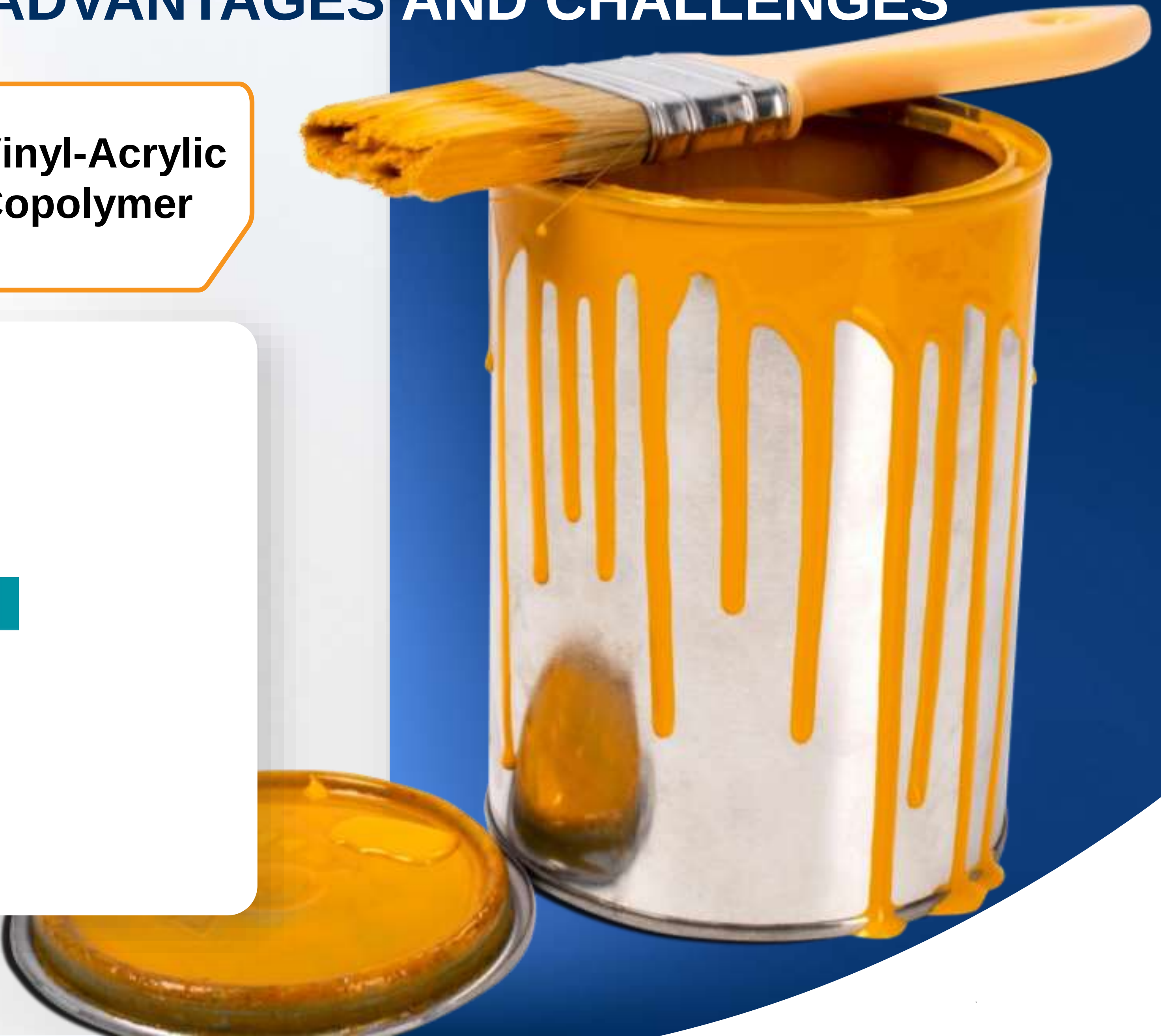


- ✓ Large **availability** and **low cost**
- ✓ Hydroplasticization of the particles
- ✓ MFFT << Tg

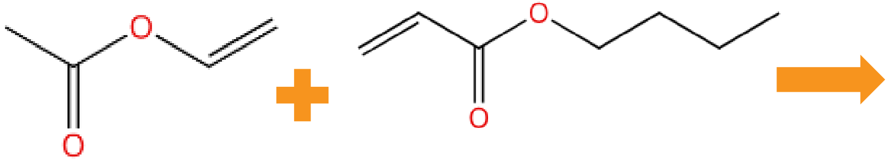


$T_{environment}$ > MFFT $T_{environment} > T_g$

- ✓ **Low coalescing agent** demand
- ✓ **Low VOC** Paints



VINYL-ACRYLIC POLYMER: ADVANTAGES AND CHALLENGES



Vinyl-Acetate Monomer

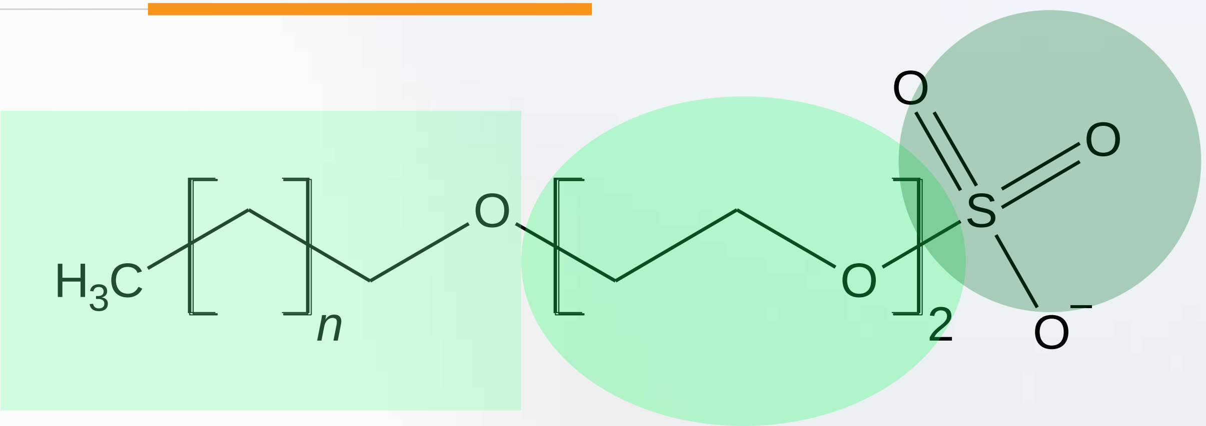
Butyl Acrylate Monomer

Vinyl-Acrylic Copolymer

- ✓ High solubility of the vinyl-acetate monomer in water
- ✓ Difficulty to adsorb surfactants on the Surface of the particles to improve stability
- ✓ Replacement of APE-based surfactants
- ✓ Market Scenario – difficult to find raw material hence improving the toolbox of solutions is key.

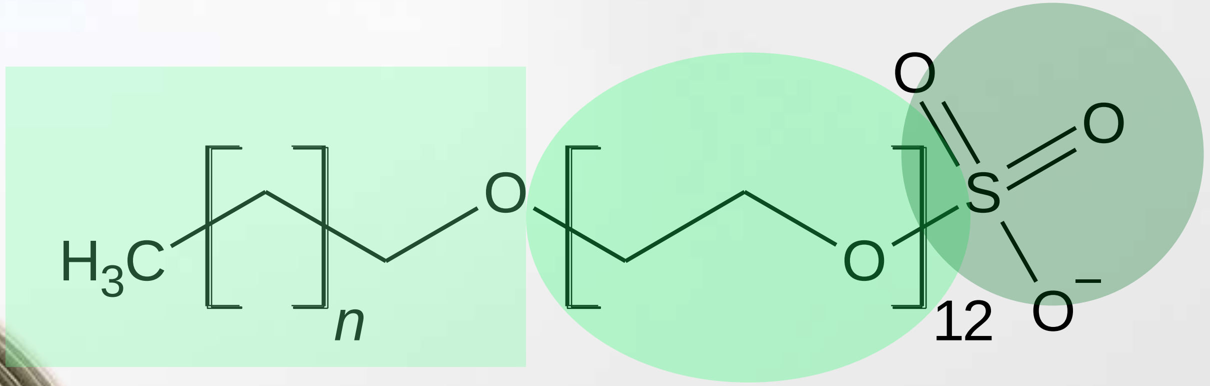
Surfactants studied - Anionic

CODES:



Linear Hydrophobe | 2 Ethylene Oxide repetitions | Sulfate

L2S

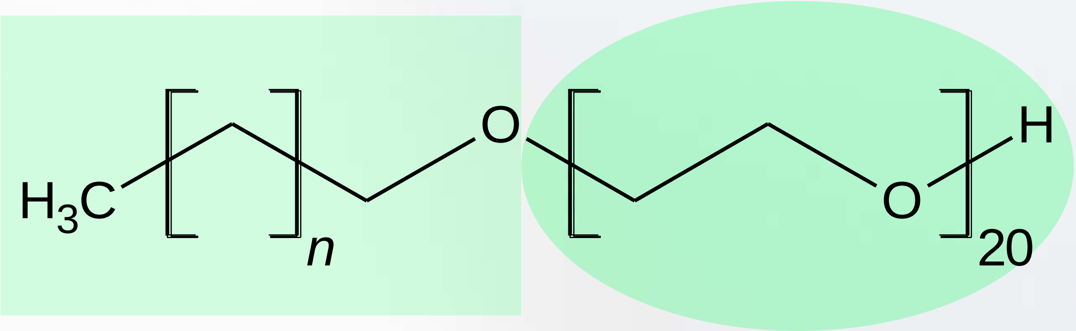


Linear Hydrophobe | 12 Ethylene Oxide repetitions | Sulfate

L12S

Surfactants studied - Nonionic

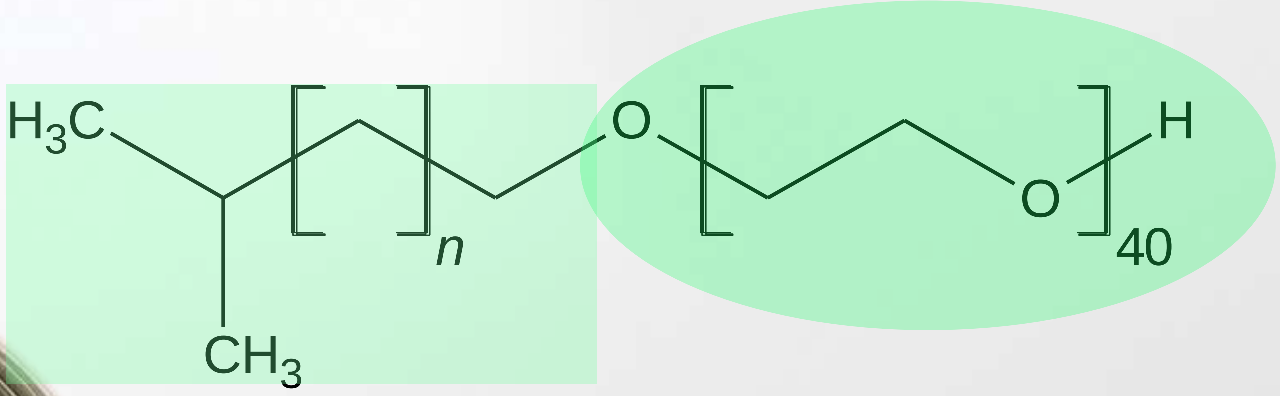
CODES:



Linear Hydrophobe

20 Ethylene Oxide repetitions

L20



Branched Hydrophobe

40 Ethylene Oxide repetitions

B40

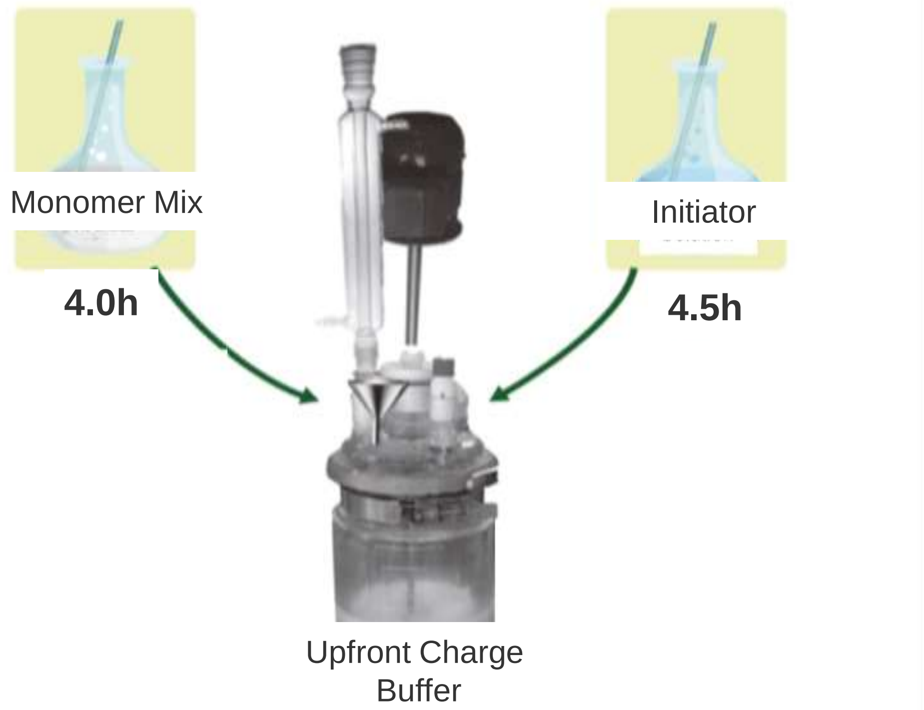
Emulsion Polymer Formulation

Goal: to evaluate different ratios of nonionic to anionic surfactant

95:5 / 85:15 / 70:30

Components (phm)	Formulation 1
Vinyl Acetate	80 %
Butyl acrylate	20 %
	Active Content (phm)
Surfactant L20	3.08 – 4.18
Surfactant L2S	0.22 – 1.32
Persulfate initiator	
Chase Redox	

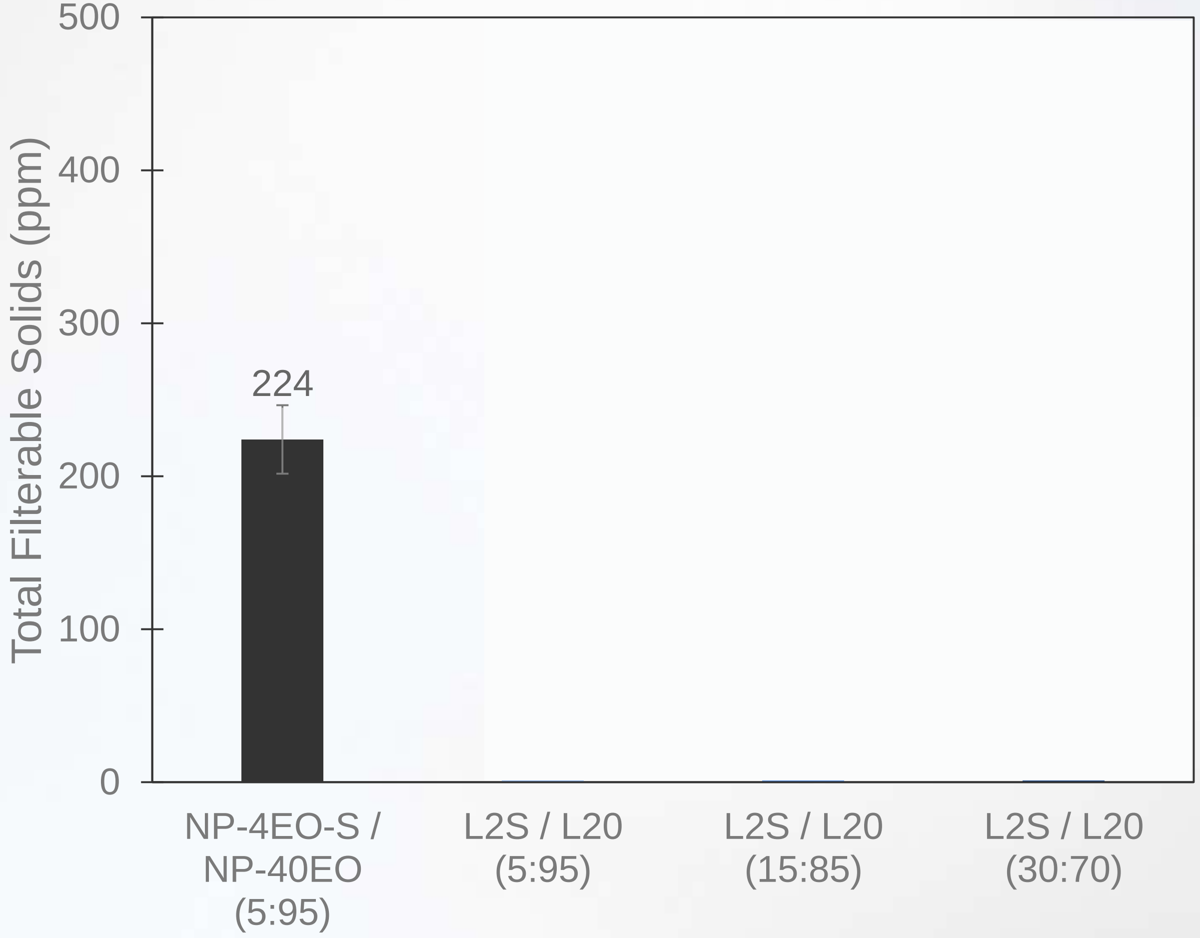
PROCESS

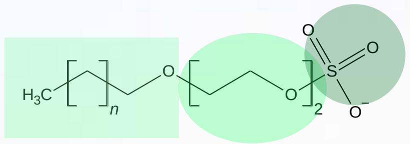


- **Thermal initiator:** 4.5h at 70 °C
- **Solid content:** 55 wt.%

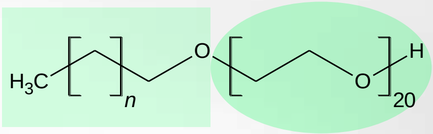
Effect of different ratios of nonionic to anionic

Reactor Cleanliness





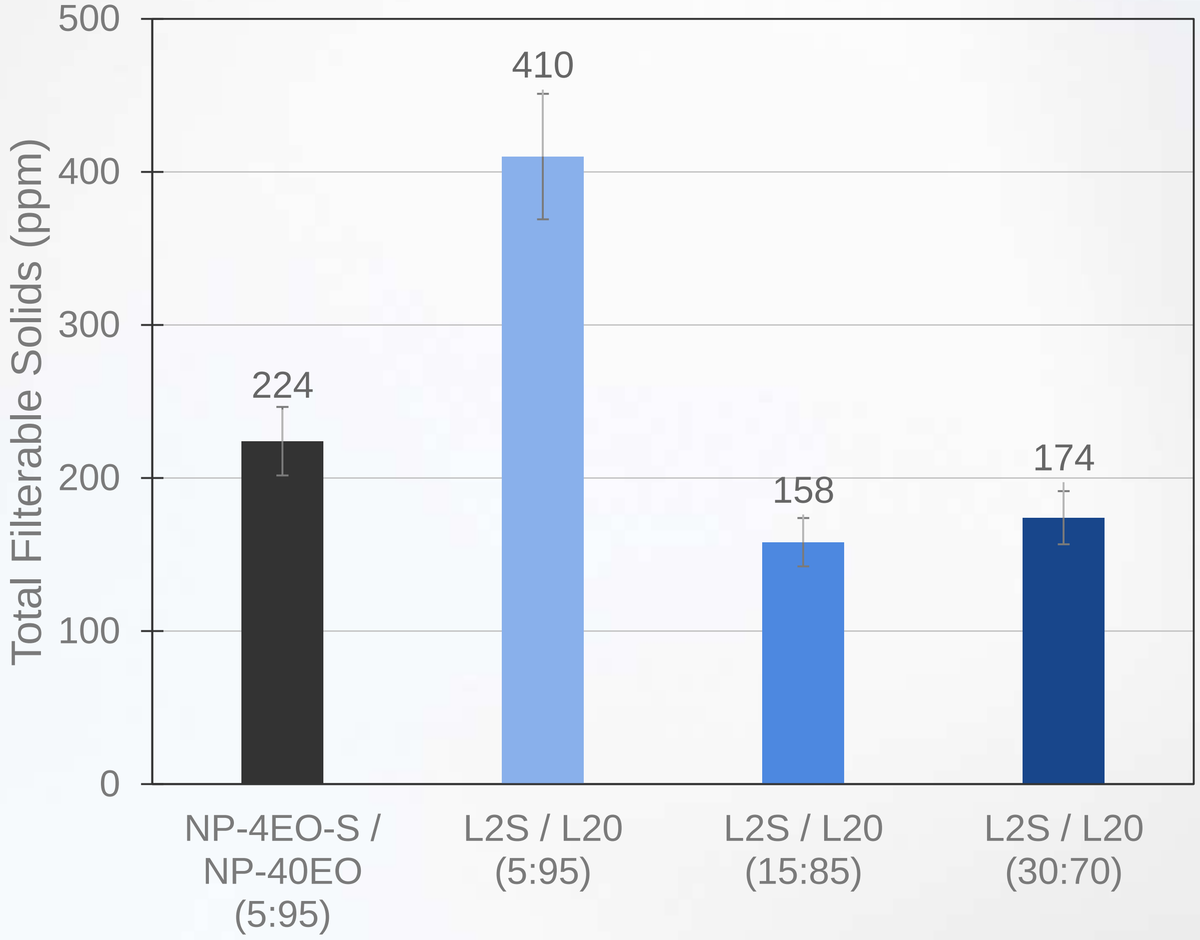
L2S



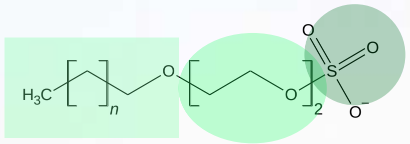
L20

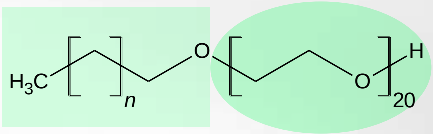
Effect of different ratios of nonionic to anionic

Reactor Cleanliness



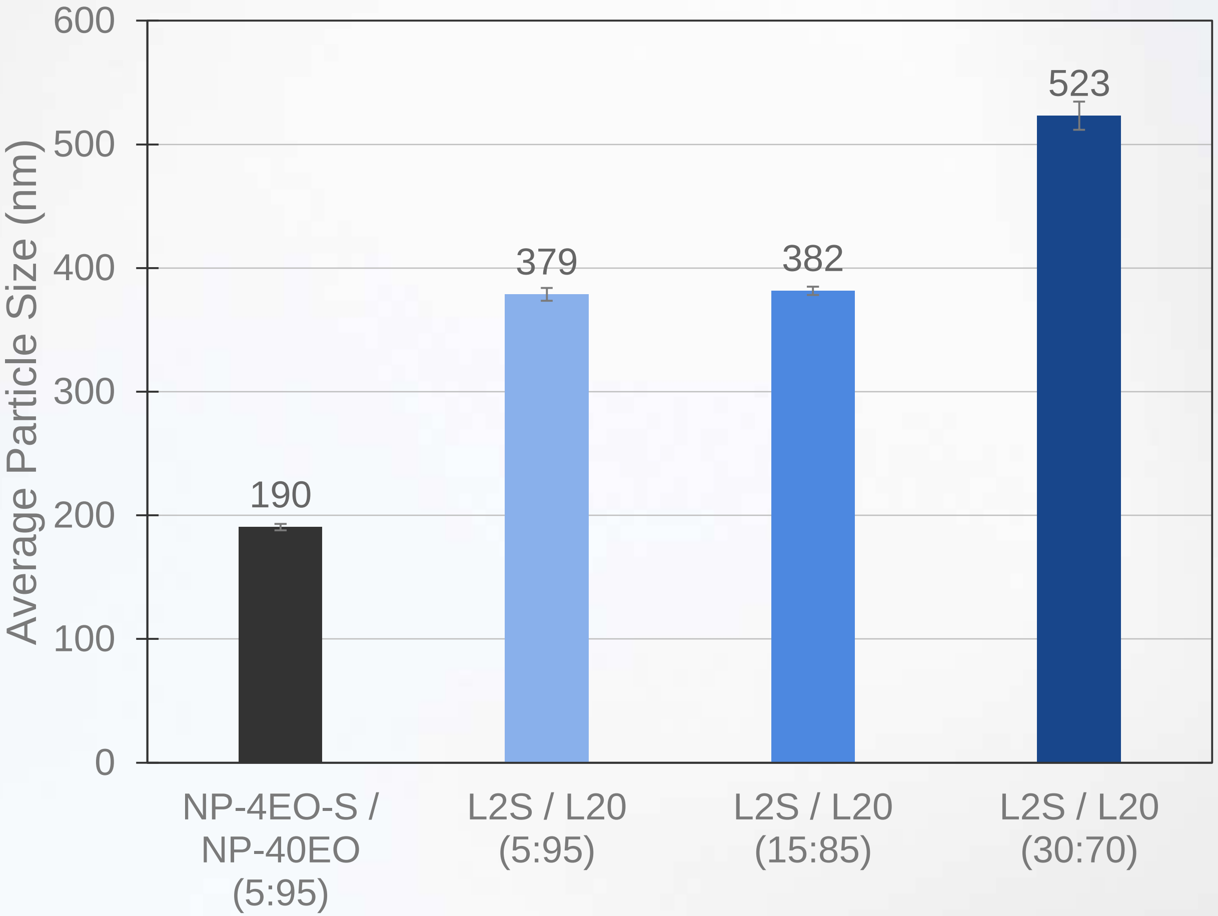
- ✓ Clot formation < 500 ppm for all formulations.
- ✓ Results comparable or better than reference.

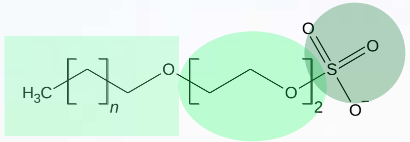




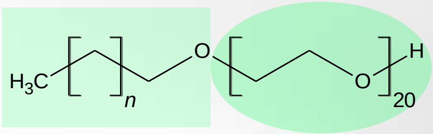
Effect of different ratios of nonionic to anionic

Particle Size





L2S

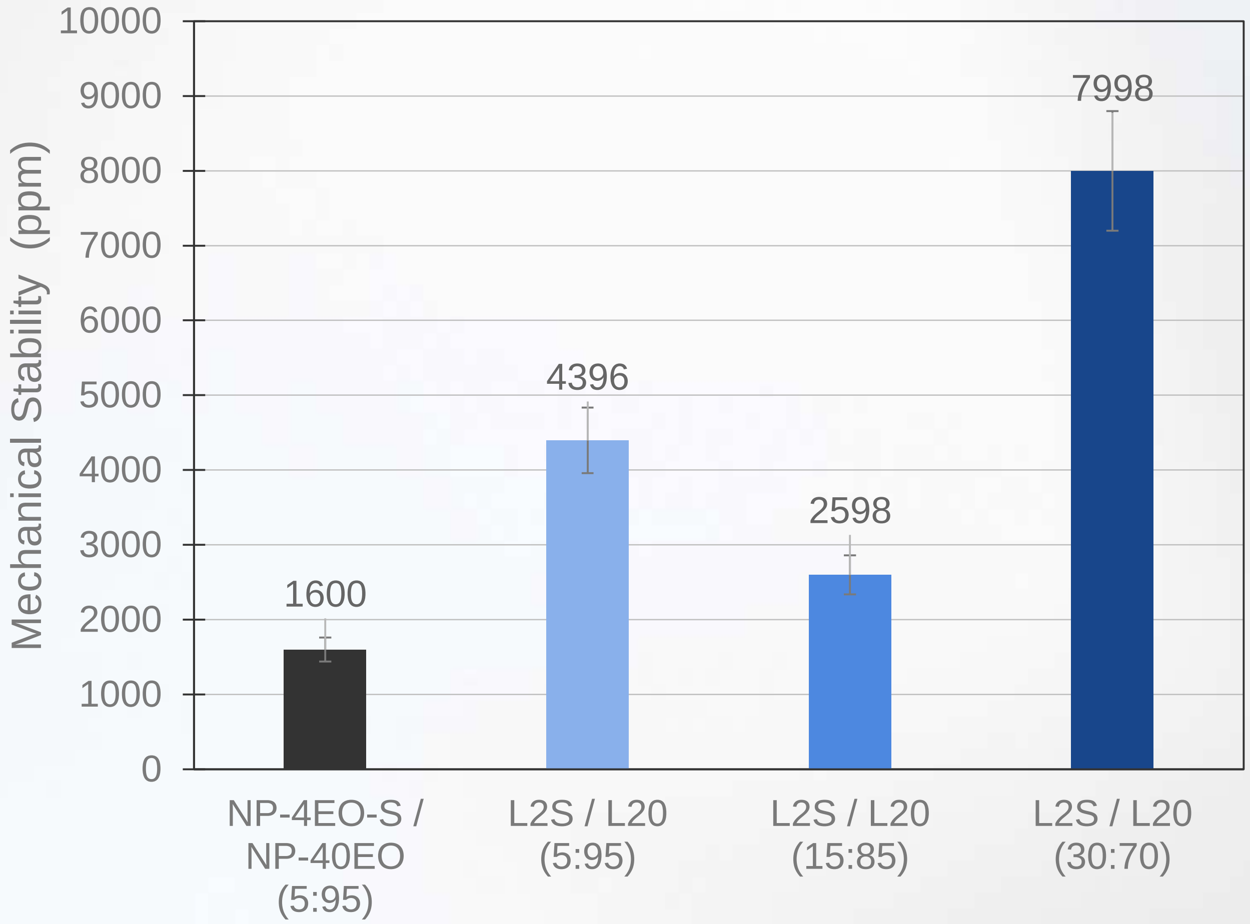


L20

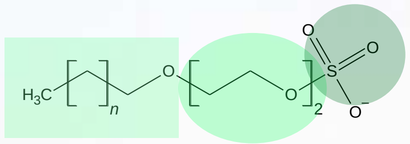
- ✓ Acceptable particle size range is 200 – 400nm.
- ✓ High nonionic content delivered better particle size control.

Effect of different ratios of nonionic to anionic

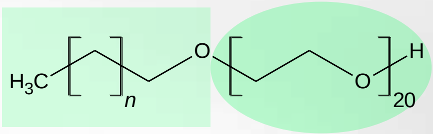
Mechanical Stability



- ✓ Less than 1.0% clot formed under shear stress.
- ✓ High nonionic content delivered better stability.



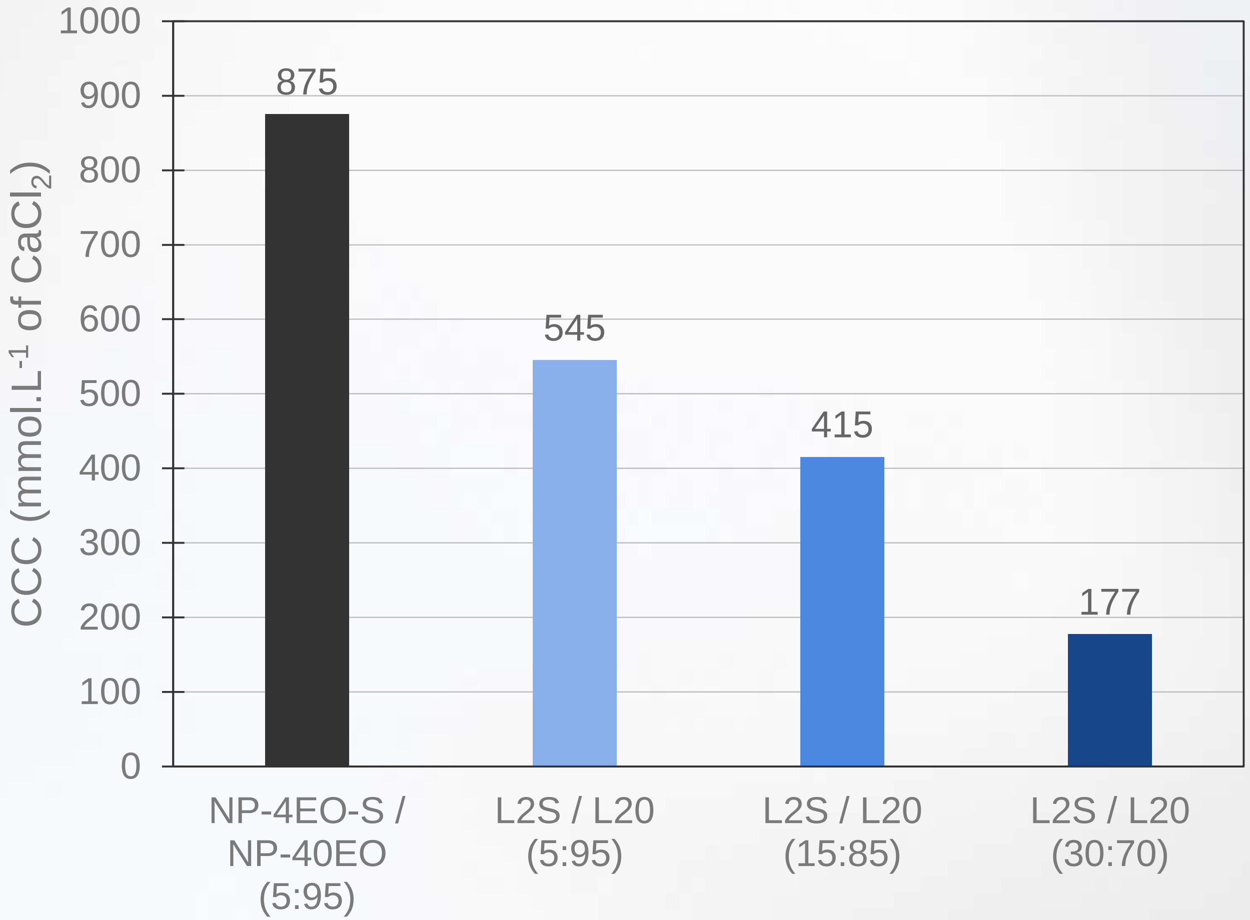
L2S



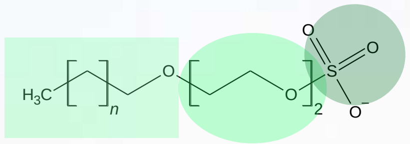
L20

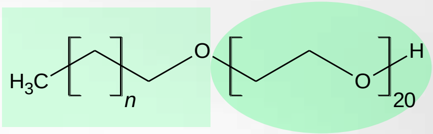
Effect of different ratios of nonionic to anionic

Electrolytic Stability



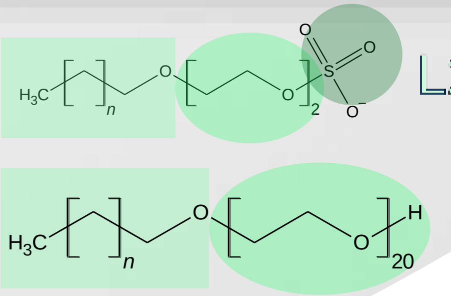
- ✓ Very high electrolytic stability for all formulations.
- ✓ High nonionic content improves steric barrier and delivered better stability.





Wrap up

- Surfactants L2S and L20 delivered a clean reactor, low particle size and stable vinyl-acrylic emulsion polymer;
- Even being less ethoxylated than the reference APE-based surfactant, the results indicated that they are suitable alternatives;
- Adjustments in the composition might improve the result. There might be an optimized composition between 5:95 and 15:85 ratio of nonionic to anionic.



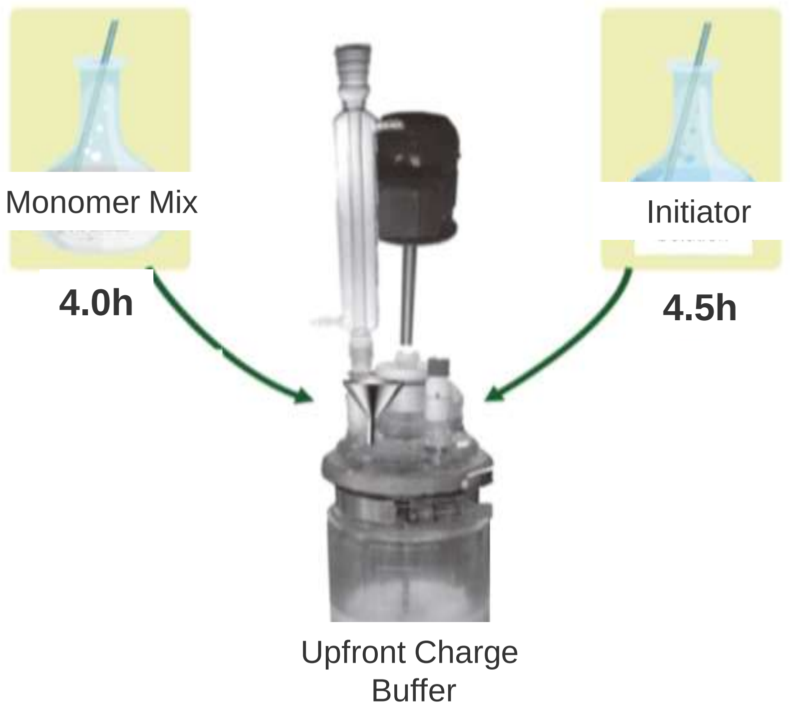
L2S
L20

Emulsion Polymer Formulation

Goal: to evaluate different anionic surfactants at two different nonionic:anionic ratio 95:5 and 85:15

Components (phm)	Formulation 2
Vinyl Acetate	80 %
Butyl acrylate	20 %
	Active Content (phm)
Surfactant L20	3.74 – 4.18
Surfactant L2S or L12S	0.22 – 0.66
Persulfate initiator	
Chase Redox	

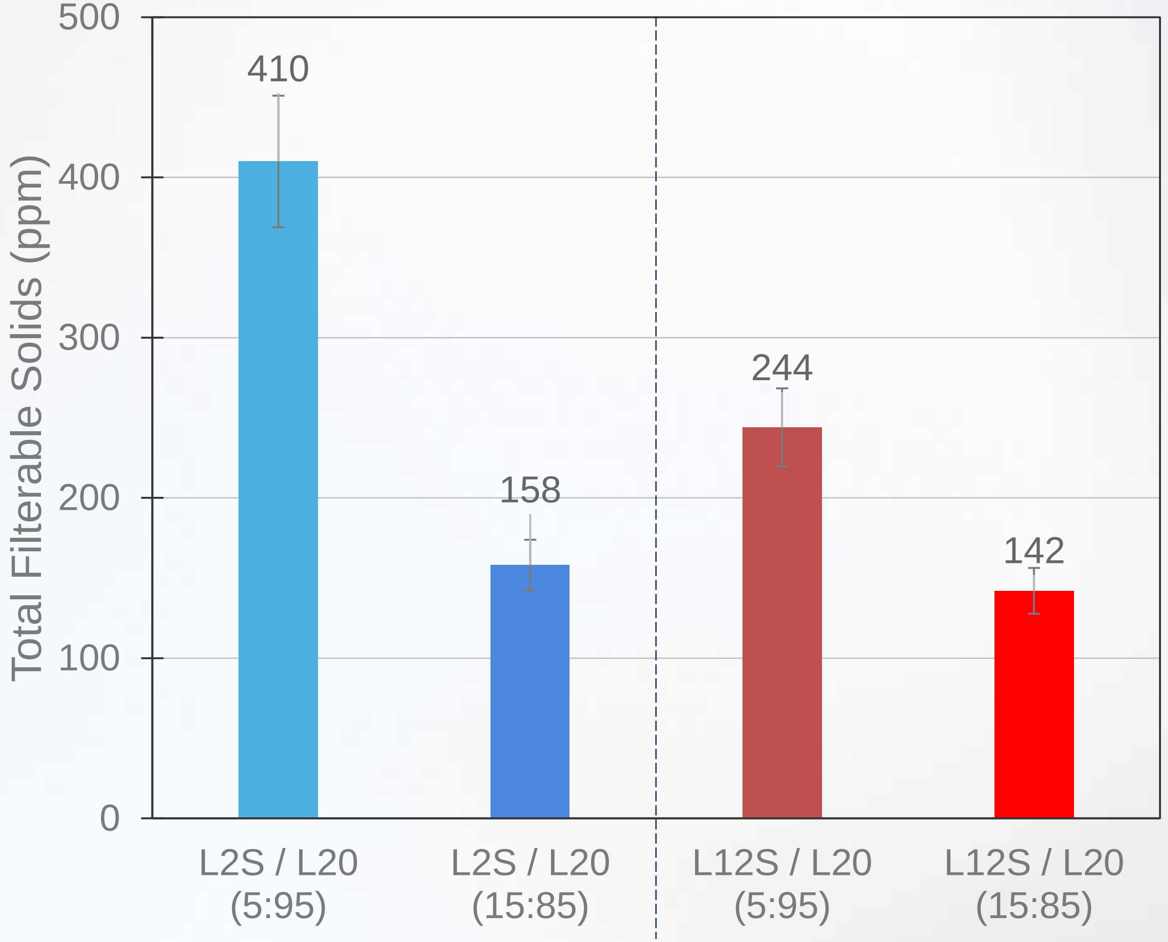
PROCESS



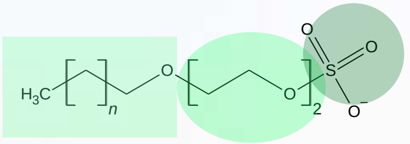
- **Thermal initiator:** 4.5h at 70 °C
- **Solid content:** 55 wt.%

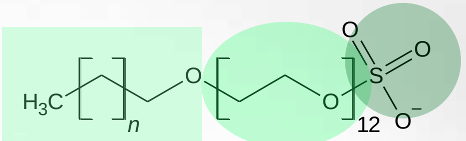
Effect of different anionic surfactants

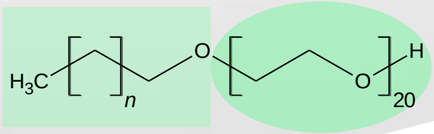
Reactor Cleanliness



- ✓ Clot formation < 500 ppm for all formulations.
- ✓ Longer ethylene oxide chain in the anionic improved the performance even at a low dosage.

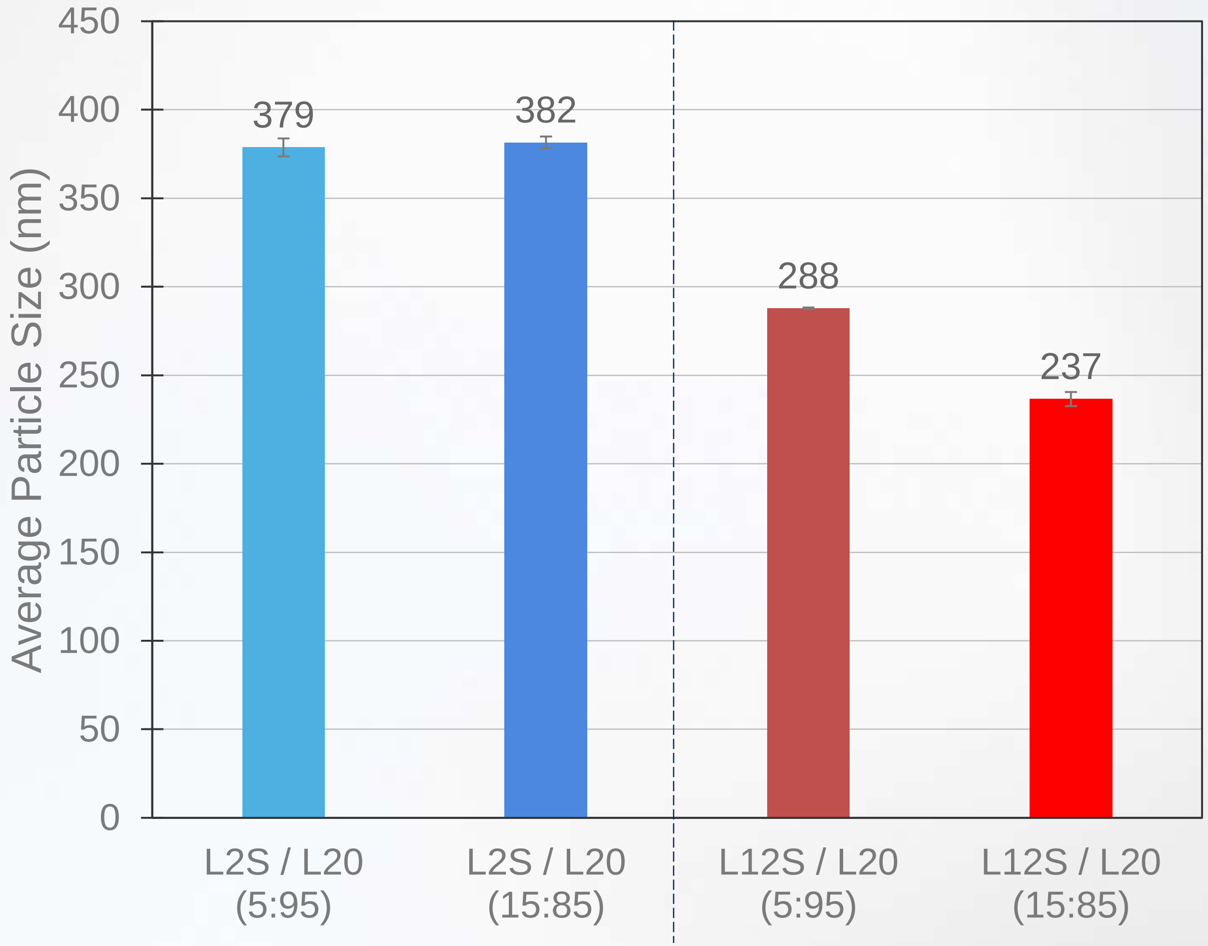




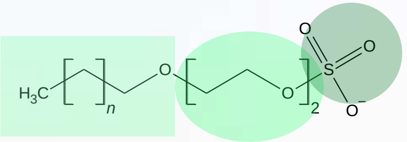


Effect of different anionic surfactants

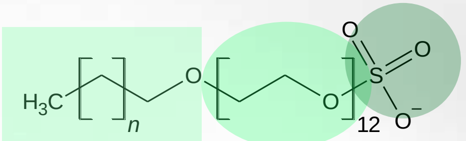
Particle Size



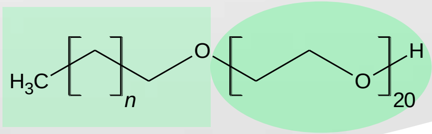
- ✓ Acceptable particle size range is 200 – 400nm;
- ✓ Longer ethylene oxide chain tends to decrease the particle size.



L2S



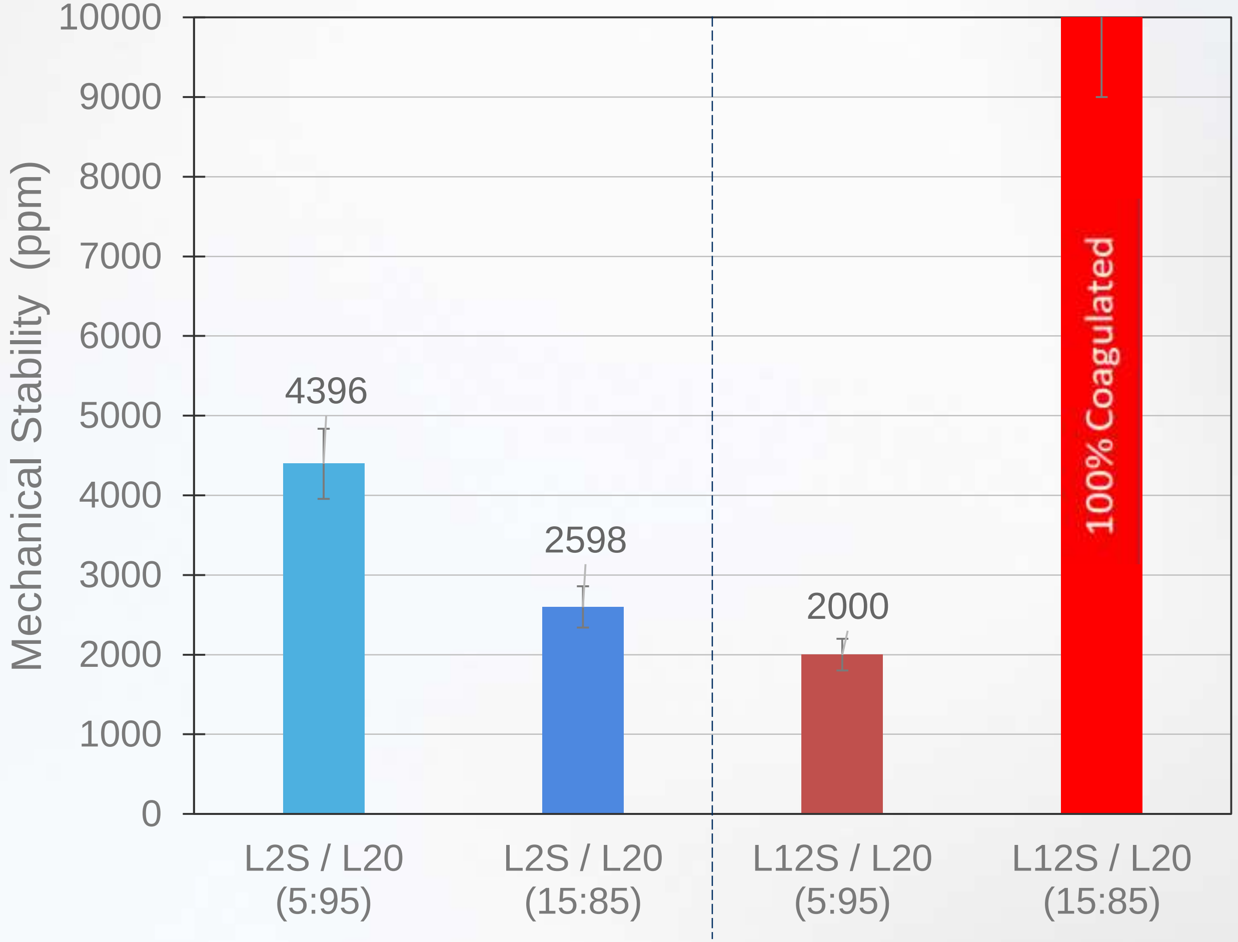
L12S



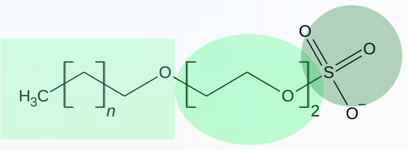
L20

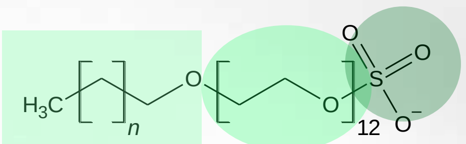
Effect of different anionic surfactants

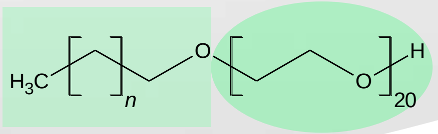
Mechanical Stability



- ✓ Longer ethylene oxide chain improved the mechanical stability for low anionic content formula;
- ✓ High anionic content with longer EO chain destabilized the latex.

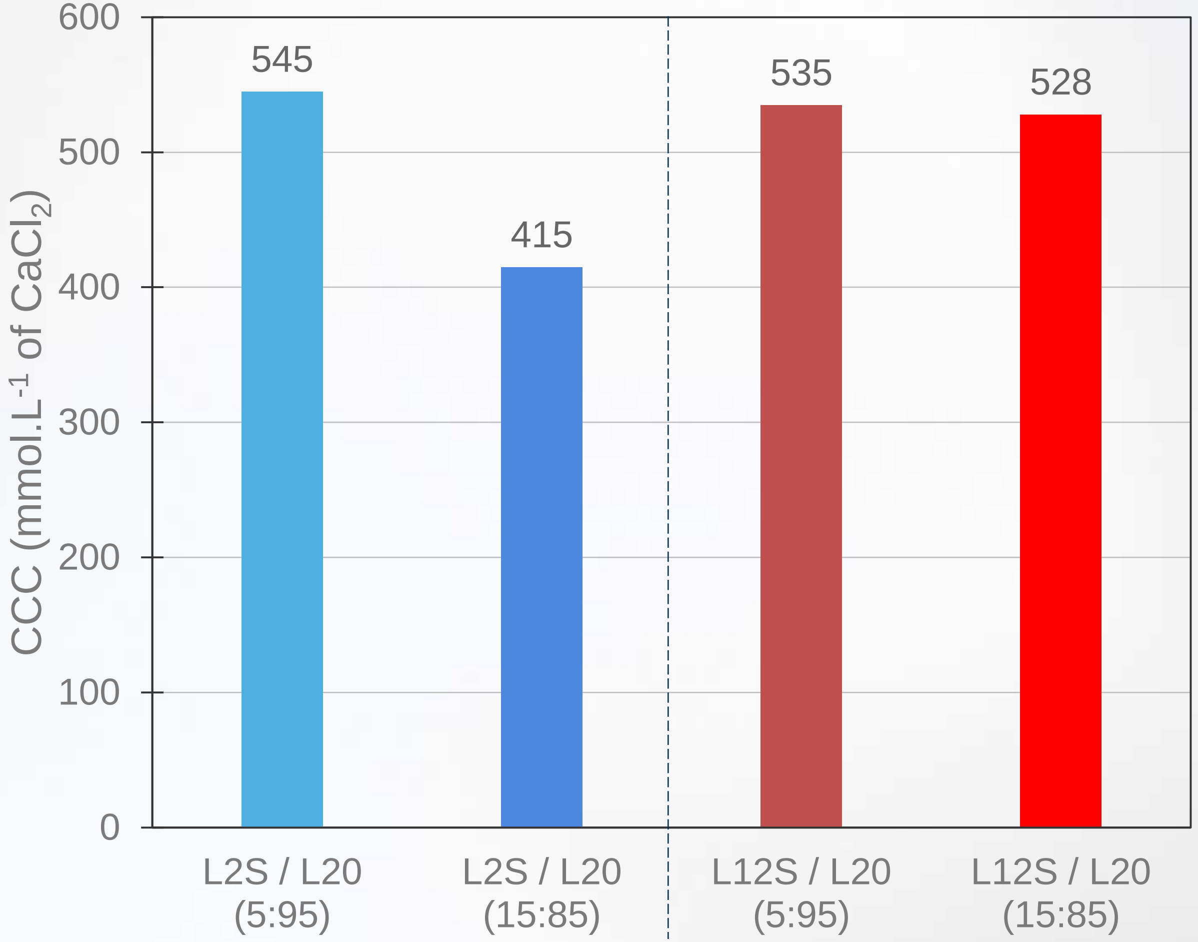




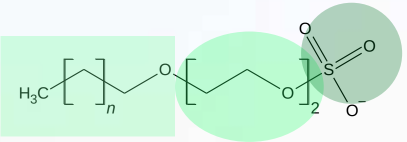


Effect of different anionic surfactants

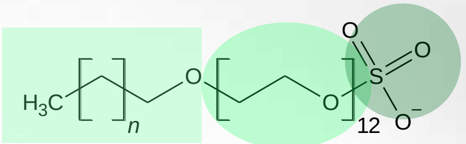
Electrolytic Stability



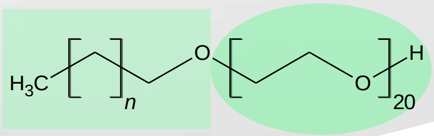
- ✓ Very high electrolytic stability for all formulations.
- ✓ Little effect when increasing the EO chain in the anionic surfactant.



L2S



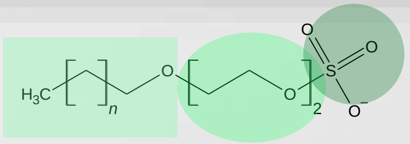
L12S



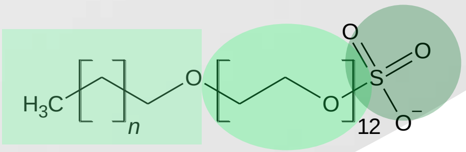
L20

Wrap up

- The longer EO chain anionic surfactant improved the overall stability of the vinyl-acrylic emulsion polymer for the same nonionic surfactant;
- Both short and long EO chain anionic delivered good results, which gives flexibility to the manufacturer;
- However, different ratios of nonionic to anionic need to be studied to fine tune the formulation. Substitution is not always a drop in.



L2S



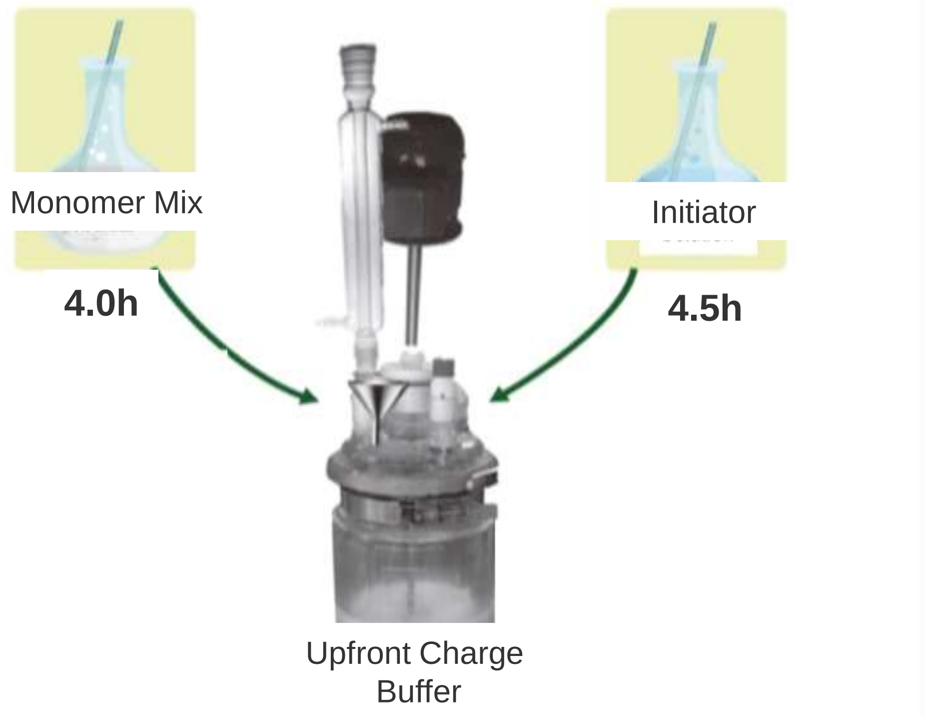
L12S

Emulsion Polymer Formulation

Goal: to evaluate different nonionic surfactants at a fixed nonionic:anionic ratio of 95:5

Components (phm)	Formulation 3
Vinyl Acetate	80 %
Butyl acrylate	20 %
	Active Content (phm)
Surfactant L20 or B40	4.18
Surfactant L2S	0.22
Persulfate initiator	
Chase Redox	

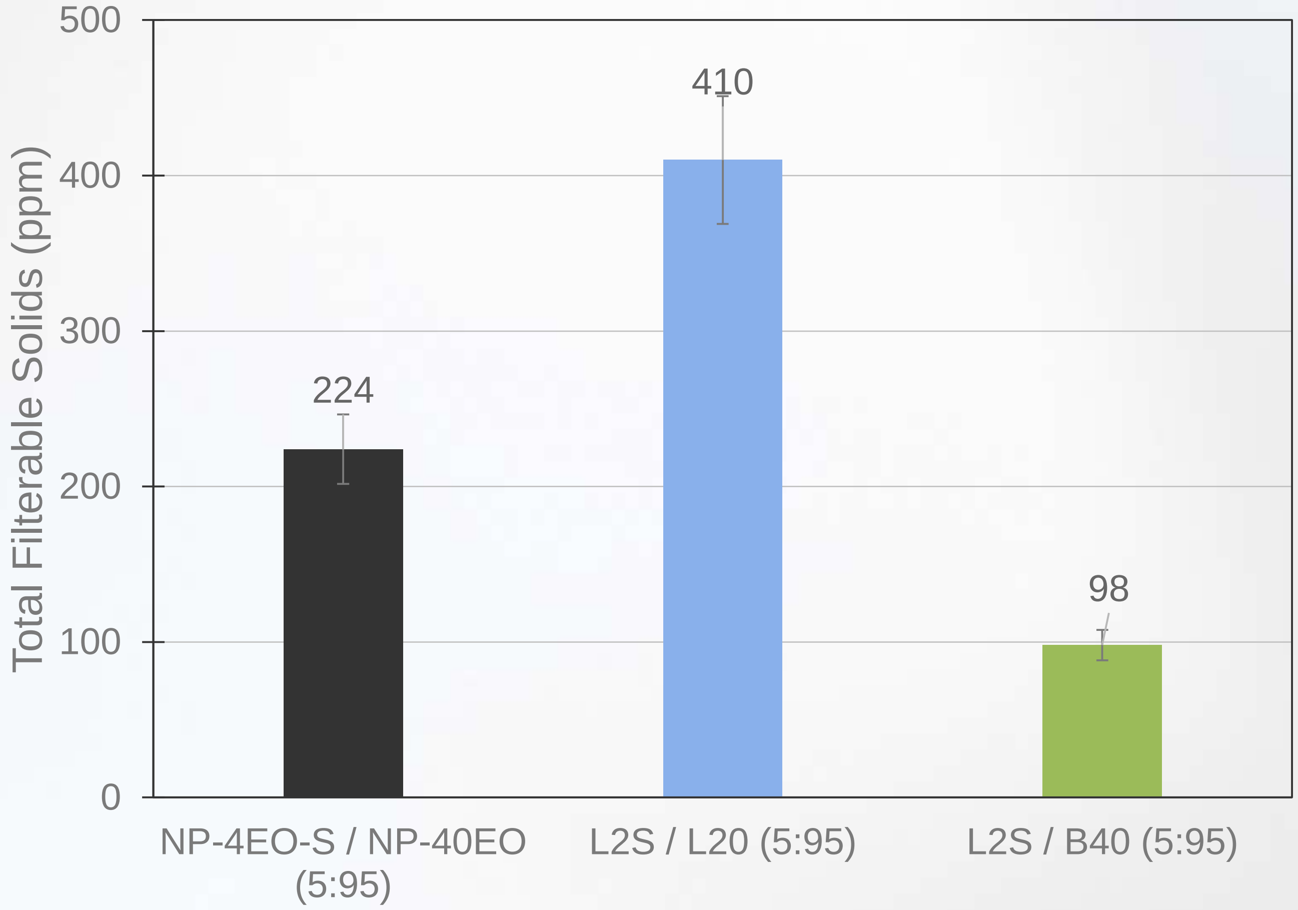
PROCESS



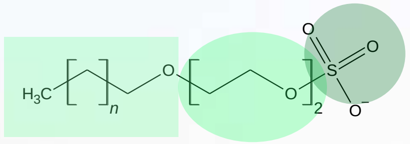
- **Thermal initiator:** 4.5h at 70 °C
- **Solid content:** 55 wt.%

Effect of different nonionic surfactants

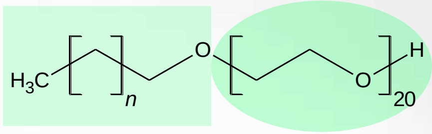
Reactor Cleanliness



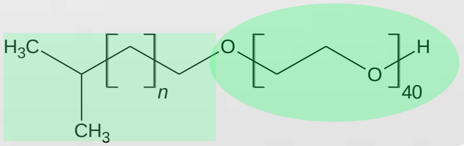
- ✓ Clot formation < 500 ppm for all formulations.
- ✓ Longer ethylene oxide chain in the nonionic improved the performance even compared against reference.



L2S



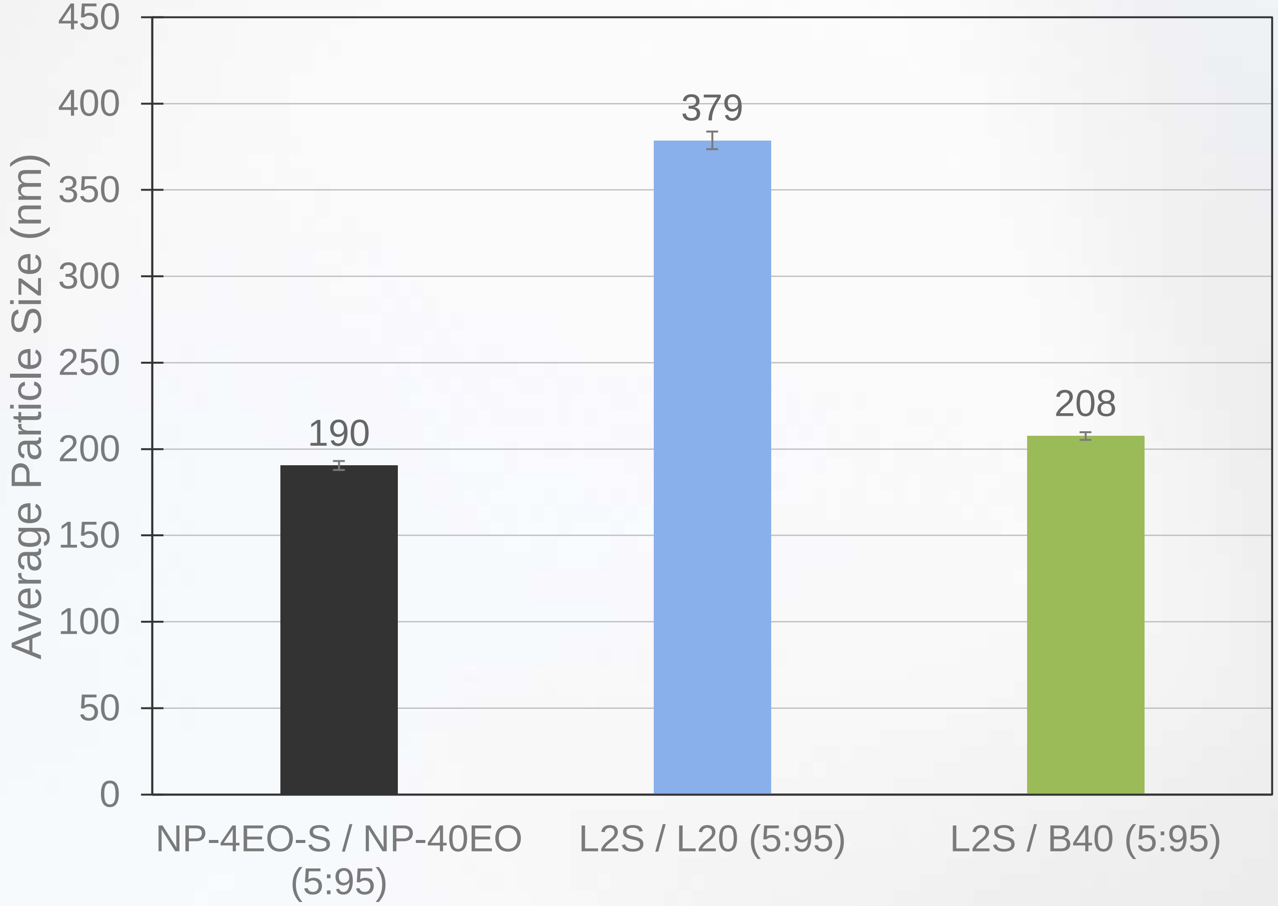
L20



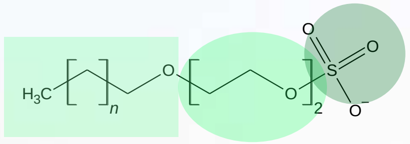
B40

Effect of different nonionic surfactants

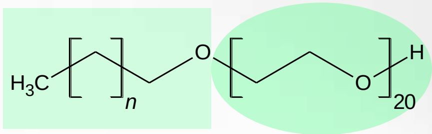
Particle Size



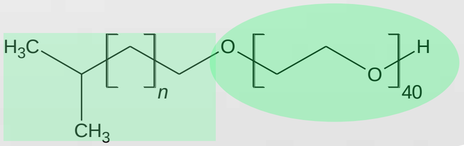
- ✓ Acceptable particle size range is 200 – 400nm;
- ✓ Longer ethylene oxide chain in the nonionic surfactant tends to decrease the particle size as seen for the anionic.



L2S



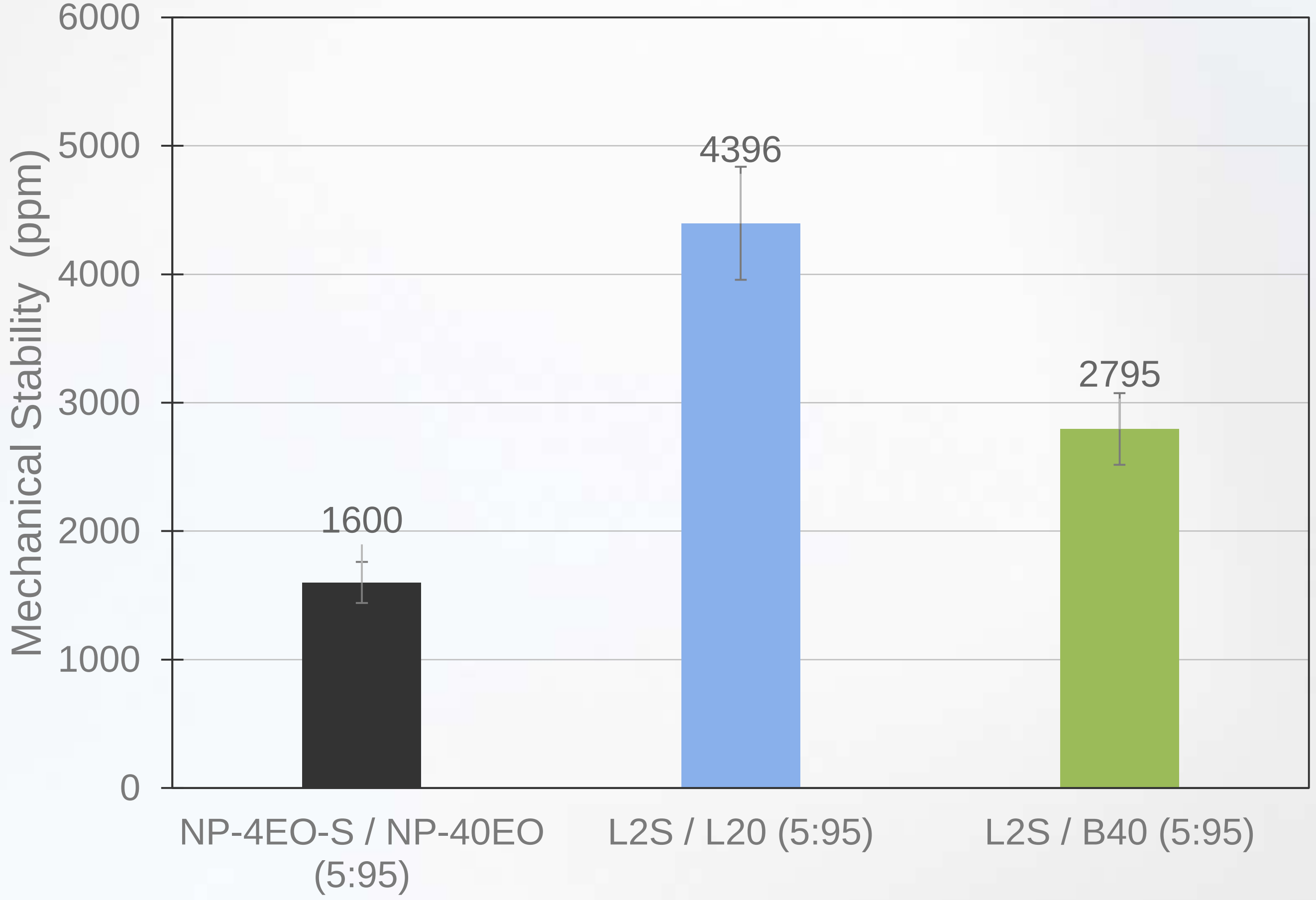
L20



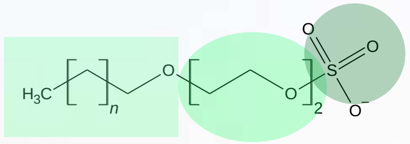
B40

Effect of different nonionic surfactants

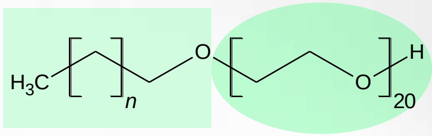
Mechanical Stability



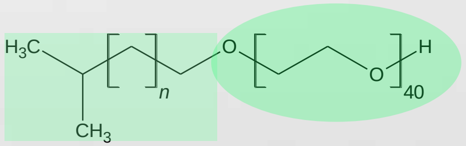
- ✓ Longer EO chain in the nonionic improved the mechanical stability;
- ✓ Combining longer EO chain in both surfactants might boost results.



L2S



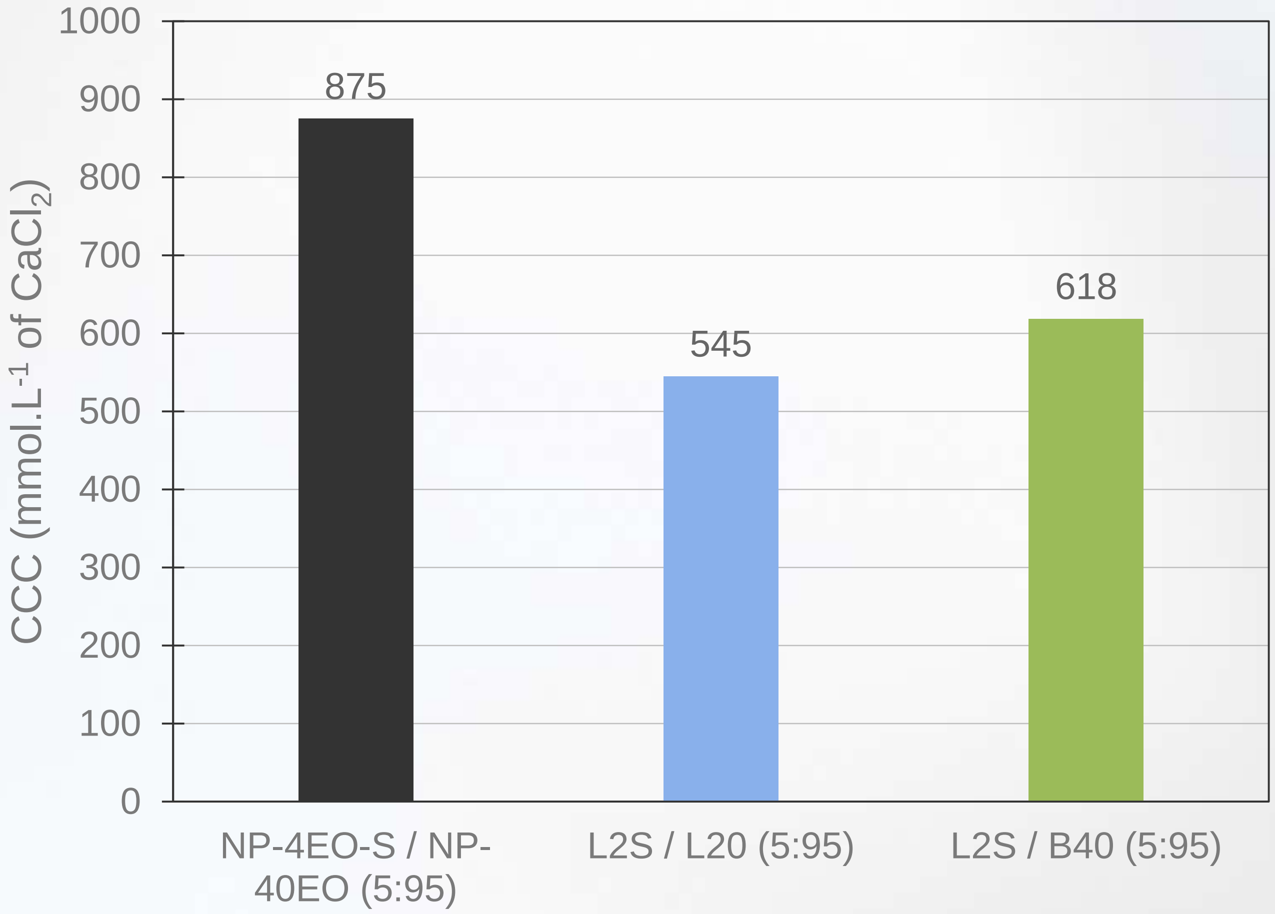
L20



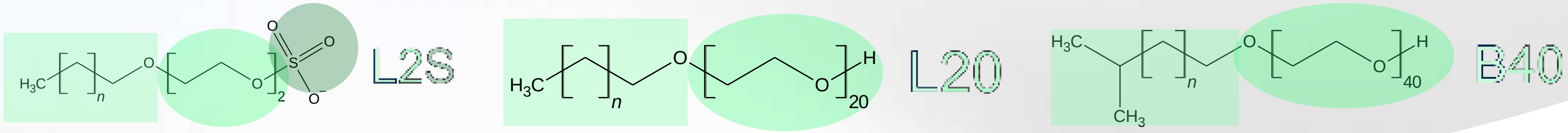
B40

Effect of different nonionic surfactants

Electrolytic Stability

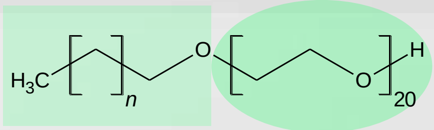


- ✓ Very high electrolytic stability for all formulations.
- ✓ Longer EO nonionic improved the steric barrier and delivered higher stability to electrolytes.

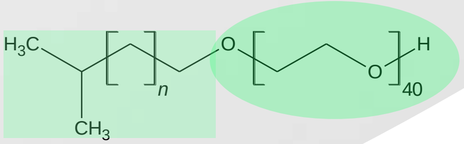


Wrap up

- The longer EO chain nonionic surfactant also improved the overall stability of the vinyl-acrylic emulsion polymer for the short EO anionic surfactant;
- Both short and long EO chain nonionic delivered good results, which gives flexibility to the manufacturer;
- Combining longer EO chain in both surfactants might boost results.



L20



B40

Paint Formulation

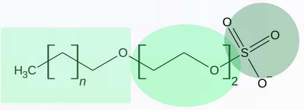
Goal: to evaluate the performance of a few of the emulsion polymers synthesized against benchmarks

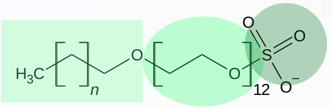
Paint Formulation

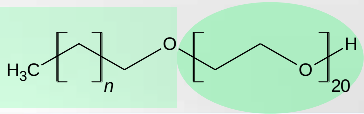
Paint Formulation
PVC ~ 45 %
Vinyl-Acrylic Emulsion ~ 35 %
Coalescing Agent ~ 2 %
VOC < 15 g/L
Viscosity = 100 ± 5 KU
pH = 9.0

Emulsion Polymers Tested

Emulsion Polymers Tested
Benchmark APE-based
Benchmark APE-free
NP-4EO-S / NP-40EO (5:95)
L2S / L20 (5:95)
L2S / L20 (15:85)
L12S / L20 (5:95)

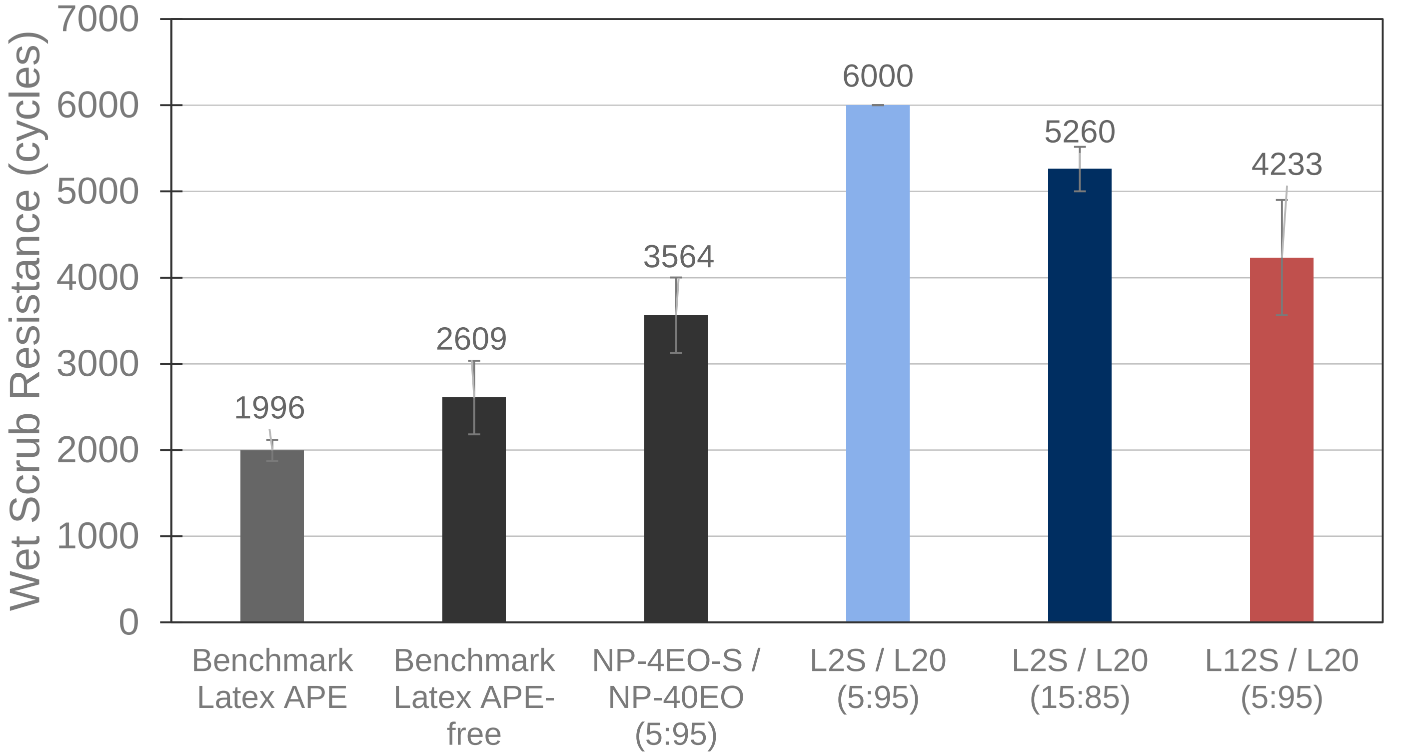

L2S

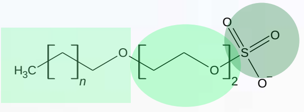

L12S


L20

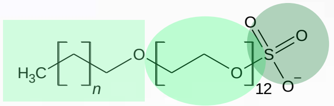
Vinyl-Acrylic Paint

Scrub Resistance – ASTM D2486

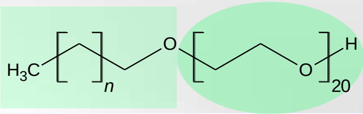




L2S



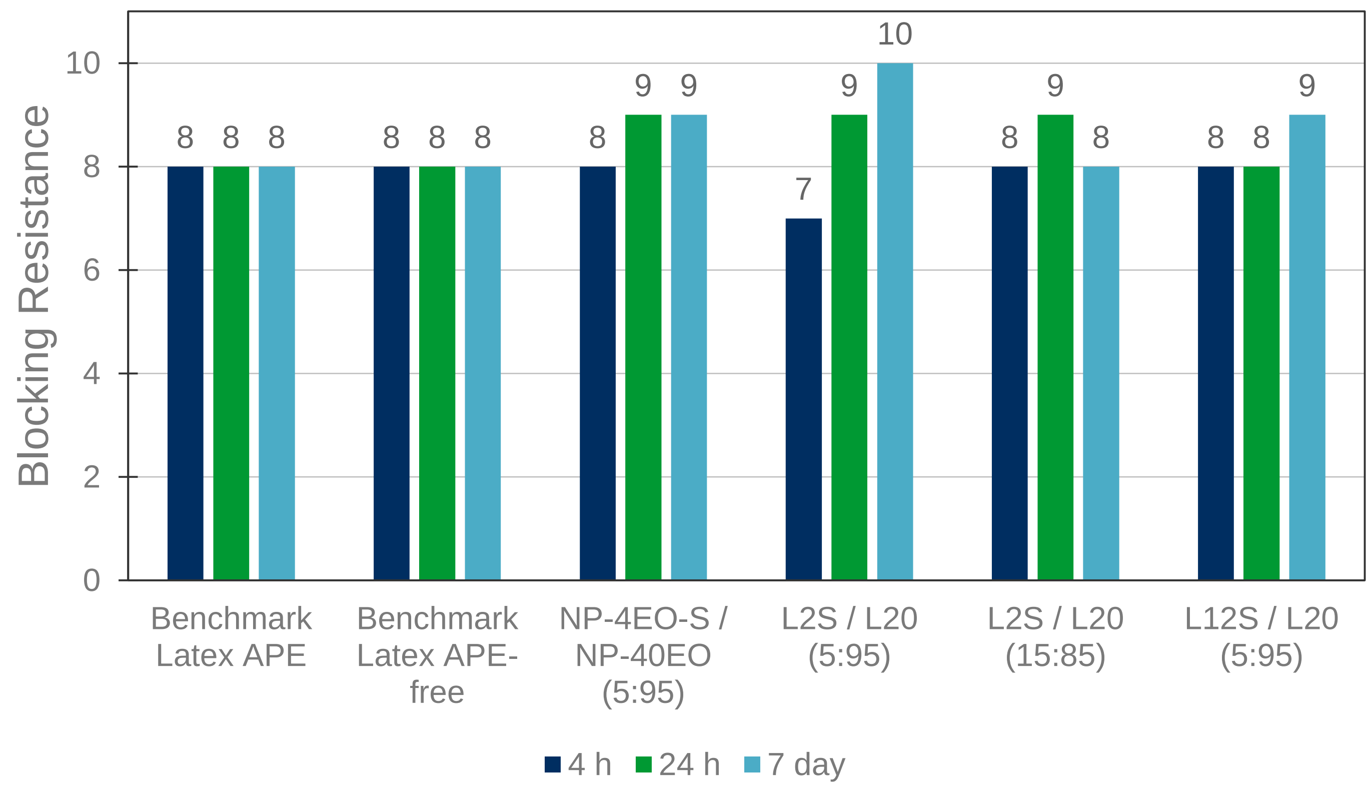
L12S

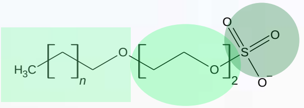


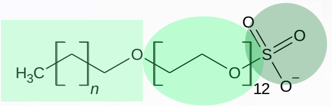
L20

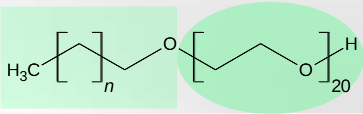
Vinyl-Acrylic Paint

Blocking Resistance – ASTM D4946



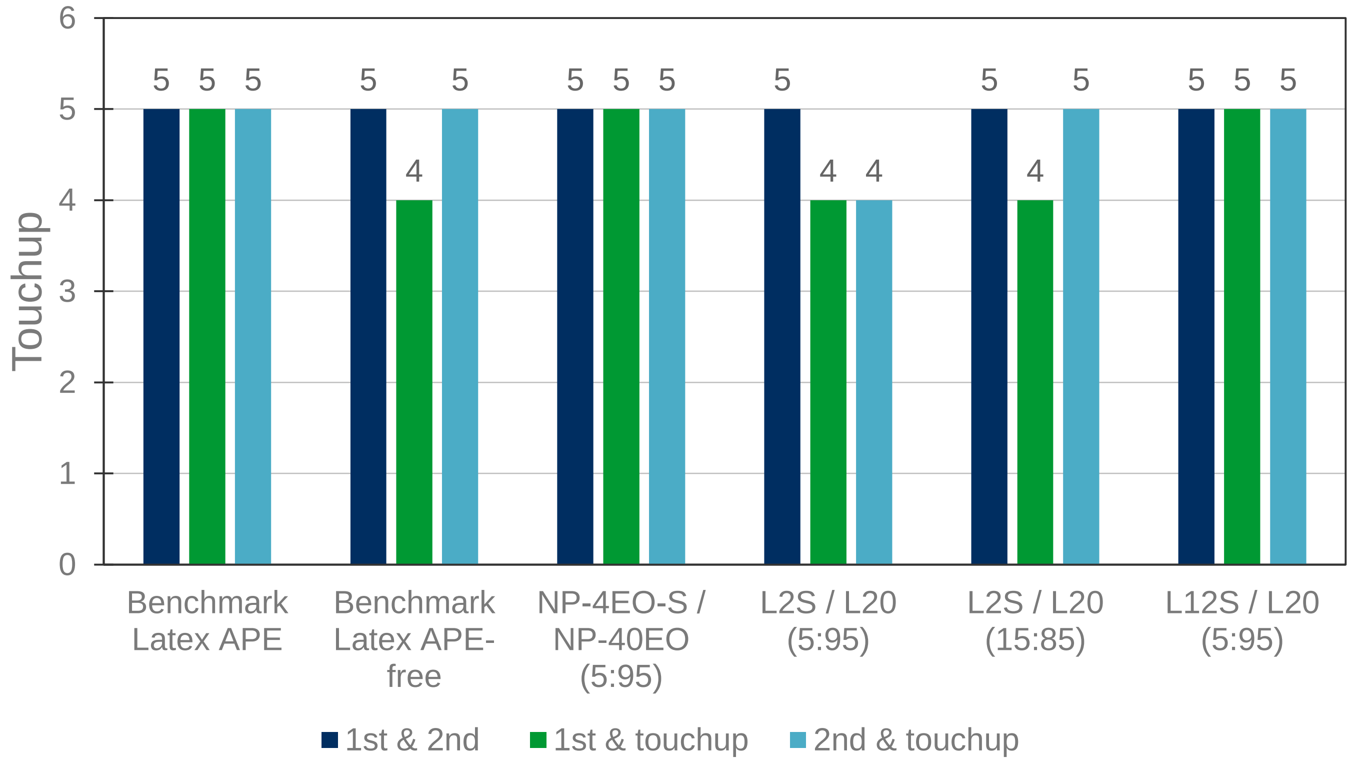

L2S

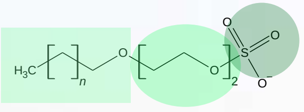

L12S


L20

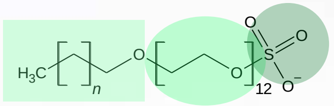
Vinyl-Acrylic Paint

Touchup – ASTM D7489

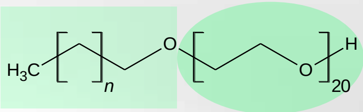




L2S



L12S



L20

Conclusions

- ✓ When replacing APE-based by APE-free surfactants, the ratio of nonionic to anionic can change. Ladder studies are advisable to fine tune composition;
- ✓ Longer Ethylene Oxide chain anionics and nonionics seem to improve overall stability BUT be careful on the ratio;
- ✓ Paint performance can be improved when replacing APE-based surfactants by APE-free ones;
- ✓ Developing a toolbox of alternatives is advisable, considering market fluctuations, and possible, considering technical performance.

THANK YOU VERY MUCH FOR YOUR ATTENTION!

Bruno Dário
TS&D Scientist
(346) 413-1152
bruno.dario@us.indorama.net

Integrated Oxides and Derivatives