BIO-ORGANIC SILICONE ADDITIVES: NON-PETROLEUM BASED ALTERNATIVE RAW MATERIALS.

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Bio-Sourced Drivers

- Current market trend for plant based, rather than petroleum based components.
- Alternate supply chain

Why Use Silicone Additives: PDMS Properties

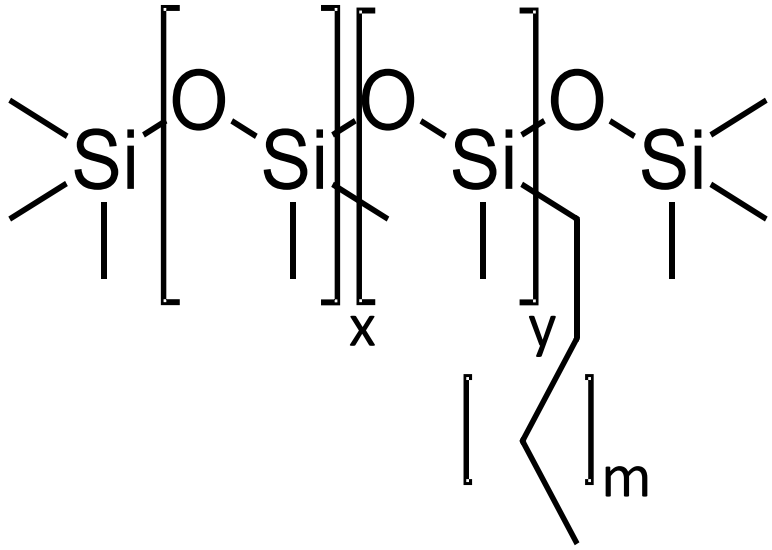
- Free Radical Stability (O_2, O_3, Sunlight)
- Insulative (Electrical and Thermal)
- High Thermal Stability: 250°C
- Low Surface Tension: 20 mN/m
- Excellent Spreading & Wetting
- Minimal Interfacial Tension
- Low Coefficient of Friction
- Low $T_{g:}$ 153°K: -120°C
- Low Odor & Toxicity
- Water Repellent
- Gas Permeable
- **Incompatible**

Affects other properties to differing degrees

To remedy incompatibility: react with an organic moiety

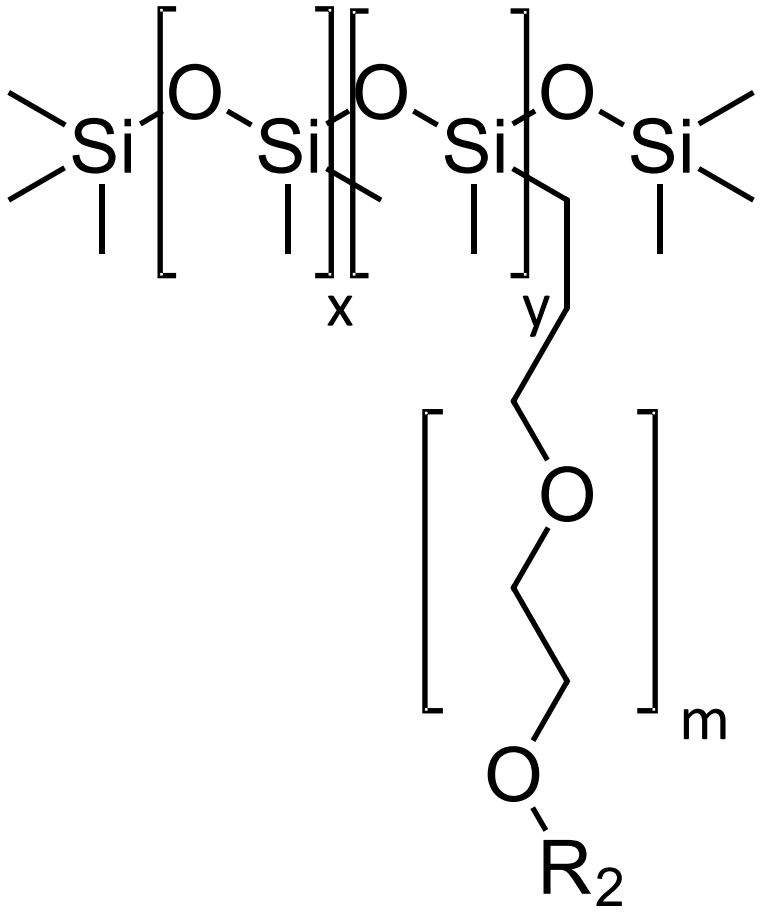
Silicone Hydrocarbon Copolymers: Tend to Increase Compatibiltiy in Solvent-Based and Other Non-Aqueous Systems

- CH_2=CH-R can vary from Ethyl to $C_{32}H_{65}$
- Variables include molecular weight, weight percent silicone, chain length of hydrocarbon
- Additional proprietary treatments



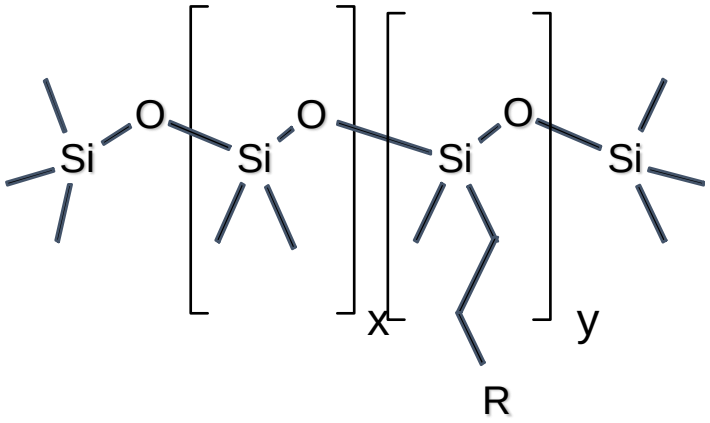
SPE Copolymers: Tend to Increase Compatibility in Solvent and Water-Based Systems

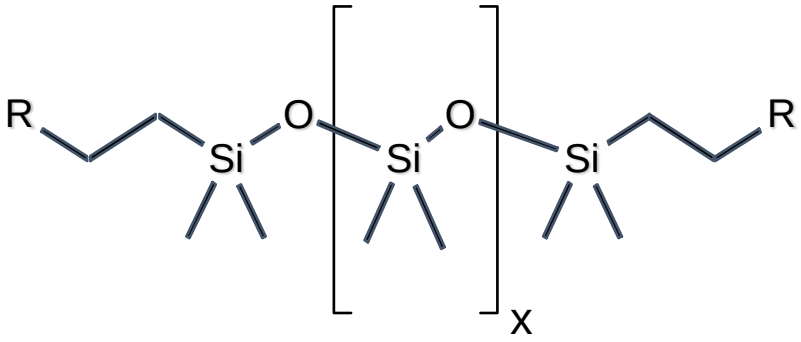
- Increasing x over y increases slip and decreases solubility.
- Increasing m increases water solubility and foaming.
- R_2=H is more water soluble and reactive

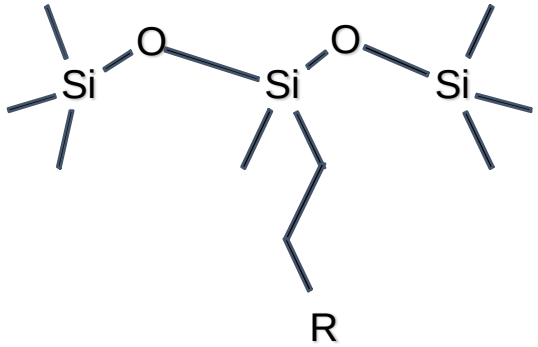


Organomodified Silicone backbones

- Pendant (Comb) Type
- Linear (ABA)
- Trisiloxane







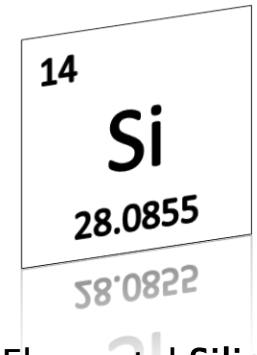
Castor Oil Derivatives. An old approach with a new reason.

- Siltech have offered a castor oil modified silicone which is described as: The castor oil triglyceride is attached to the silicone backbone making these more soluble in triglycerides.
- Non-TSCA
- In the past we showed these high bio-content silicones to have some utility in coatings.
  - Gave slip, mar resistance, anti-graffiti, but F&L not optimized.

Castor Oil Silicones Best in UV systems

1.75%	Gloss	Static COF	Kinetic COF	Marker Removal	Antigraffiti Rating	Surface Appear.
A	95	0.713	0.633	5.5	2.6	Orange peel
B	89	0.648	0.557	5.8	2.9	Orange peel
C	95	0.416	0.307	7.8	4.4	Mild waves
Control	96	1.311	1.306	3.8	1.5	Lots of craters

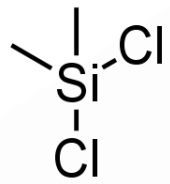
The Road from Silicon to Silicone



Elemental **Silicon**:
Abundant in the earth's crust predominately as oxide minerals; silica, sand, quartz, or gemstones.

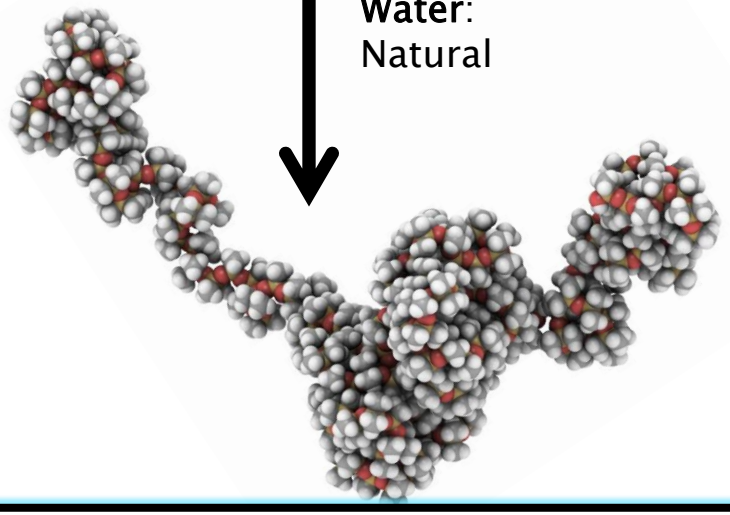
1) **Methanol**: A naturally occurring biochemical very common in nature. Generally made from Natural Gas.
2) **HCl**: a naturally occurring mineral acid

Catalysts:
From the Earth



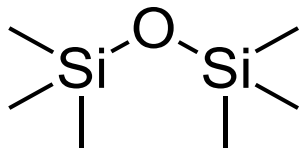
A variety of **chlorosilanes**: man-made, highly reactive intermediates. These are only used by chemical companies.

Water:
Natural

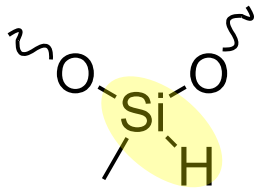


Silicone. a.k.a. **polydimethylsiloxane**, **PDMS**, **simethicone** or **dimethicone**. This man-made polymer is used in a very wide range of medical, food, personal care, household and industrial uses. It is among the most toxicologically studied and low toxicity polymers known to man.

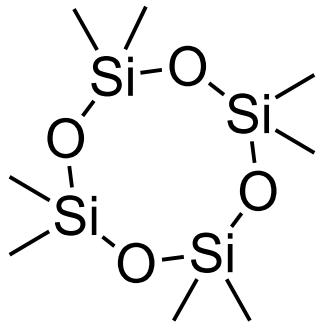
Silicone Hybrid Chemistry



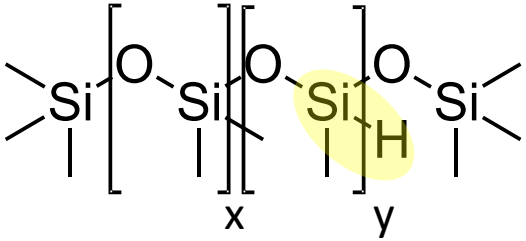
End Capper (MM)



Reactive Site (D*)

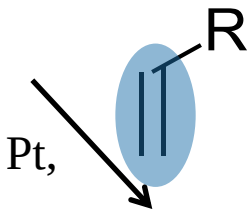


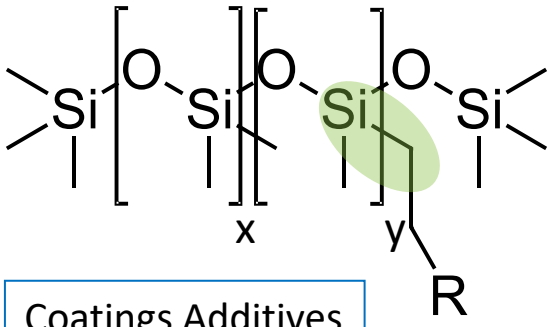
Chain Extender (D_4)



Silanic H type

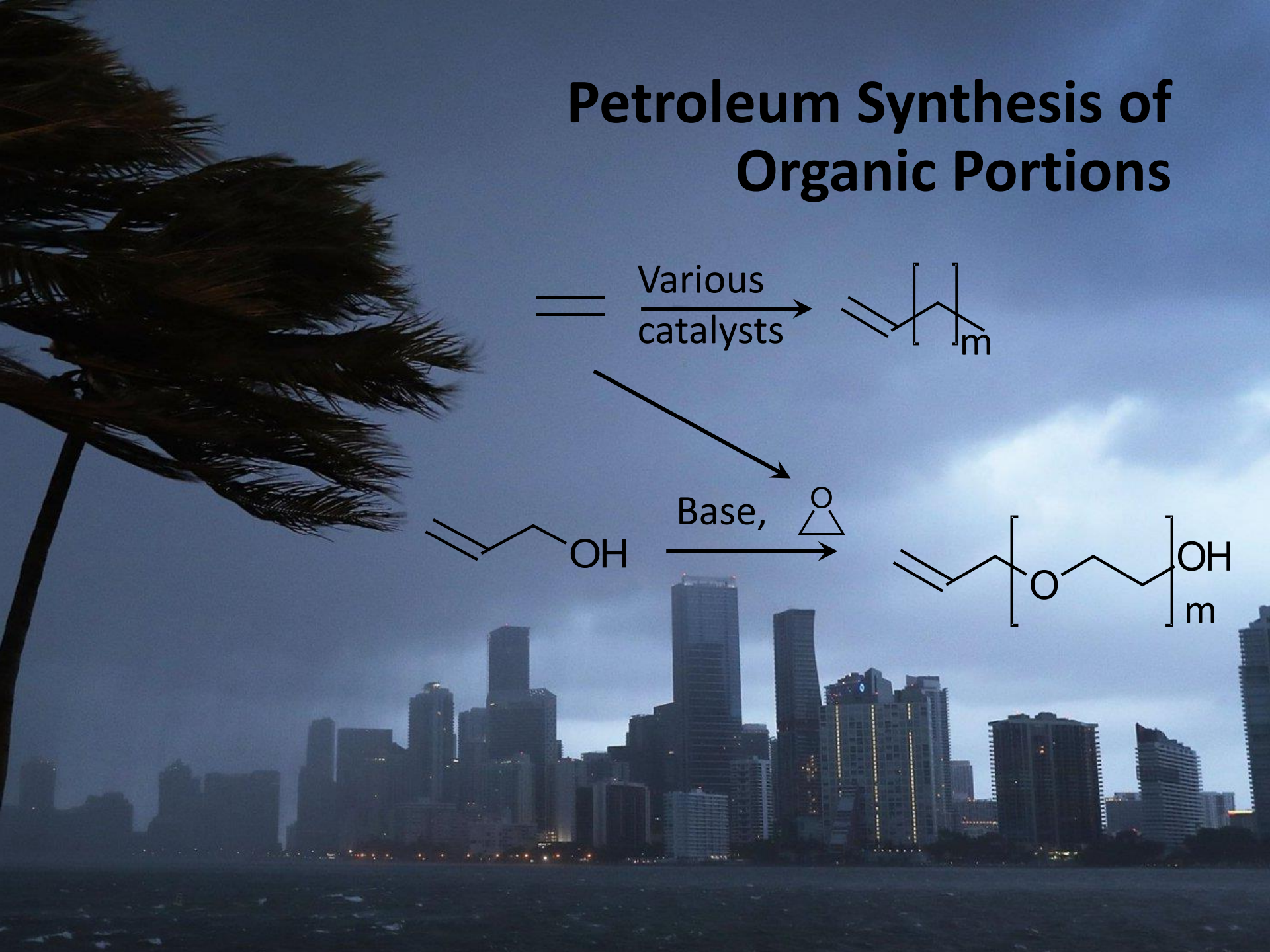
Bio source



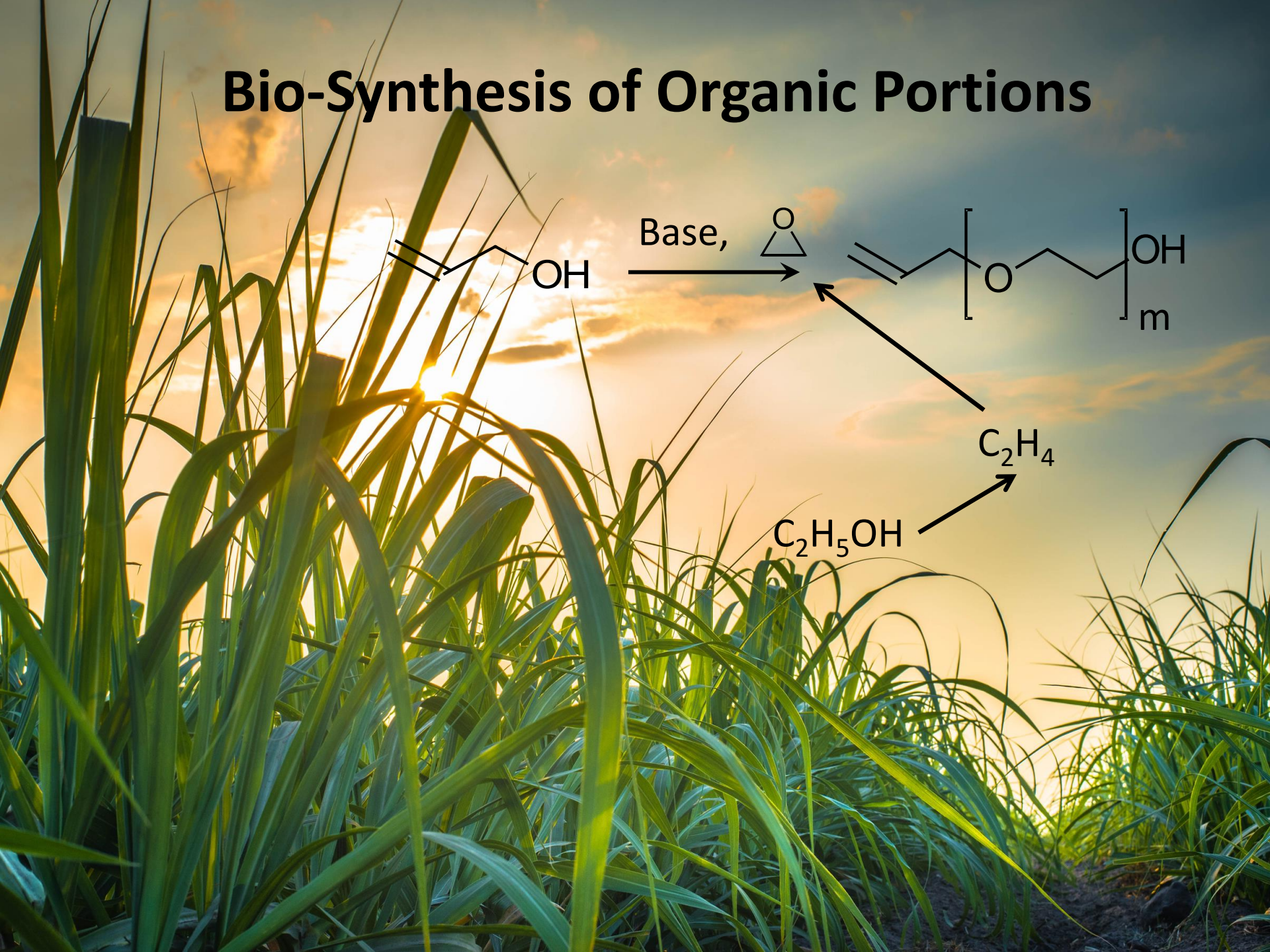


Coatings Additives

Petroleum Synthesis of Organic Portions



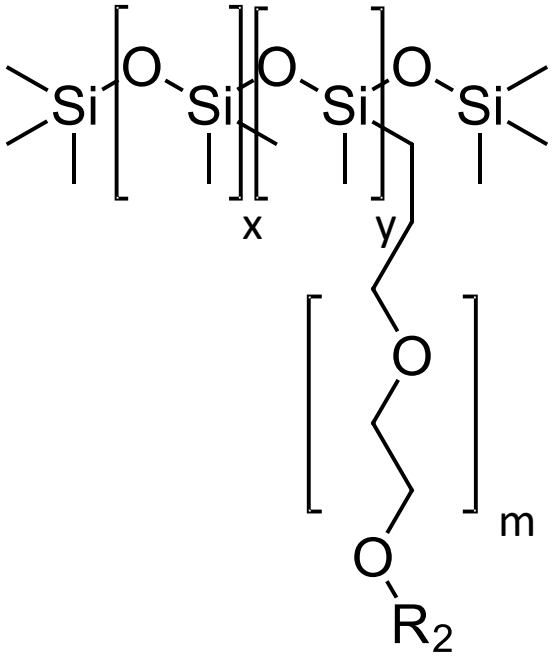
Bio-Synthesis of Organic Portions

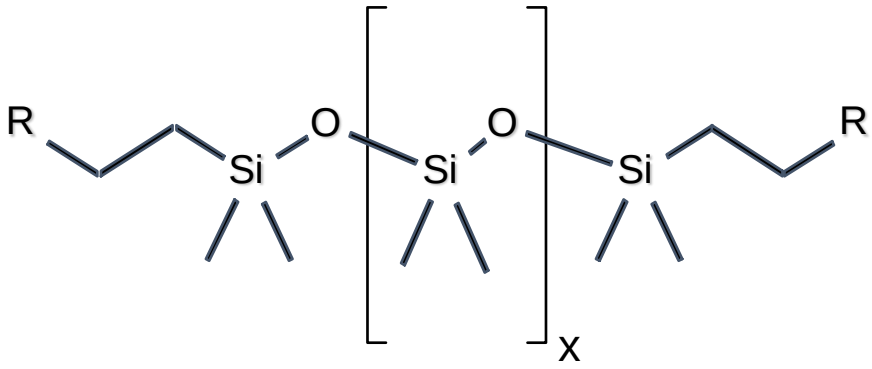


Hypothesis

The coatings additives, which were laboratory synthesized using bio-based organic components, will behave the same as the corresponding commercial petroleum feedstock sourced additives.

Structures:





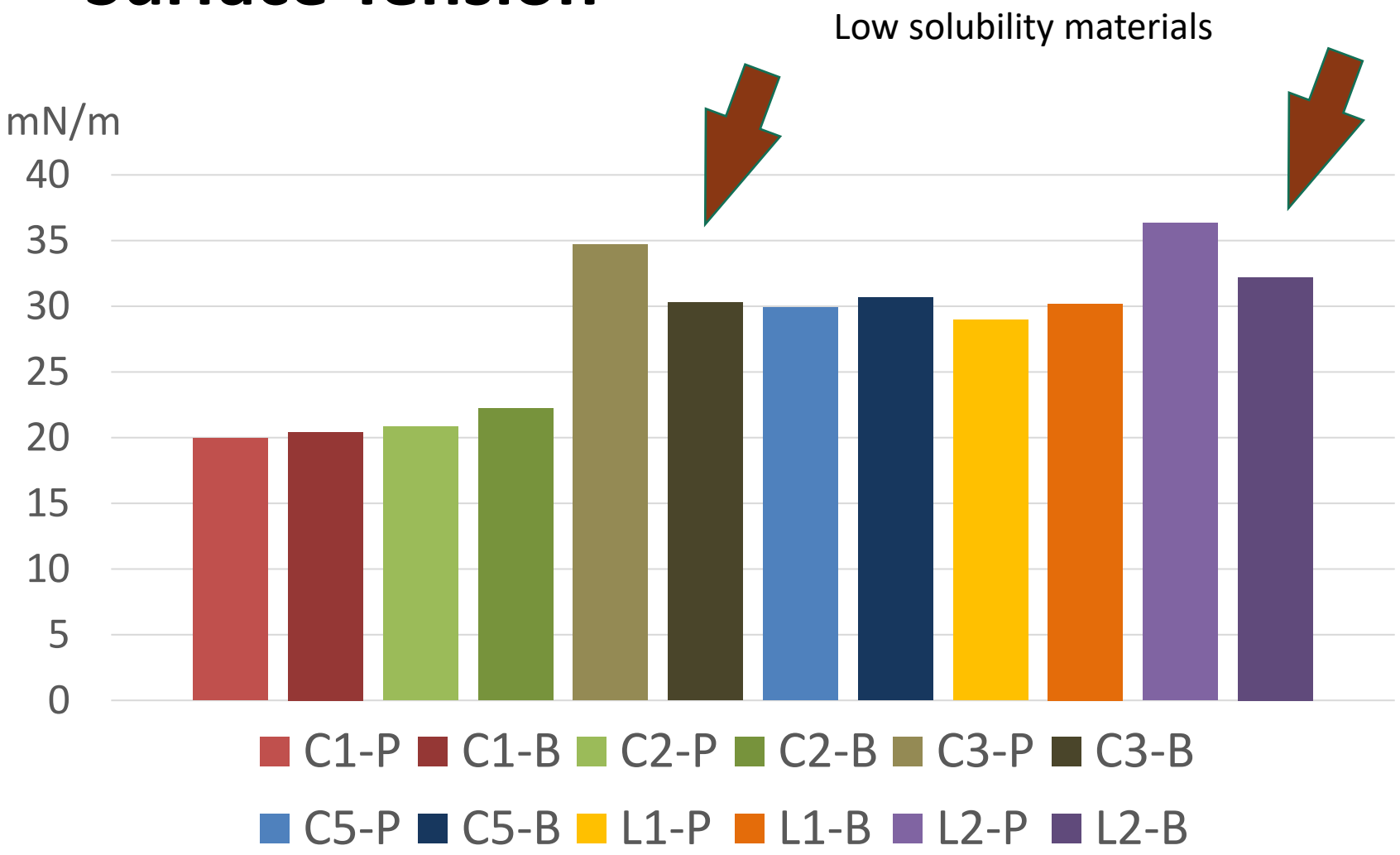
C: comb
L: linear
P: petro
B: Bio

Material	x	y	m	R	Water Solubility
C1-P & C1-B	0	1	8	H	Dispersible
C2-P & C2-B	1	1	8	H	Soluble
C3-P & C3-B	12	2	8	H	Dispersible
C4-P & C4-B	22	2	10	Acetyl	Dispersible
C5-P & C5-B	8	4	8	H	Soluble
L1-P & L1-B	10	0	10	H	Soluble
L2-P & L2-B	25	0	10	H	Dispersible

Physical Properties

Sample	Viscosity, cP	Visc. History / spec., cP	S.T. mN/m	Appearance
C1-P	41	45±5 / 30-70	20.0	Clear liquid
C1-B	51		20.4	Clear liquid
C2-P	103	101±15 / 70-150	20.8	Clear liquid
C2-B	170		22.2	Clear liquid
C3-P	220	227±24 / 100-350	34.7	Clear liquid
C3-B	252		30.3	Clear liquid
C4-P	300	267±12 / 175-390	N.D.	Clear liquid
C4-B	343			Clear liquid
C5-P	307	302±11 / 150-400	29.9	Clear liquid
C5-B	313		30.7	Clear liquid
L1-P	210	205±5 / 150-400	29.0	Clear to hazy liquid
L1-B	292		30.2	Clear to hazy liquid
L2-P	480	471±18 / 300-600	36.3	Clear to hazy liquid
L2-B	567		32.2	Clear to hazy liquid

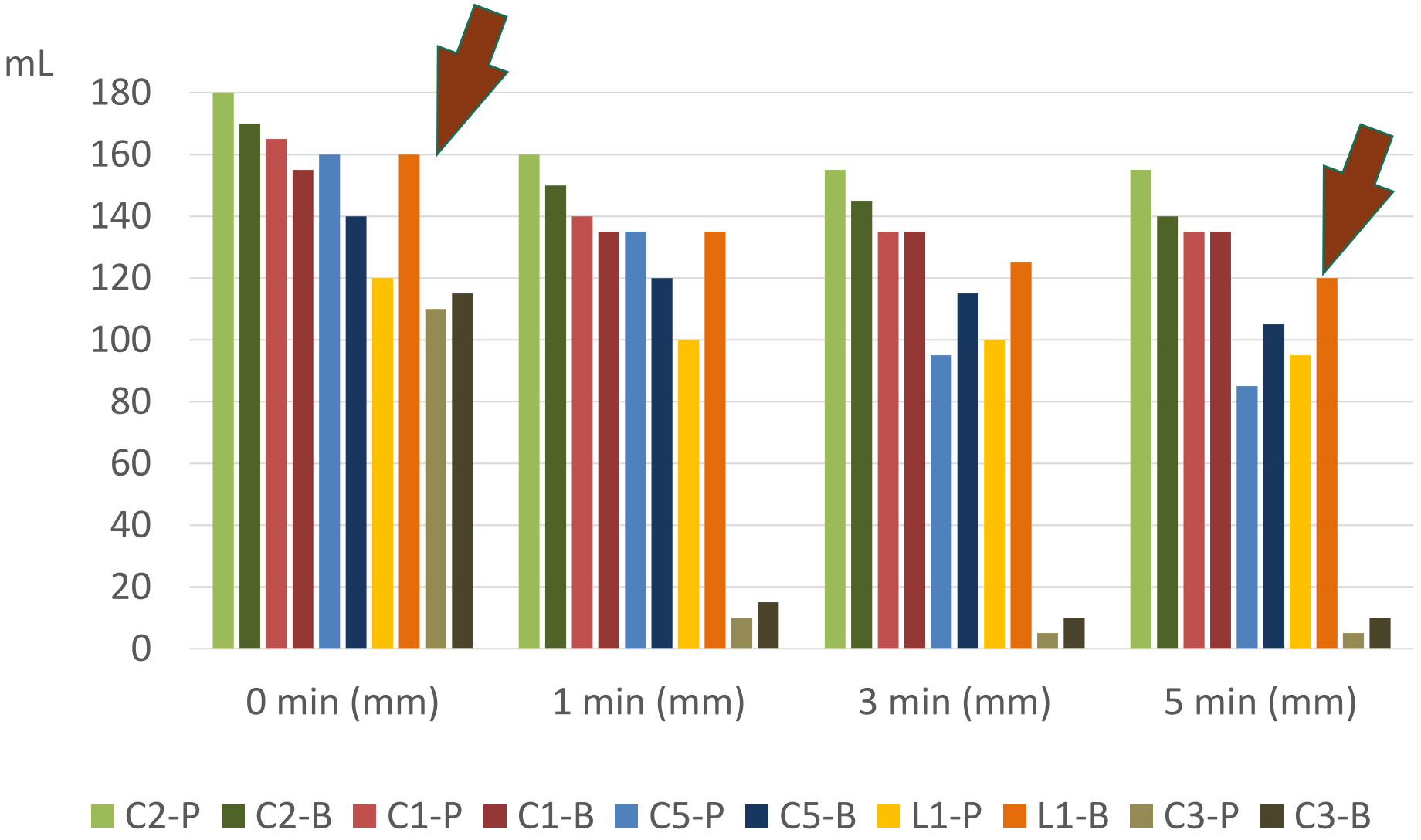
Surface Tension



Aqueous Foam Height

Sample	0 min (mL)	1 min (mL)	3 min (mL)	5 min (mL)	Comments	
C1-P	165	140	135	135	Loose	Hazy
C1-B	155	135	135	135	Loose	Hazy
C2-P	180	160	155	155	Tight	Clear
C2-B	170	150	145	140	Tight	Clear
C3-P	110	10	5	5	None	Hazy
C3-B	115	15	10	10	None	Hazy
C5-P	160	135	95	85	Loose	Clear
C5-B	140	120	115	105	Loose	Clear
L1-P	120	100	100	95	Loose	Clear
L1-B	160	135	125	120	Loose	Clear

Aqueous Foam Height



Coatings Evaluations

0.5% additive in PR-1245 (1 K WB PUD) from Quaker Color

- Appearance and foam generation were similar except with the soluble products. Some of the dispersible ones had poor F&L.
- Results were the same for –P and –B samples

PUD Appearance

C4-P and C4-B
coating appearance

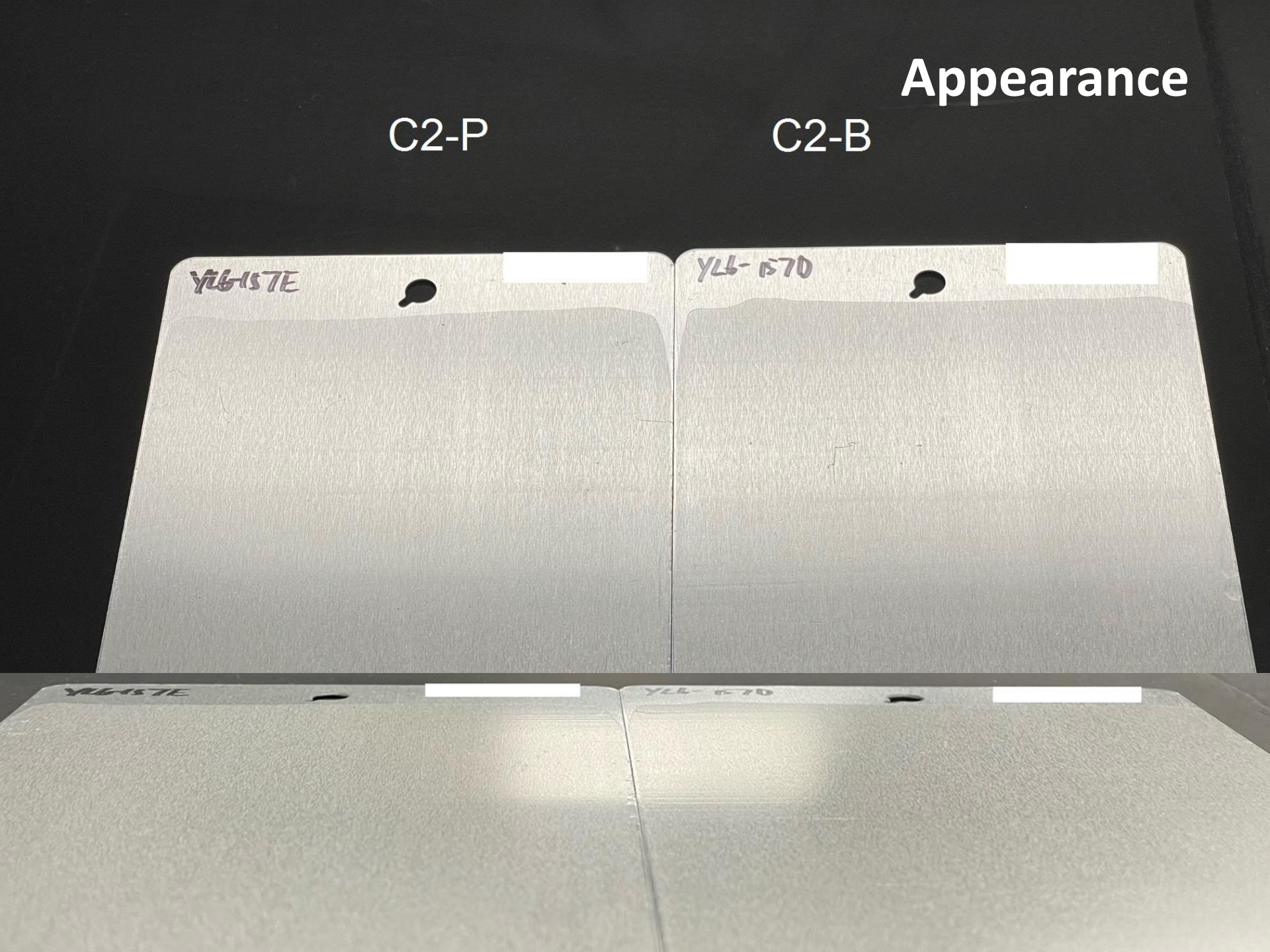
All other PUD
coating appearance
with additives

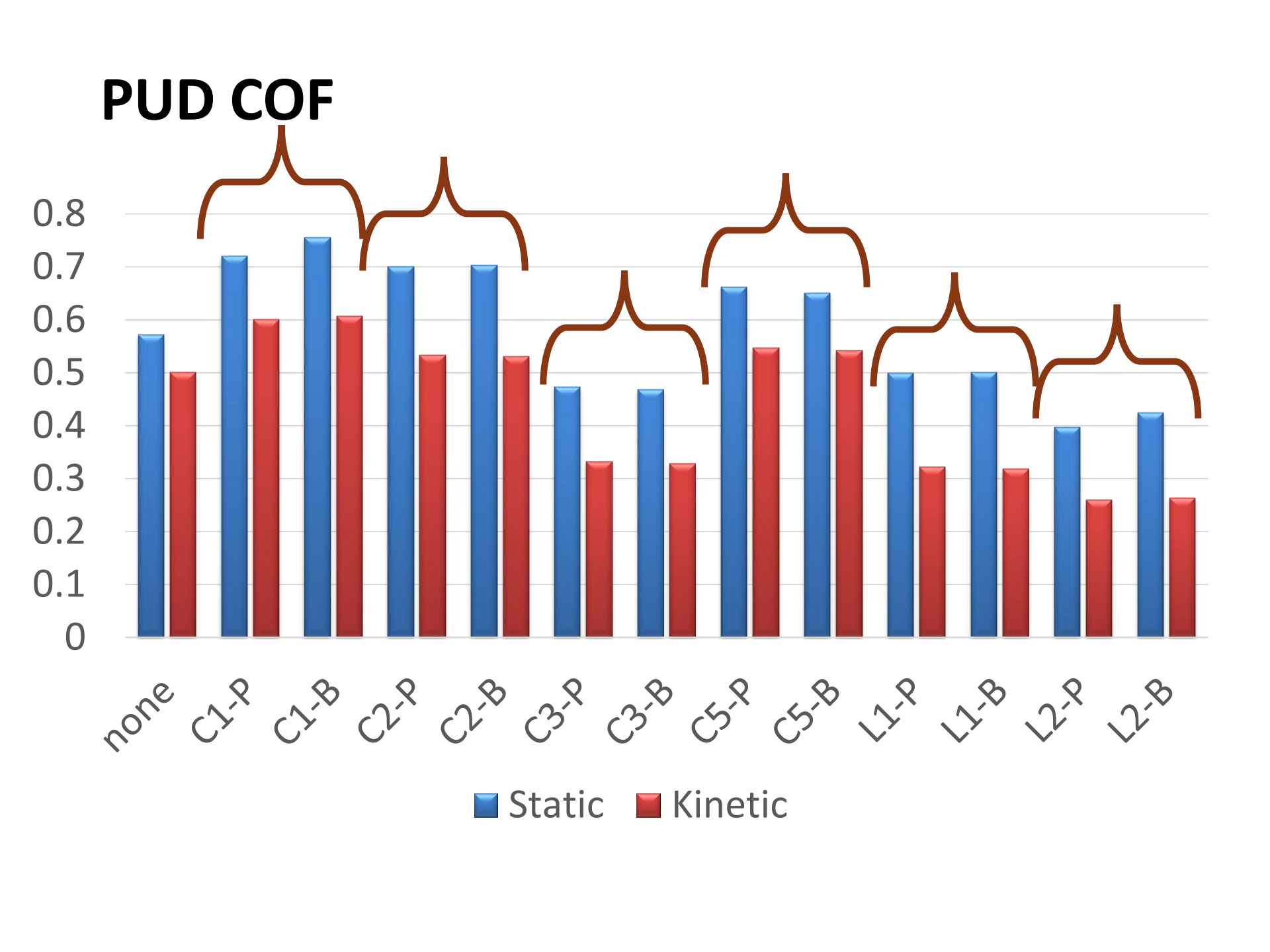
uncoated Al

Appearance

C2-P

C2-B

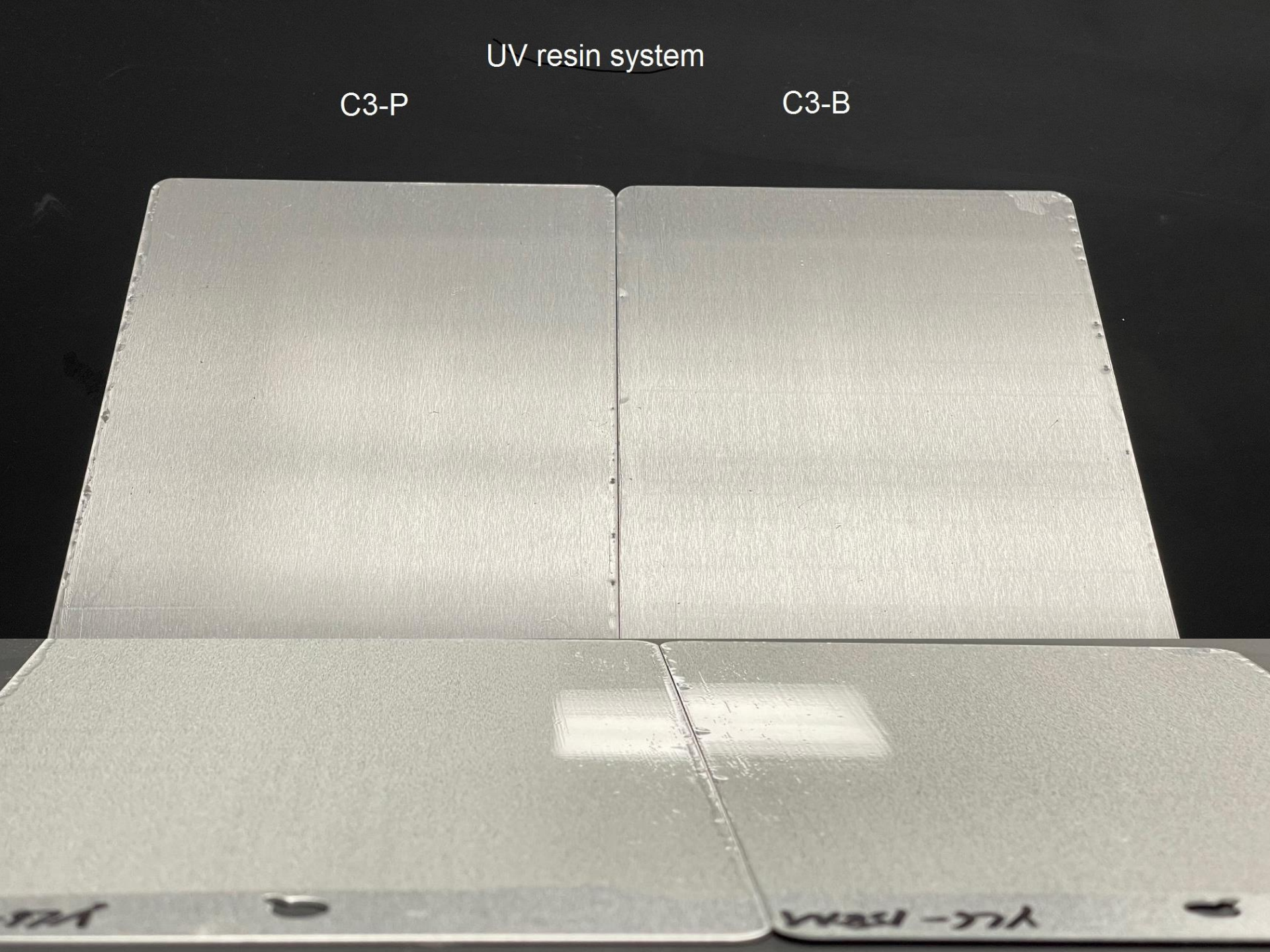


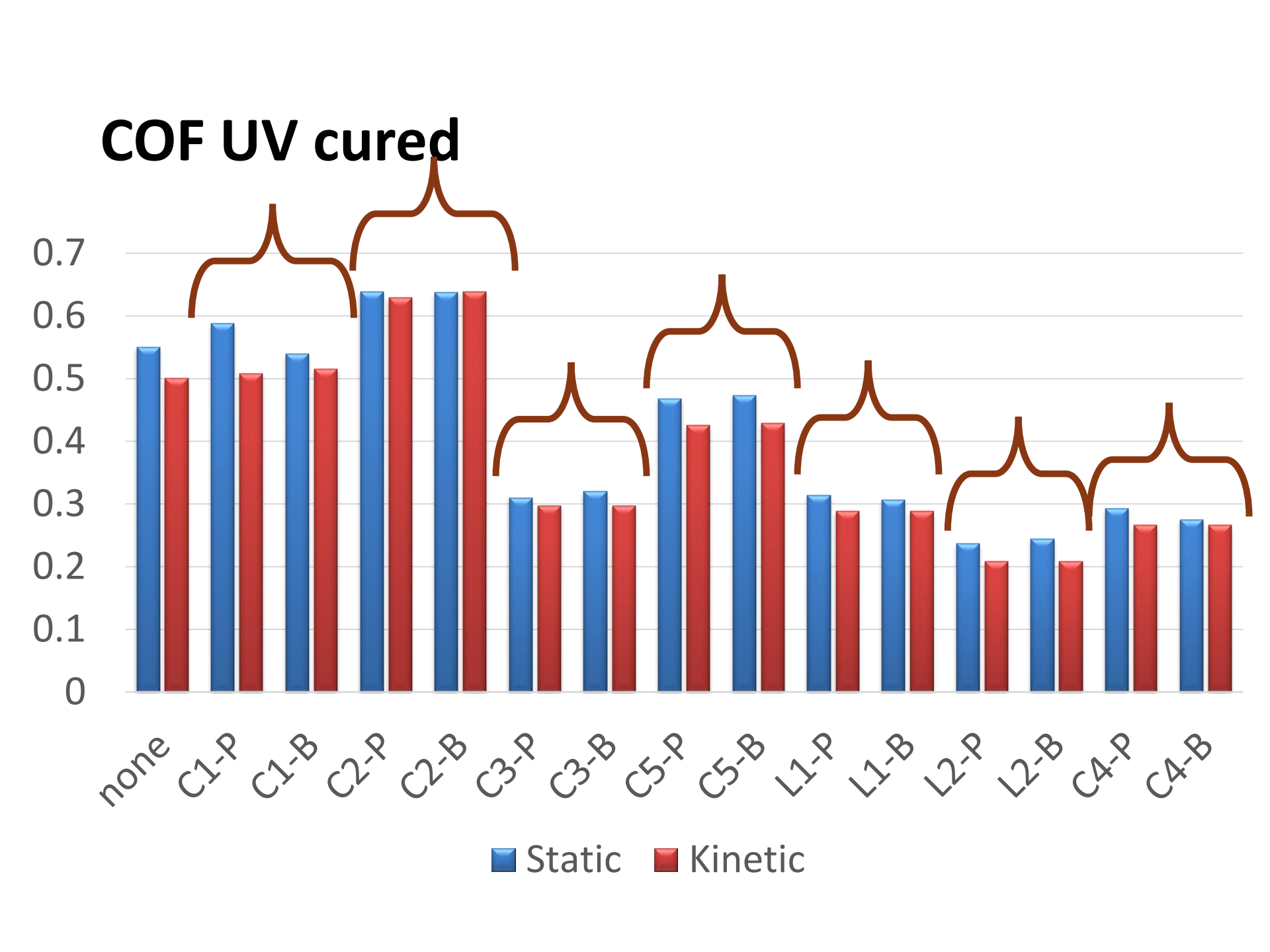

PUD COF
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
none
C1-P
C1-B
C2-P
C2-B
C3-P
C3-B
C5-P
C5-B
L1-P
L1-B
L2-P
L2-B
Static
Kinetic

Coatings Evaluations

0.5% additive in a 1K proprietary UV cured clear varnish based on Epoxy Acrylate resin and reactive diluents.

- Appearance, foam generation, were all good. Differences in COF were seen structure to structure but similar for –P vs. –B trends.


UV resin system
C3-P
C3-B


COF UV cured
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
none
C1-P
C1-B
C2-P
C2-B
C3-P
C3-B
C5-P
C5-B
L1-P
L1-B
L2-P
L2-B
C4-P
C4-B
Static
Kinetic

Conclusions

- There is some bias towards higher viscosity and higher aqueous surface tension with the bio-sourced samples relative to the petroleum sourced samples.
- The bias is consistent within a polyether sample and differing among 8, and 10 EO materials. This perhaps is due to minor differences between the processes of the two suppliers rather than the bio vs. petro-sourcing
- These differences were within lot to lot variation of the commercial histories.
- No significant differences were seen in the coatings or their drawdowns.

Conclusions

Silicone Polyether Derivatives made from newly available bio-sourced EO chain compare favorably to products made from the traditional petro-chemical sources.


Thank
You