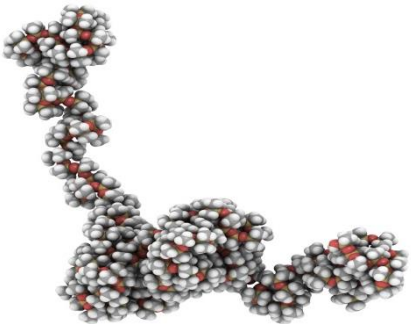


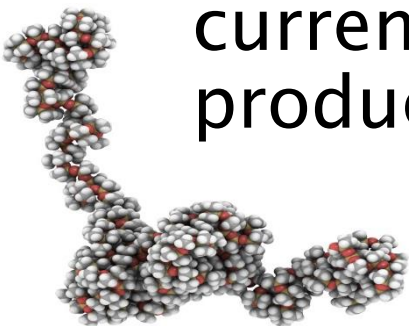
# Regulatory Driven Innovation

Siltech Corporation  
Bob Ruckle, Joel Valencony,  
Steve Wilkowski, Dave Wilson



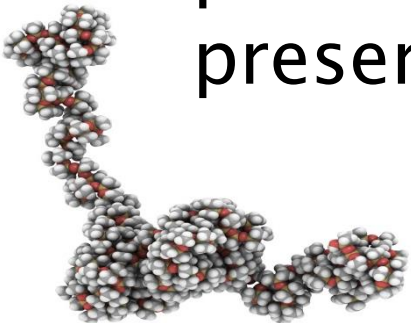
# Reality

- ▶ In today's world, instant communication and a desire to lessen our impact on the environment and society drive regulatory and market changes.
- ▶ Perception is the new reality.
  - Man-made chemicals are guilty until proven Innocent
  - Market perception is as or more important than regulations. It nearly always precedes.
- ▶ Manufacturers scramble to stay ahead of the current hot topics with innovation and new product development.



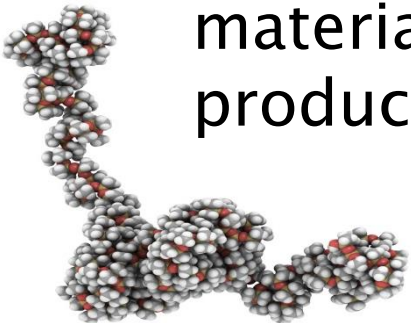
# Overview

- ▶ Green driver has driven us to Silwax D02 which allows bio-oils to replace silicones
- ▶ Perception of toxicity has driven us to APEO and EO free emulsifiers
- ▶ EU and Canadian regulations drive NPE free emulsions
- ▶ Regulation is driving the replacement of parabens and formaldehyde donor based preservatives.



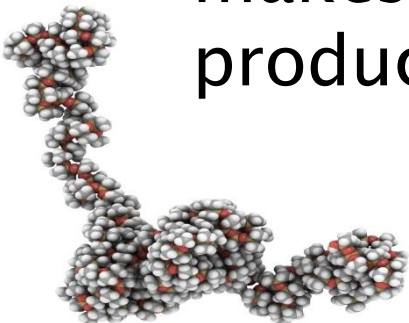
# Overview

- ▶ CARB drives volatiles reduction and additives to allow for solvent free formulations. Also CARB has driven us to aromatic solvent free processes, and changing to acceptable solvents where needed.
- ▶ Perceived toxicity has driven Volatile Silicones (D4/D5) below 0.1%
- ▶ Regulation is driving the replacement of tin as a catalyst
- ▶ US EPA consent order to replace PFOS based materials spurs renewed focus on our Fluorosil products.



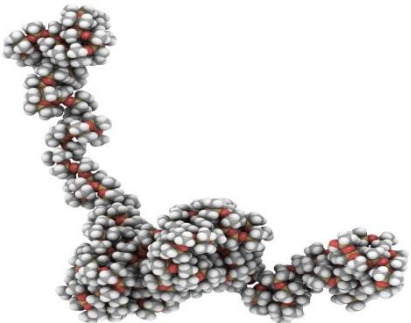
# Green Trend

- ▶ At first not well defined, green in the chemical industry has come to mean non-petroleum, preferably naturally, derived.
- ▶ Silicone itself is derived from silicon – the main component of the earth's crust – and small chemicals, which are currently petroleum derived.
- ▶ As long as we use petroleum for fuel sources, it makes practical sense to use the available by-products rather than waste them.



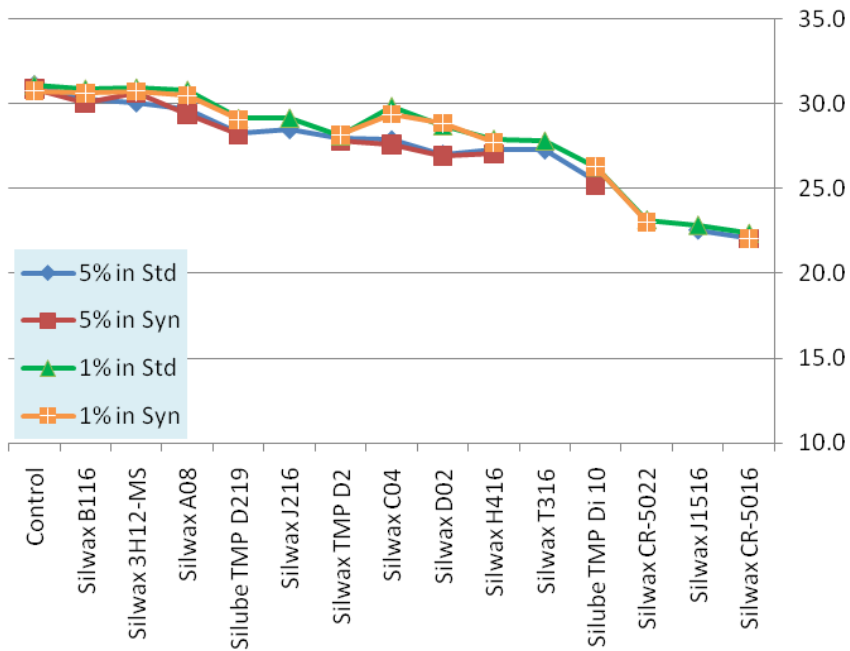
# Green Trend

- ▶ However, there is a market need for more natural products.
- ▶ Siltech has a variety of products based on castor oil, aliphatic hydrocarbon and essential oils.
- ▶ Silwax D02 was developed to enable botanical oils to replace silicone oil in personal care lotions and creams.

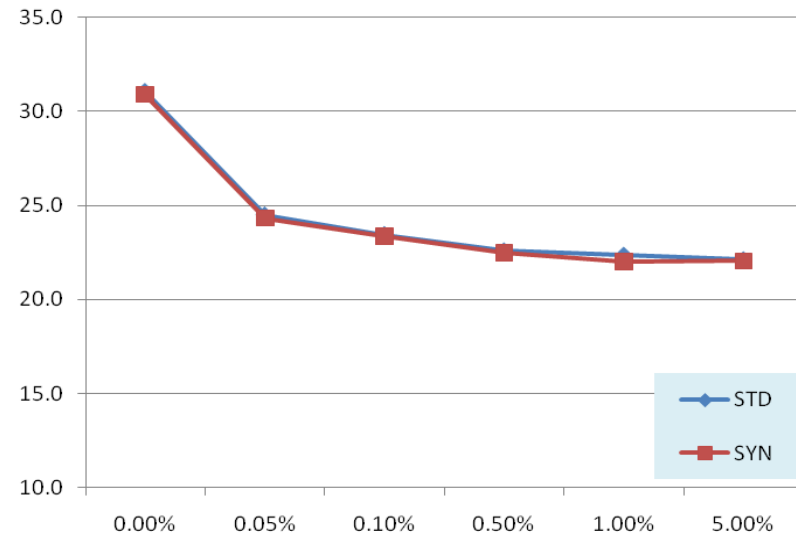


# Surface Tension (ST) Reduction in Motor Oil

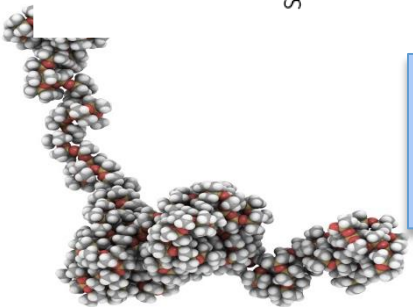
ST of Various Silicones in Standard and Synthetic 10W-30 Motor Oil



ST of Silwax CR-5016 in Motor Oil at 0-5%

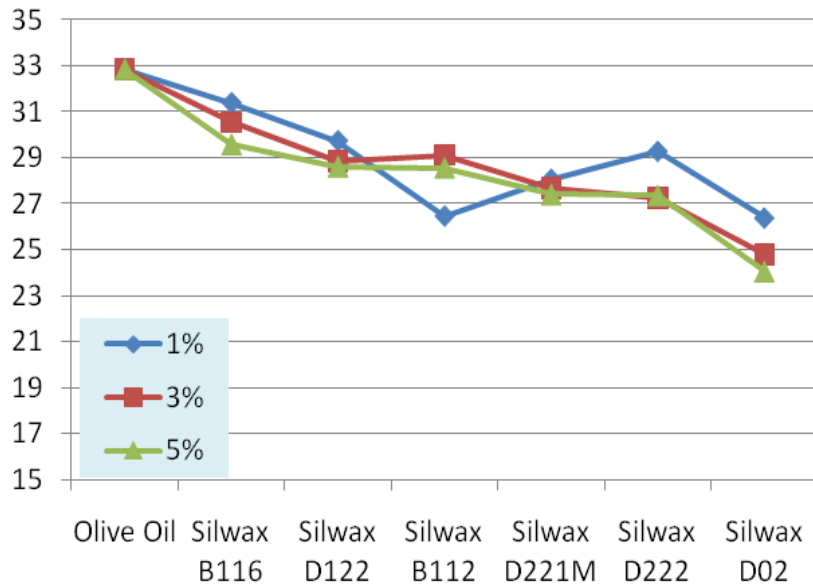


With a small amount of the right Silwax® or Silube® product, one can cause motor oil to have a surface tension close to that of silicone oil



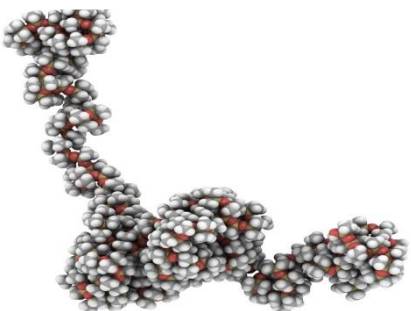
# Surface Tension Reduction in non-Petroleum Oils and Solvents

ST of Various Silicones at 1,3,5% in Olive Oil



	pure	w/ 0.5% silicone	Silicone
Toluene	28.9	25.0	Silwax D026
2-butoxy ethanol	29.1	22.0	Silwax C18
methanol	23.4	22.2	Silube C8 PEG-8
isopropanol	21.7	20.5	Silsurf A008
motor oil	31.0	22.6	Silwax CR-5016
Siltech F350	20.0	NA	

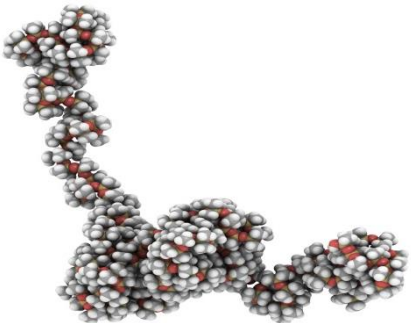
In general:  
 Silwax® CR-5016 good for petroleum oils  
 Silwax D02 good for ester type oils  
 Silwax D026 is also good sometimes





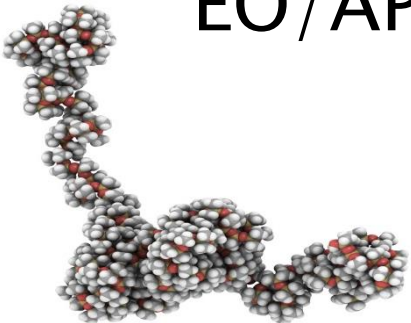
# NPE Free

- ▶ EU and Canadian regulations have driven NPE free emulsions, now becoming law in the US as well.
- ▶ Being a Canadian manufacturer, Siltech has never used NPE emulsifiers and rely on linear alcohol ethoxylates and silicone emulsifiers to stabilize our emulsions.

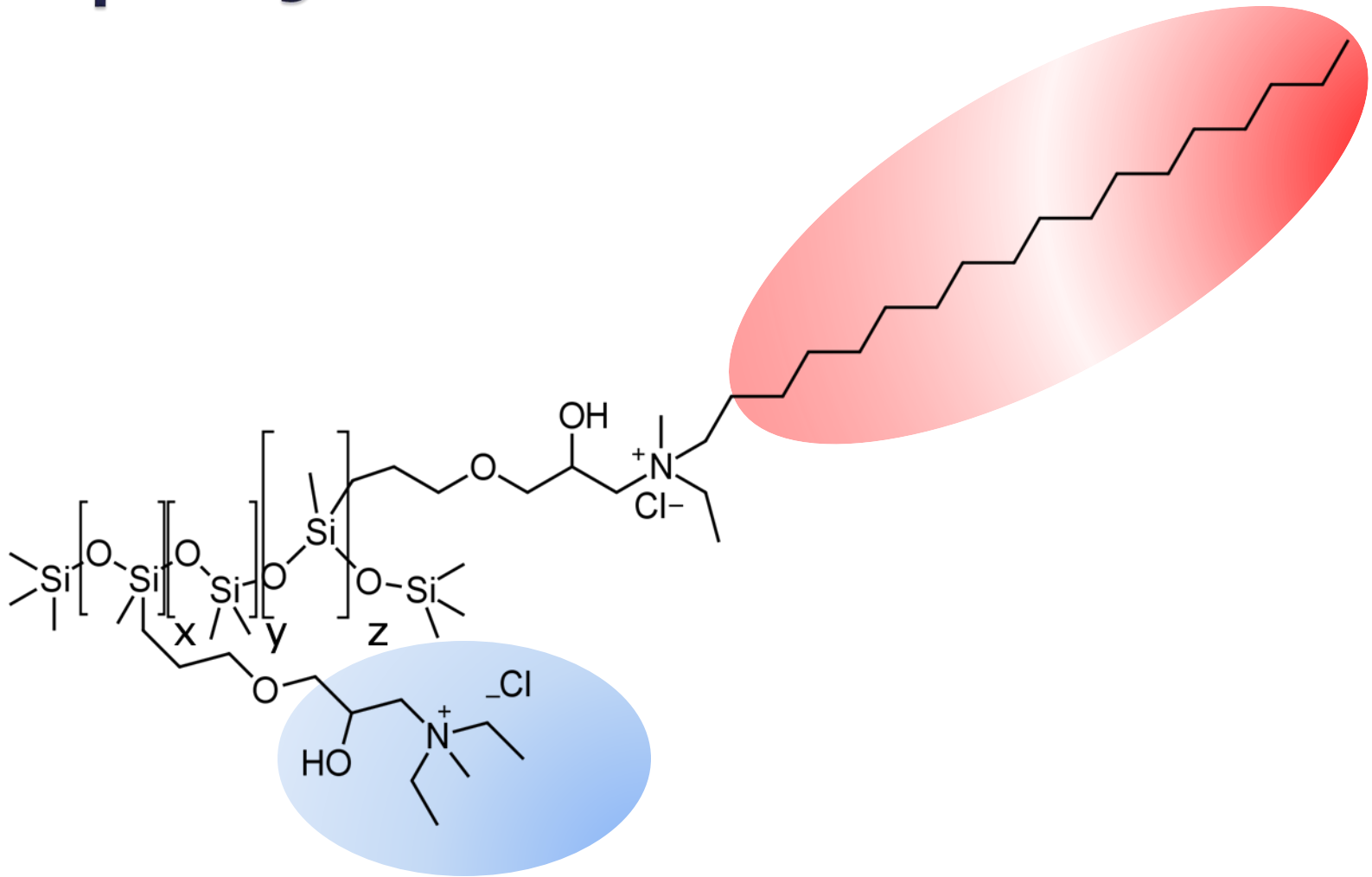


# APEO and EO free surfactants

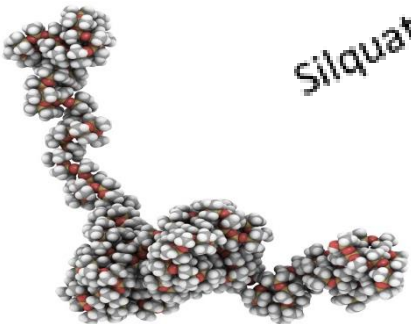
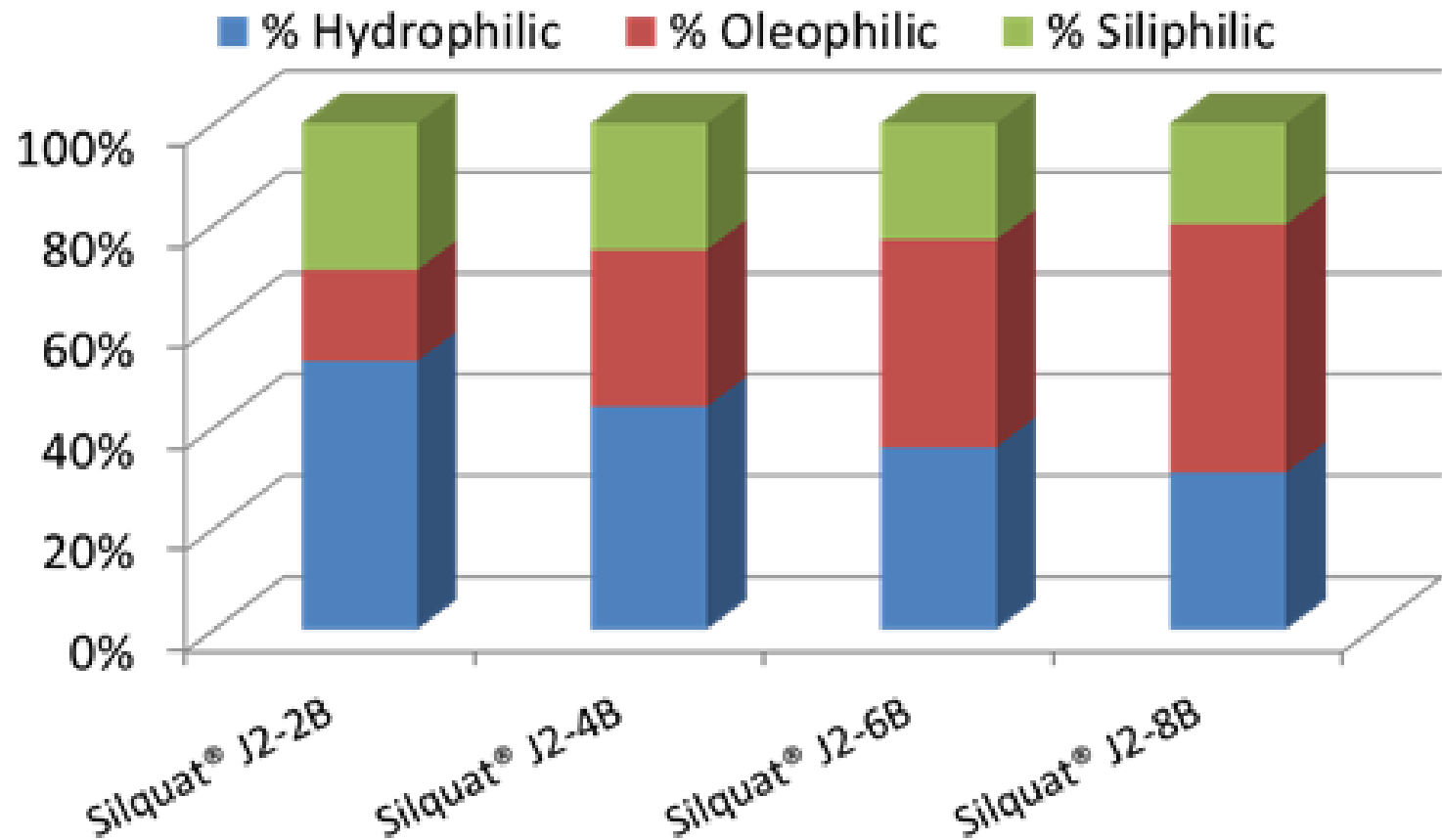
- ▶ There is a market driver for allyl ethoxylate free surfactants due to believed toxicity of these materials. Also for non-ethoxylate hydrophiles.
- ▶ Siltech have recently developed a series of quaternary ammonium silicone -based emulsifier which have no EO. These materials are excellent emulsifiers, EO/APEO free and multi-functional.



# Silquat J2-xB series

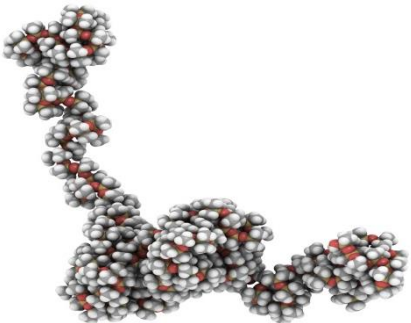


# Silquat J2-xB series



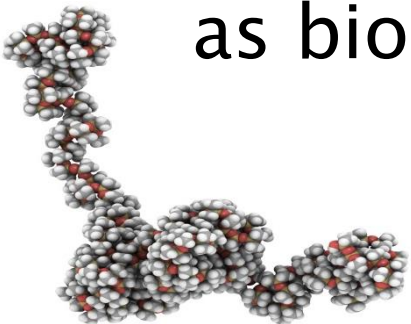
# Excellent EO Free O/W Emulsifiers

Product	Emulsion Type	HLB	Viscosity	Shear needed	Processing Temperature	Applications					Secondary Benefits				
						Make Up	Sun Care	Skin Care	Hair Care	Hydroalcoholic Emulsion	Ease of application	water resistance	Lubricity and Release	Pigment dispersion	Sensory Claims
Silquat J2-2B	O/W	11	7000	H	H	Y			Y	Y					
Silquat J2-4B	O/W	9	7500	H	H	Y	Y	Y	Y	Y					rich non-greasy,
Silquat J2-6B	O/W	7	7500	H	H	Y	Y	Y	Y	Y					luxurious, very soft,
Silquat J2-8B	O/W	5	6700	H	H	Y	Y	Y	Y	Y	Y	Y	Y		smooth powdery feel



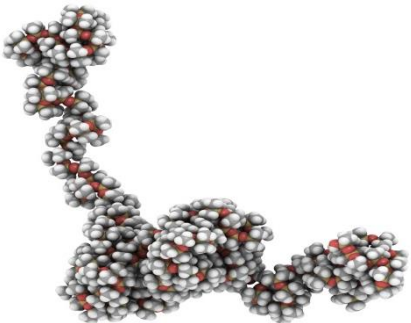
# Biocide Aversion

- ▶ Biocides are implicated in a variety of human maladies and some have been limited or ruled out, particularly in the EU.
- ▶ Siltech uses pH and other alternative biostats when possible and constantly assesses the available biocide options for our emulsion products.
- ▶ We are assessing the quaternary emulsifiers as biostats



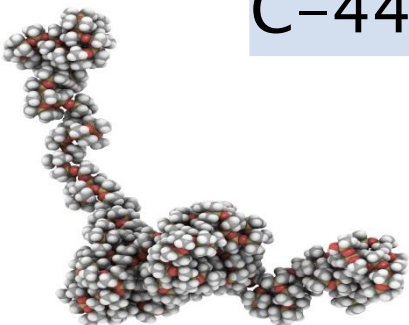
# EU anti-Sn Sentiment

- ▶ EU concerns against tin (Sn) catalysts commonly used in many emulsions and other condensation reacted silicones.
- ▶ Siltech is actively looking at titanium based and other catalysts as well as systems that don't need to be catalyzed.



# Emulsion Properties

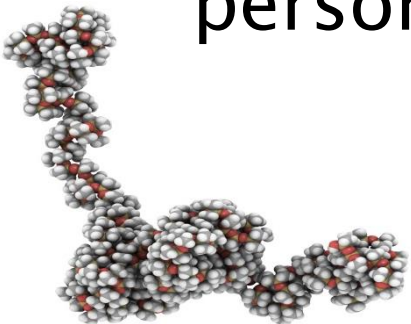
Siltech	Emulsifier Type	Biocide Type	Cross-linker
E-600	LAE	none	none
E-660	LAE	none	none
E-2140	LAE	none	Sn
E-2145	LAE	none	Sn
E-3050	LAE	none	none
E-3132	LAE	none	none
C-4405	LAE	none	Sn
C-4425	LAE	none	none
C-4435	LAE	none	none





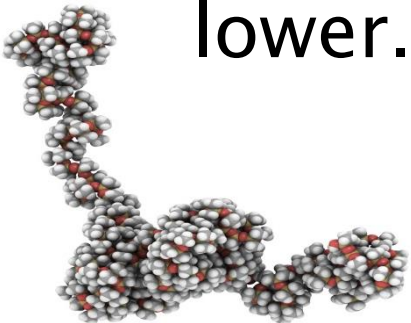
# Volatile Silicones

- ▶ An unprecedented level of toxicological testing and scrutiny was given to silicones after the US breast implant litigations of 1990's and concurrent FDA actions.
  - In 2013, with all of the data in, FDA again allowed silicone gel implants.
- ▶ Some early testing results led to concern over volatile silicones D<sub>4</sub>/D<sub>5</sub> especially in personal care products.



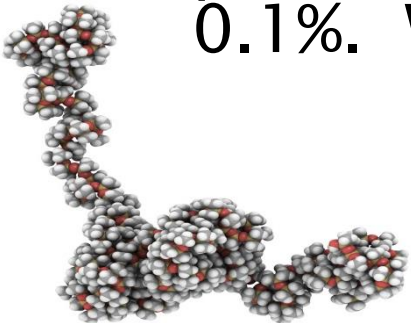
# Volatile Silicones

- ▶ Canadian concerns over environmental fate caused consideration of limits on  $D_4/D_5$ .
- ▶ Although few current regulations require this, Siltech has responded to the market need for low VS content silicones.
- ▶ Siltech have installed a state of the art WFE and procedures to routinely drive volatile levels below 0.1%. Where needed we can go lower.



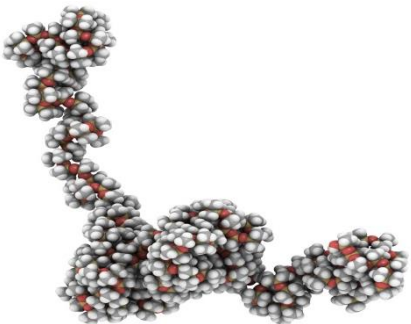
# Other Volatiles

- ▶ Early CARB regulations led the way for current regulations against volatile organic compounds in multiple geographies and end uses.
- ▶ Siltech has developed a series of organomodified silicones to enable the effective use of waterborne and other non- or low-VOC systems.
- ▶ Siltech have eliminated aromatic solvents from our processes and routinely change out solvents to acceptable alternatives as more is learned.
- ▶ Siltech have installed a state of the art WFE and procedures to routinely drive volatile levels below 0.1%. Where needed we can go lower.

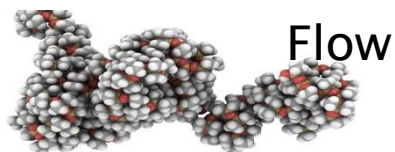
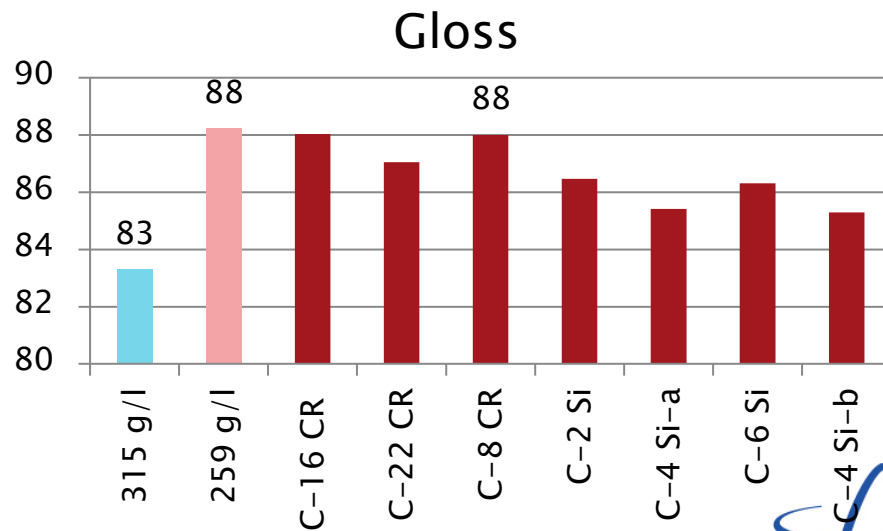
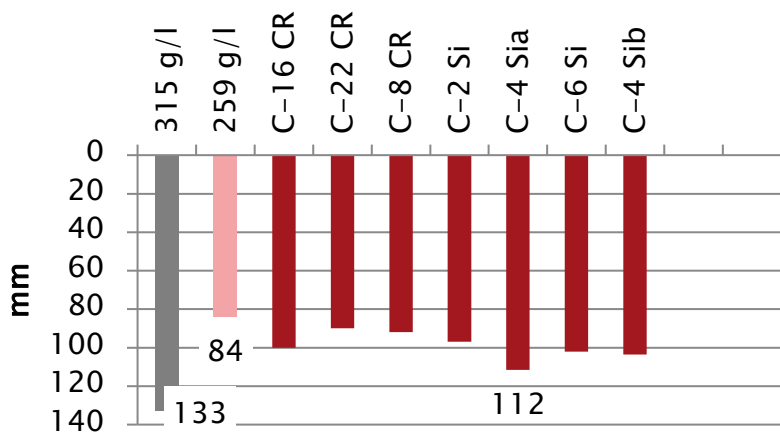
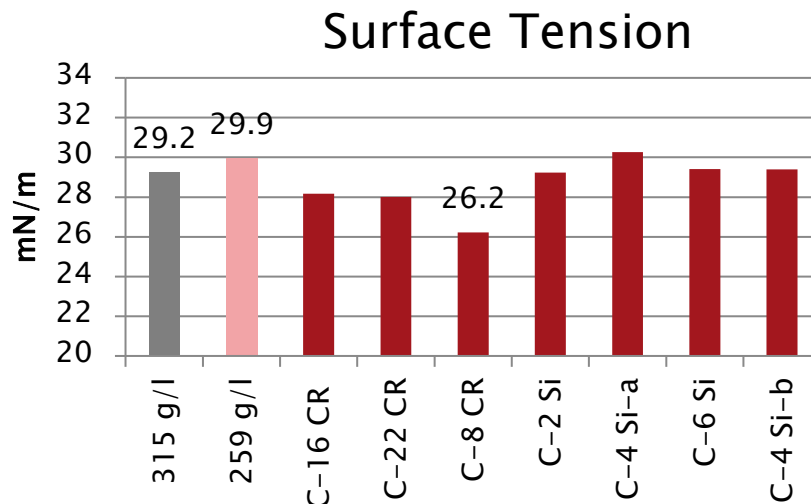
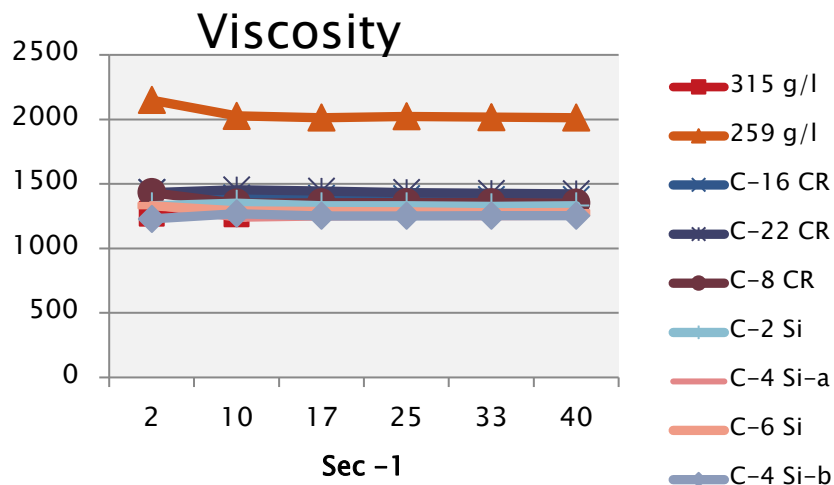


# Solvent borne surface tension agents to reduce VOC's in a black enamel formula

	High Solids	Higher Solids	Results
High Solids Alkyd Resin	39.53%	42.75%	Appear.
Glycol Ether/Solvent Mix	28.35%	22.51%	
Special Black 4A	13.95%	15.09%	S.T.
Filler Blend	16.61%	17.96%	
Siltech Additives	0%	0 or 0.5%	Visc.
Anti-settling Agent	S.Q.	S.Q.	
Dispersing Agent	S.Q.	S.Q.	Flow
Dryer blend	S.Q.	S.Q.	
Stabilizer	S.Q.	S.Q.	Gloss
Anti-skinning Agent	S.Q.	S.Q.	
VOC	315 g/l	259 g/l	Abr. Resist.
Solid	60%	65%	

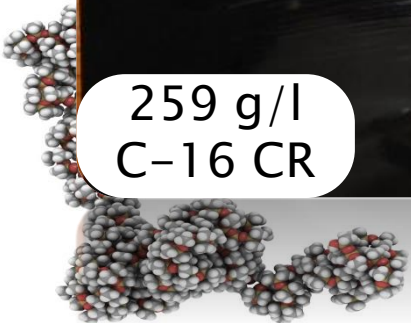
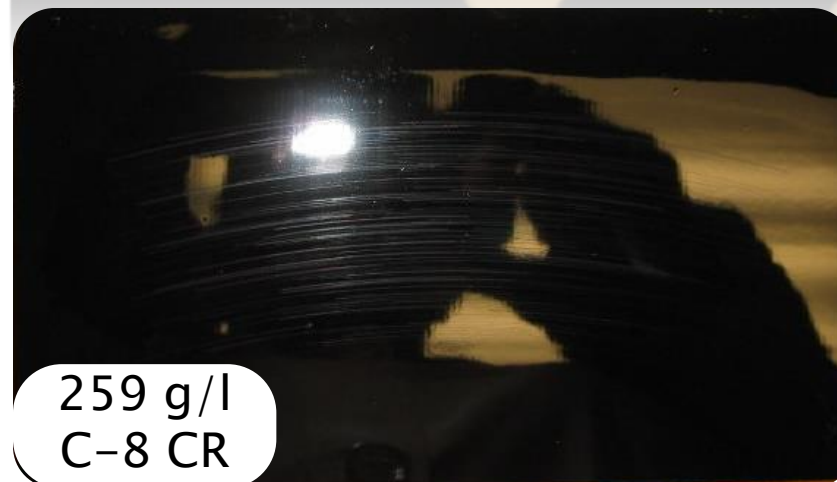
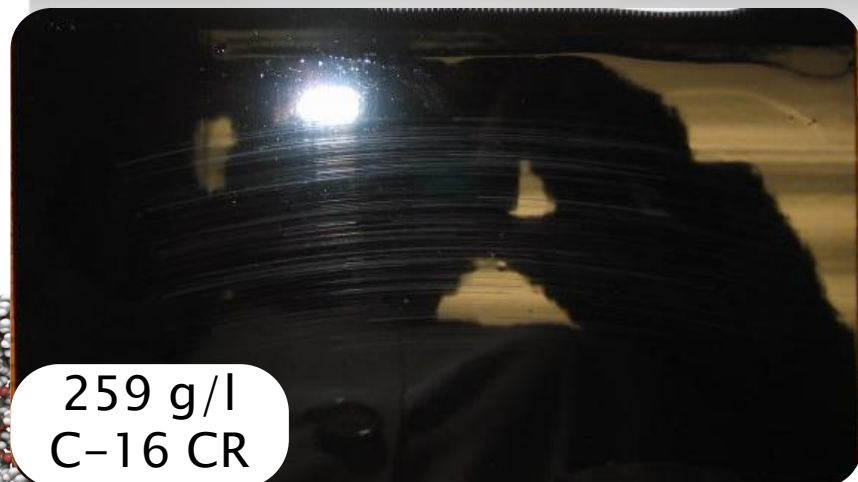
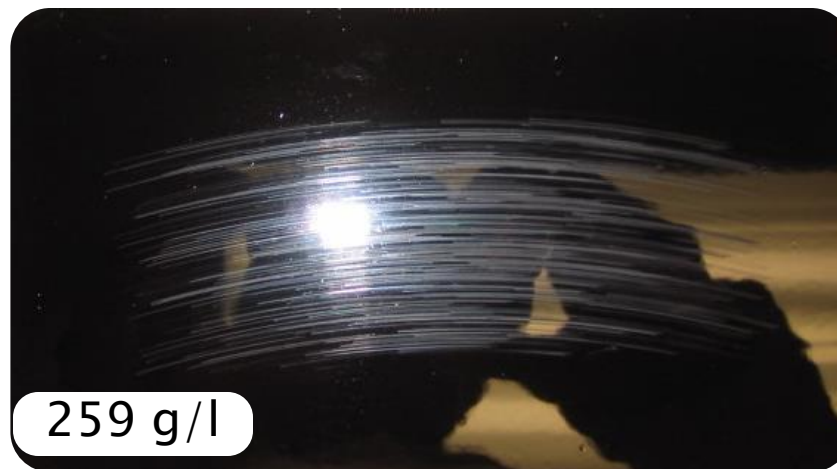
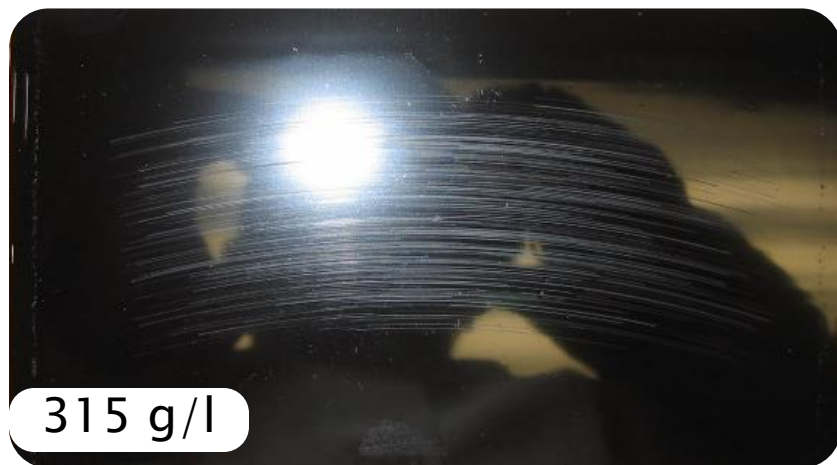


# Properties with alkyl silicones



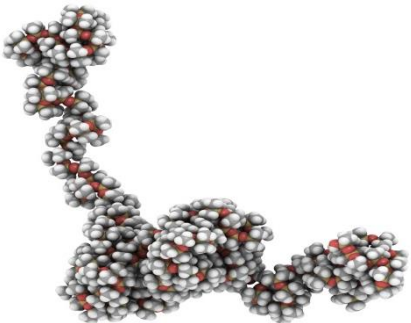
# Black Enamel

Visual

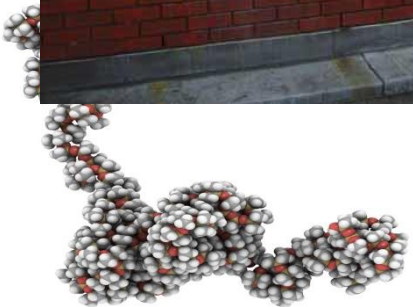


# Non-PFOS stain resistance

- ▶ US EPA consent order to replace PFOS based products spurs renewed focus on our Fluorosil  $C_6H_4F_9$  materials.
- ▶ Besides the inherently safer lower chain length fluoroalkyl group used, we believe there is a synergy between the silicone and fluoroalkyl groups that lower the fluoroalkyl usage level.



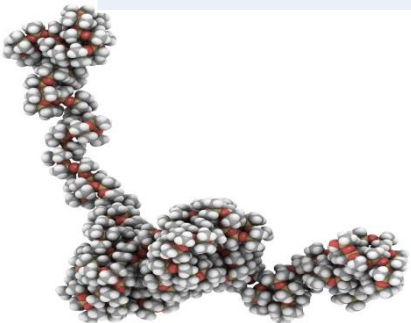
# Challenges from Staining, Fouling, Graffiti, Fingerprints, Chemicals....





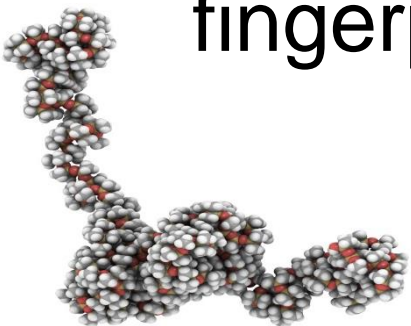
# Comparison of Selected Properties of Silicone and Fluoropolymer

Silicone	Fluoropolymer
✓ Low surface energy	✓ Very low surface energy
✓ Very good thermal flexibility	✓ Marginal thermal flexibility
✓ Good chemical resistance	✓ Very good chemical resistance
✓ Marginal oil resistance–swelling	✓ Very good oil resistance
✓ Very good water resistance	✓ Good water resistance
✓ Marginal abrasion resistance	✓ Low abrasion resistance
✓ High cost (\$/lb.)	✓ Very high cost (\$/lb.)
✓ Effective at low use levels	✓ Effective at low use levels



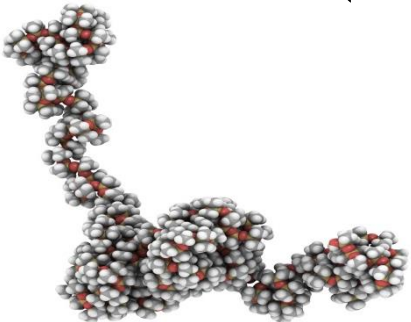
# Experimental Design and Methods:

- ▶ The overall design used five systems:
  - *SB 2k Urethane*
  - *UV cured urethane acrylate*
  - *UV cured epoxy acrylate*
  - *Cationic UV cured epoxy silicone (in handouts only)*
  - *Commercial flat white paint (post addition)*
- ▶ Various silicones are evaluated for slip, COF, defects and mar, stain, and fingerprint and chemical resistance.

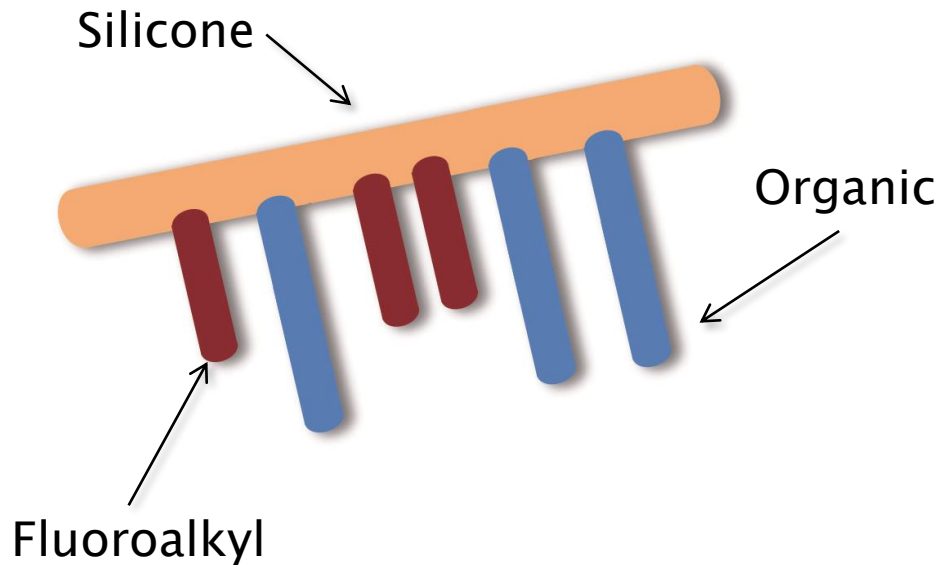


# Test Methods Utilized

- ▶ ASTM D543 (chemical resistance)
- ▶ ASTM D870 (water absorption)
- ▶ ASTM D1308 (chemical resistance)
- ▶ CoF (sled method)
- ▶ Gloss (gloss meter)
- ▶ Fingerprint (internal test method)
- ▶ Stain (variations on standard and internal test methods)



# Fluoroalkyl Silicone Variants



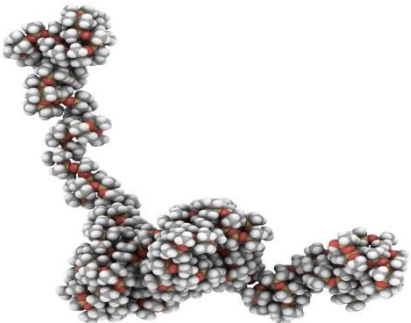
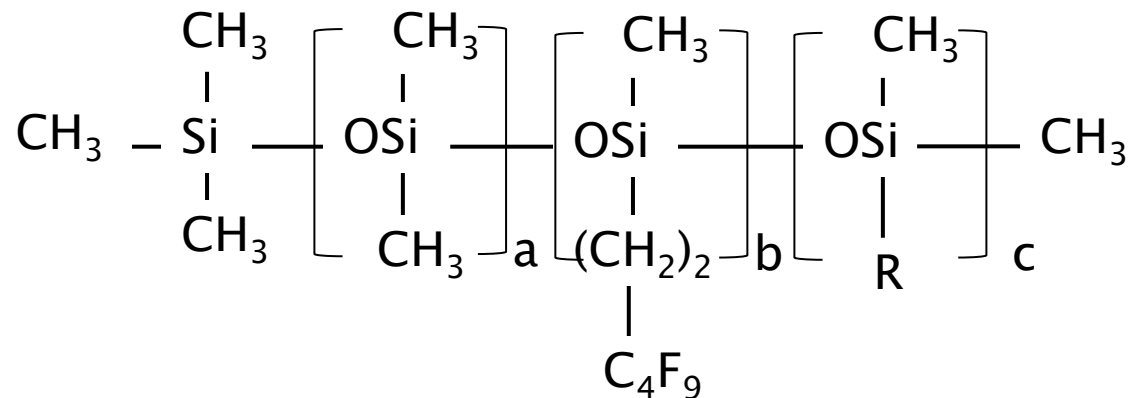
- Silicone provides slip, surface tension reduction, mar resistance, hydrophobicity.
- Fluoroalkyl provides oleophobicity, stain and chemical resistance
- Organic provides miscibility

By varying the number, length and type of fluoroalkyl and/or organic substituents covalently bound to the silicone we can control properties.



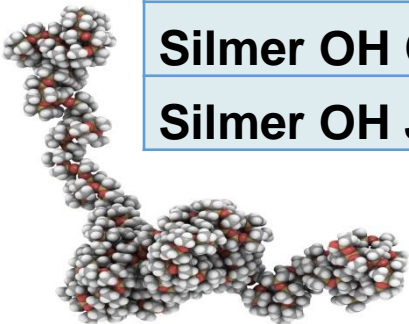
# Fluoroalkyl Silicone Variants

	c	b	R
FPE	>0	>0	$(\text{CH}_2)_3(\text{OC}_2\text{H}_4)_d(\text{OC}_3\text{H}_6)_e \text{OH}$
FS	0	>0	n/a
AF	>0	>0	$\text{C}_n\text{H}(2_n) \text{R}'$ (R = acrylate, etc.)
AS	>0	0	$\text{C}_n\text{H}(2_n) \text{R}'$ (R = acrylate, etc.)



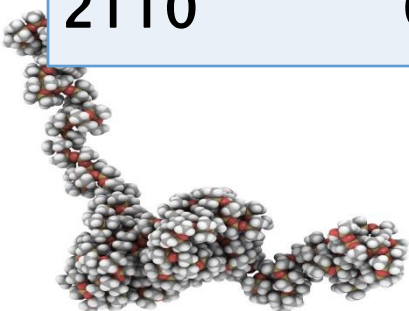
# Details On Copolymer Design

Fluorosil	Wt % Silicone	Wt % CF <sub>2</sub>	Wt % organic	Reactive Site	Water Miscible	MW	Type
<b>2010</b>	L	L	H	OH	1%	3000	fluoroalkyl polyether silicone
<b>2110</b>	L	L	H	OH	10%	7000	
<b>D2</b>	M	H	0%	no	no	2000	fluoroalkyl silicone
<b>J15</b>	H	M	0%	no	no	14000	
<b>OH G2-F</b>	H	L	M	OH	no	3000	alkyl, fluoroalkyl silicone
<b>OH E3.5-F</b>	M	M	L	OH	no	2000	
<b>ACR/OH C7-F</b>	H	L	L	ACR	no	2000	
<b>H418</b>	M	M	M	no	no	5000	
<b>Silmer OH C50</b>	VH	0%	L	OH	no	12000	alkyl silicone
<b>Silmer OH J10</b>	H	0%	M	OH	no	8000	

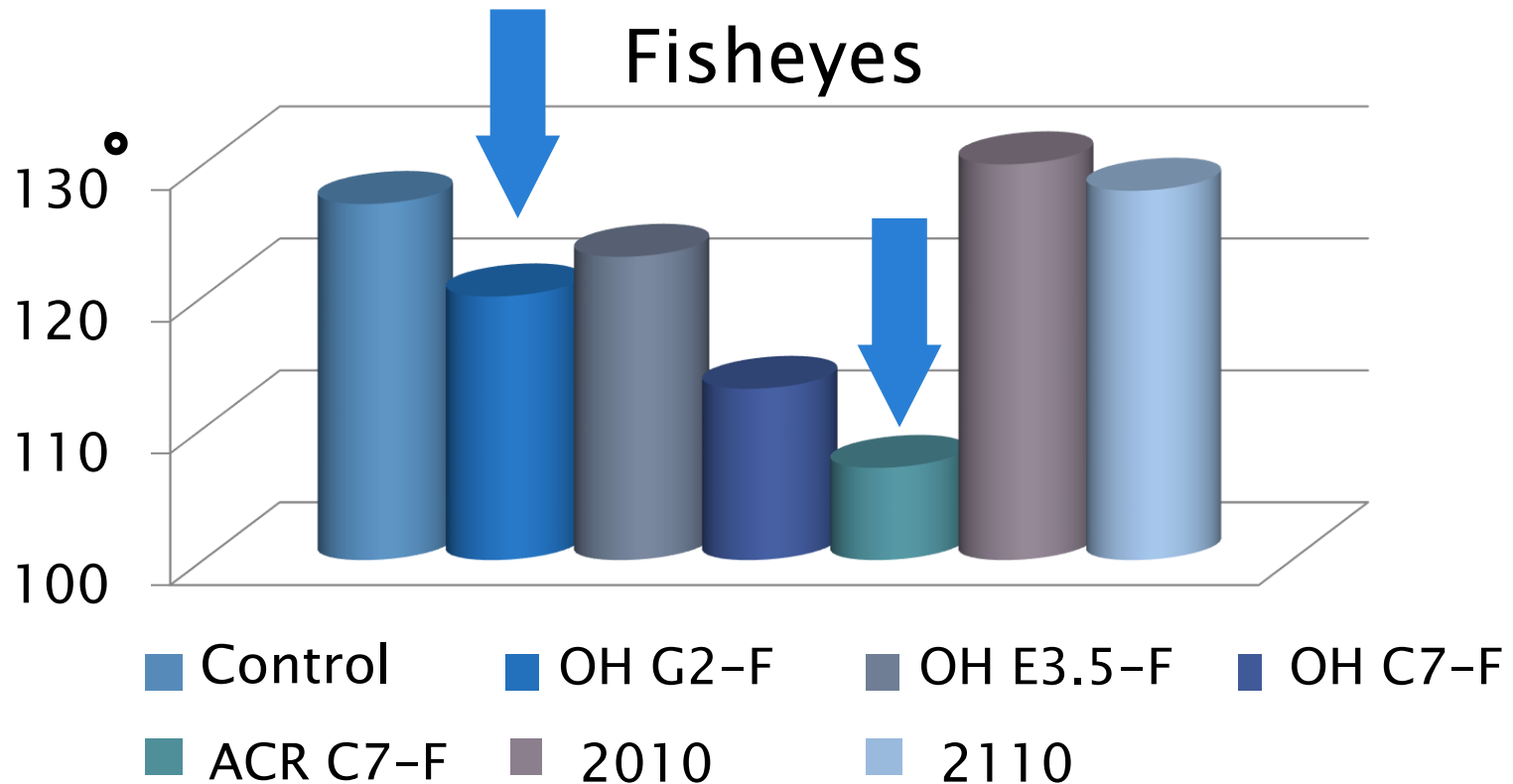


# Film Properties: SB Urethane

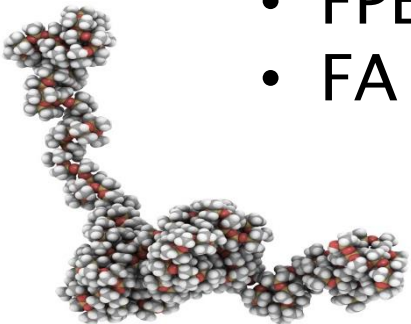
	Static COF	Kinetic COF	Gloss	%Gloss Retained	Mar Resist	Surface appearance
Control	1.397	1.500	127	77.2%	1.1	Smooth
OH G2-F	1.274	1.204	120	95.0%	6.4	Fisheyes
OH E3.5-F	0.940	1.115	123	86.2%	4.3	Smooth
OH C7-F	0.794	0.756	113	87.1%	4.3	Smooth
ACR C7-F	0.405	0.422	107	93.1%	6.4	Fisheyes
2010	0.577	0.631	130	96.7%	6.4	Smooth
2110	0.681	0.711	128	96.4%	6.4	Smooth



# Gloss: SB Urethane

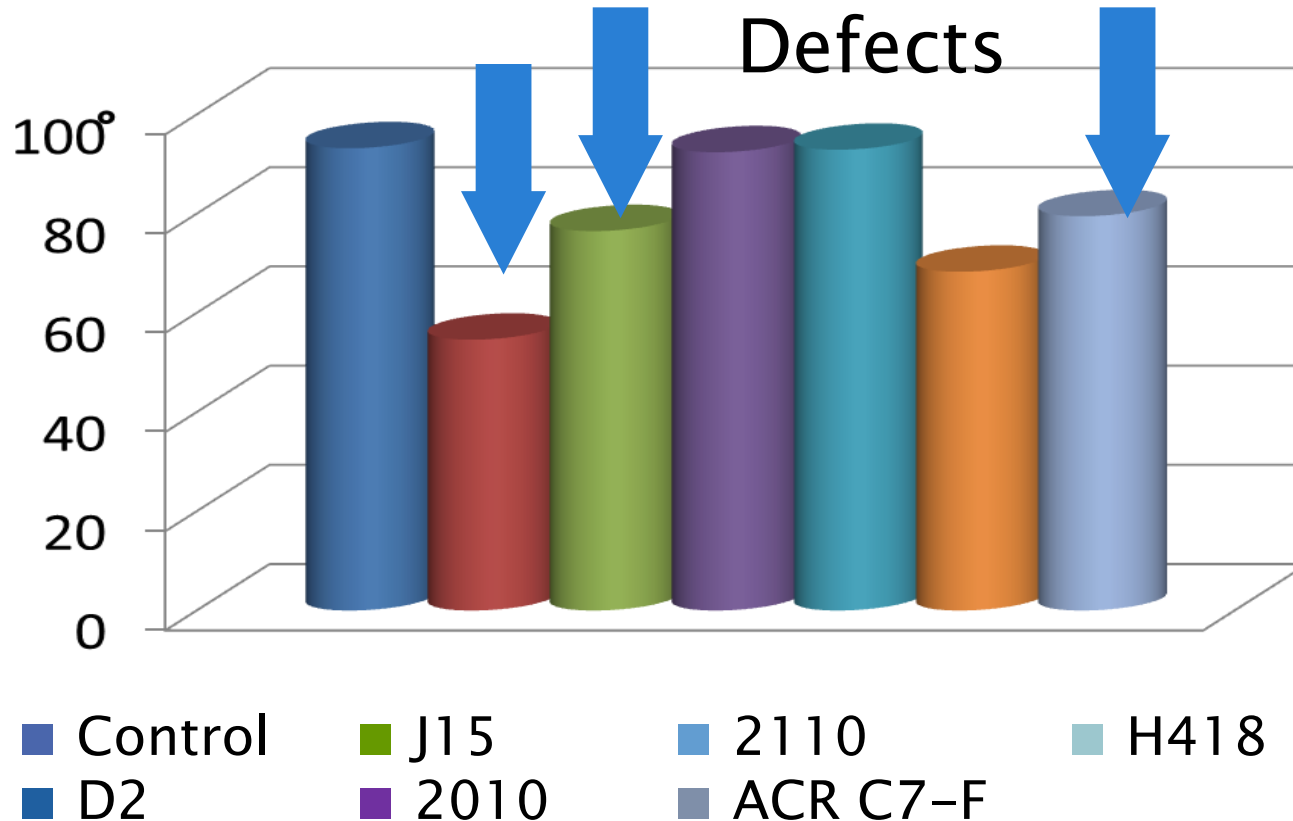


- FPE are most miscible, improve gloss
- FA type decrease gloss cause defects

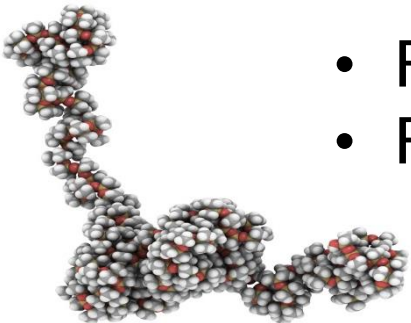




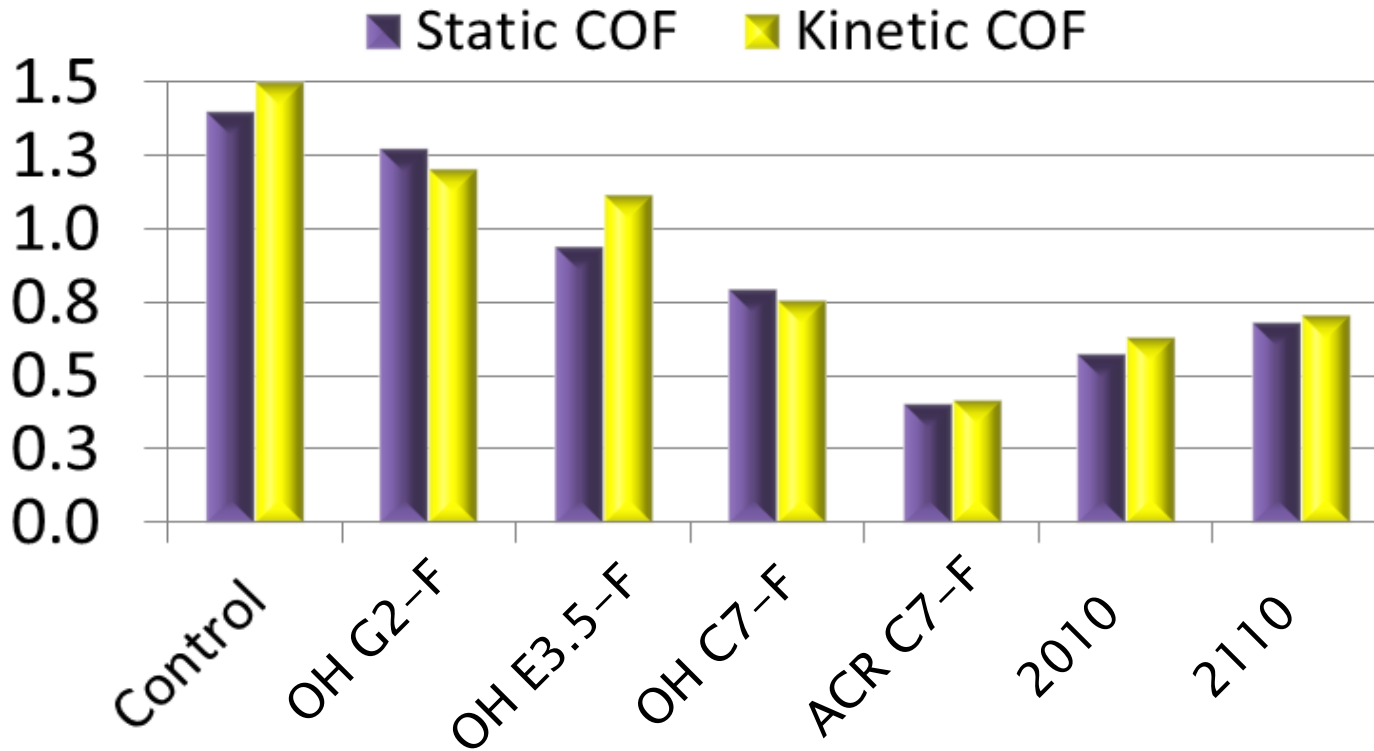
# Gloss: Urethane Acrylate



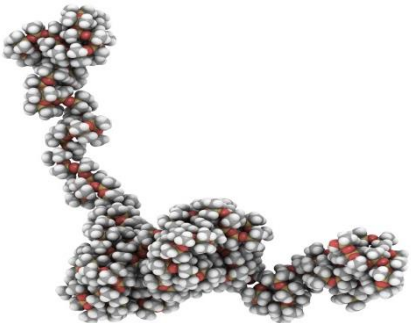
- FPE are most miscible, keep gloss
- FA and FS types decrease gloss



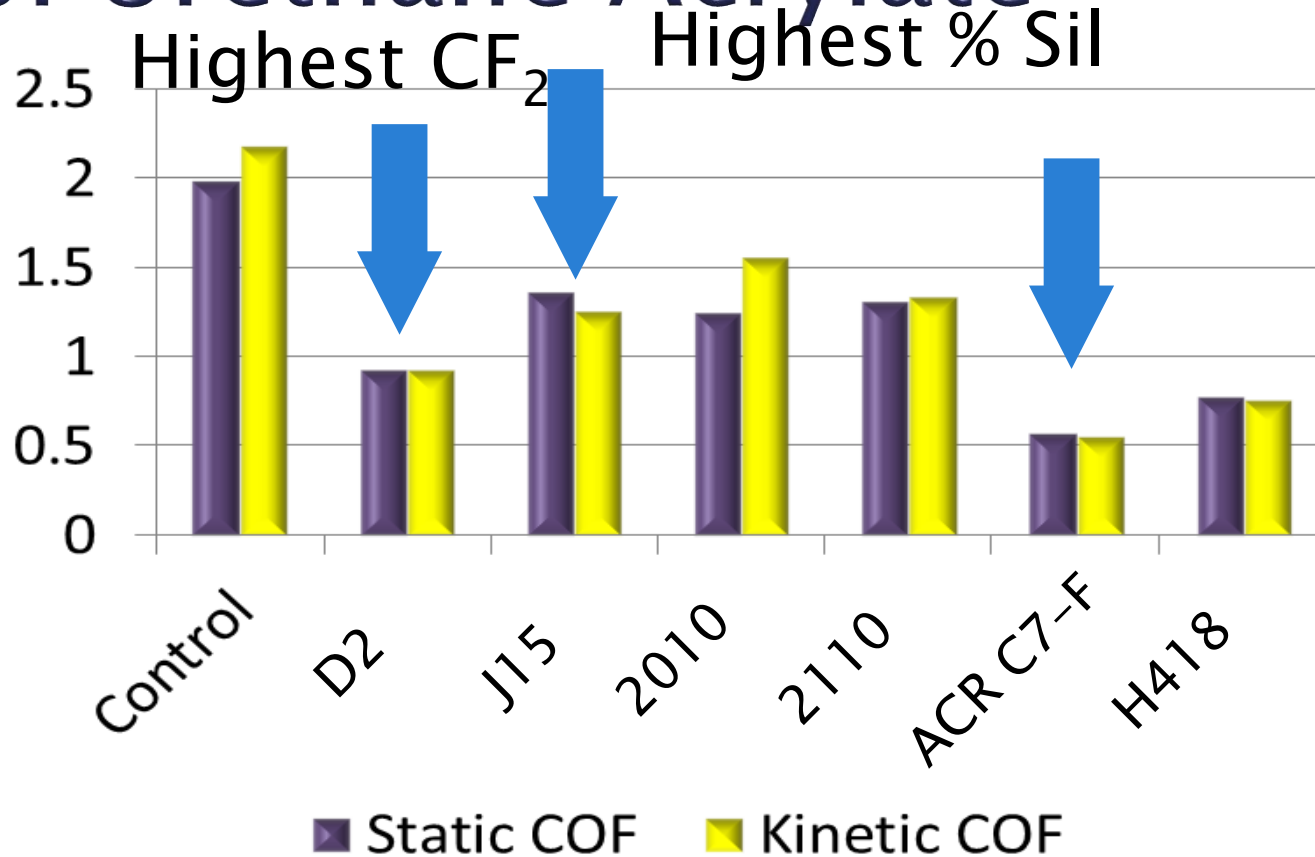
# Slip: SB Urethane



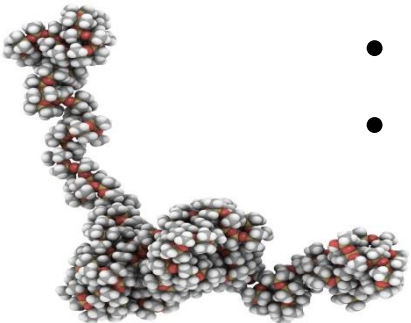
- All improve COF
- C7-F structures are best
- ACR better than OH



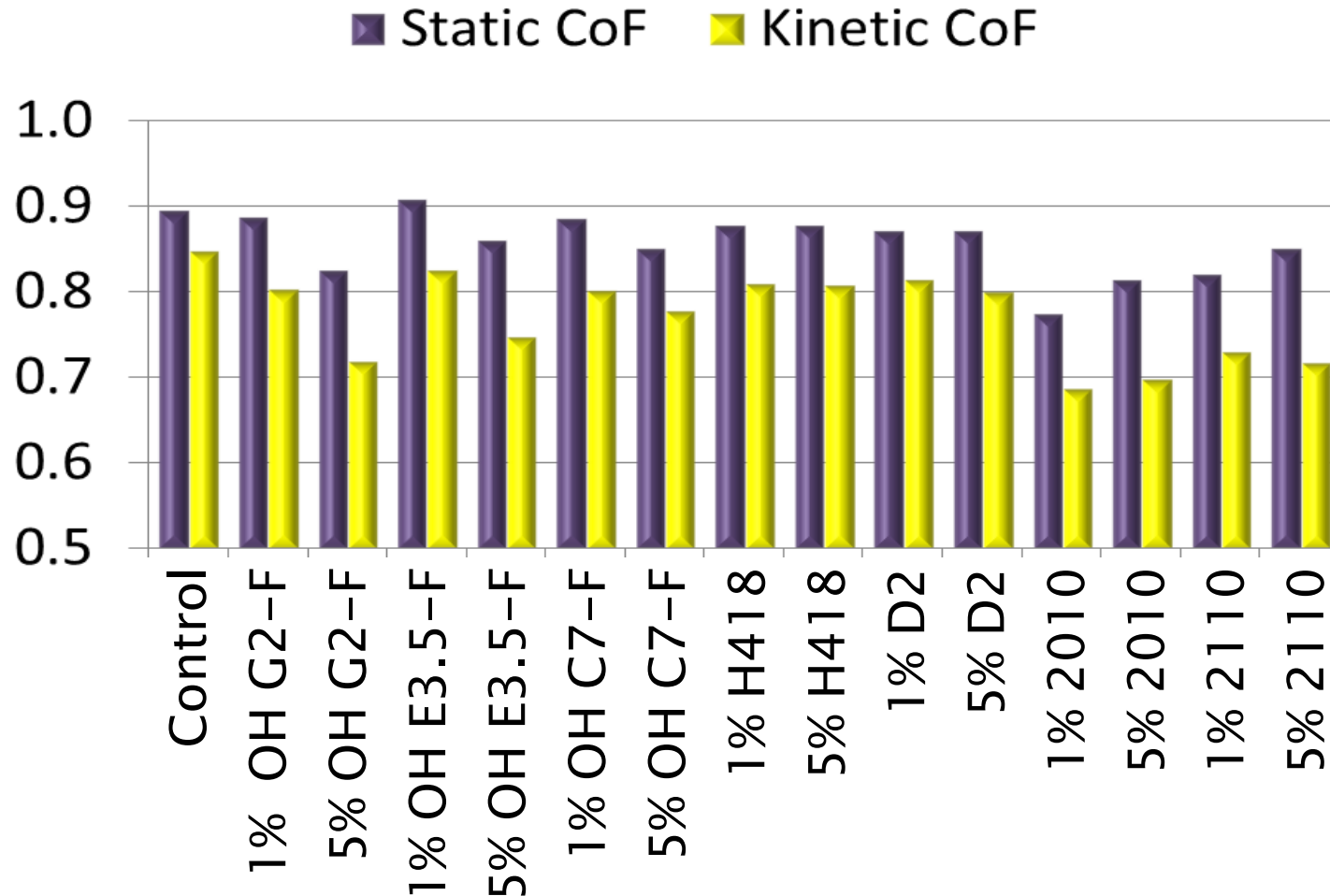
# Slip: Urethane Acrylate



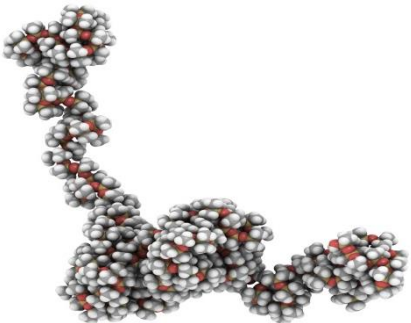
- All improve COF
- Again C7-F is best



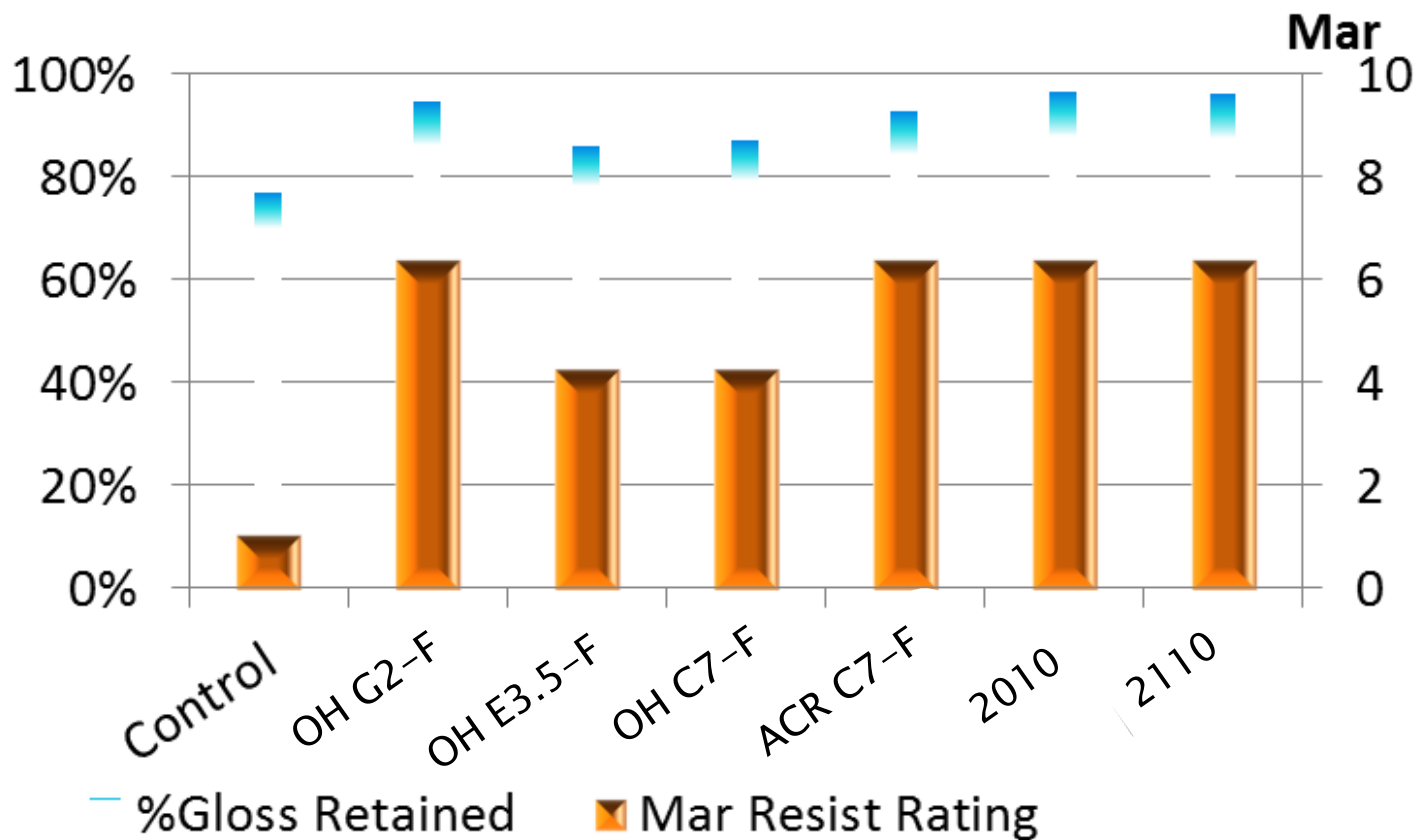
# Slip: Post add



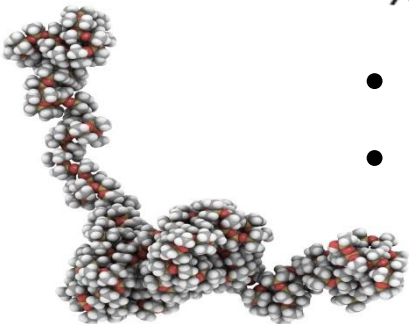
- All improve COF, more at 5%
- FPEs are very good



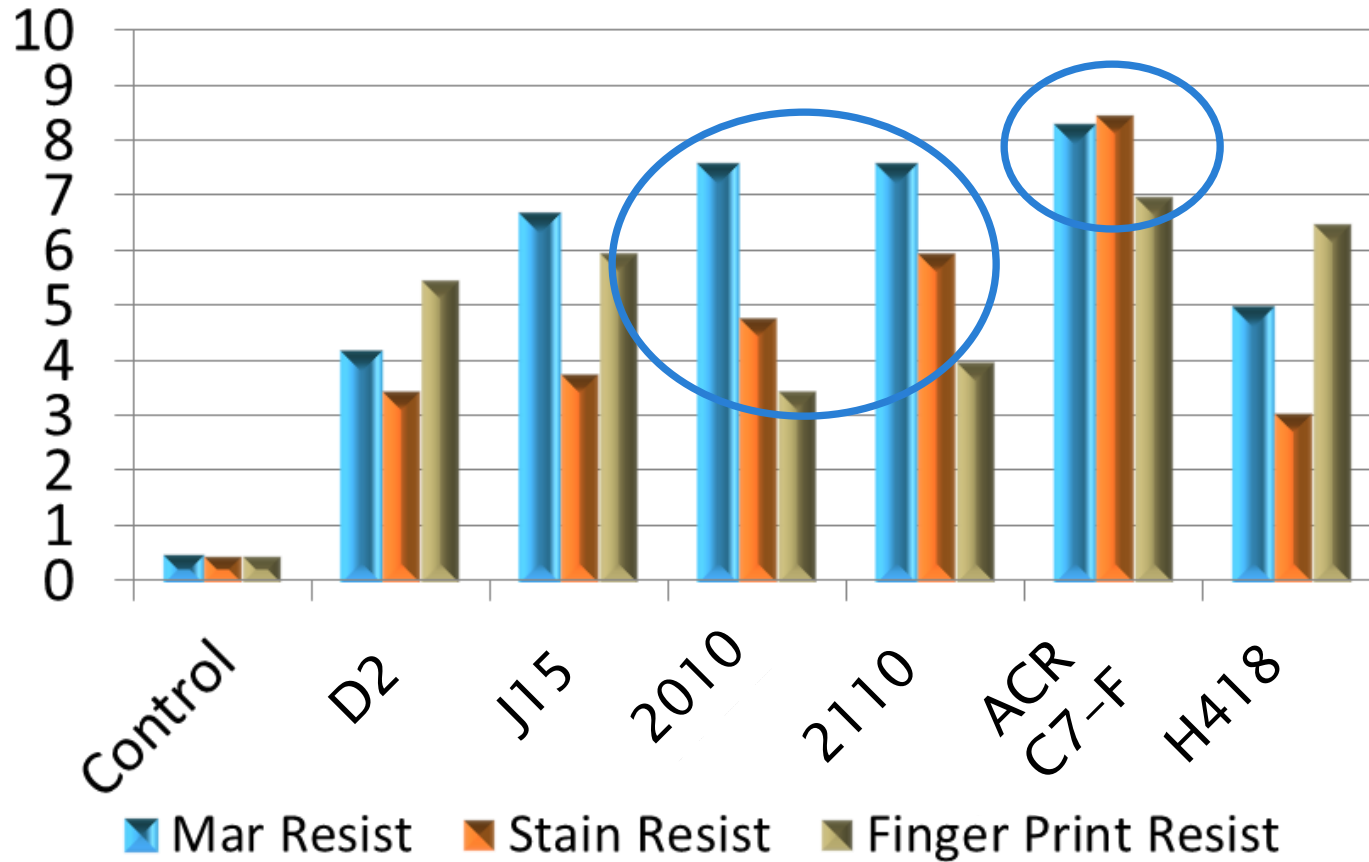
# Mar Resist: SB Urethane



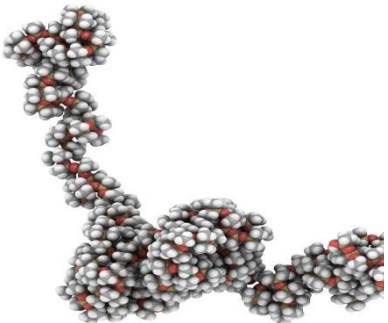
- All improve mar resistance
- FPE are better than expected



# Mar, Stain, Print: UV Epoxy Acrylate



- All are improved over control
- The high %CF<sub>2</sub> Fluorosil D2 is not best
- FPEs are weak on fingerprint
- ACR C7-F strong on all

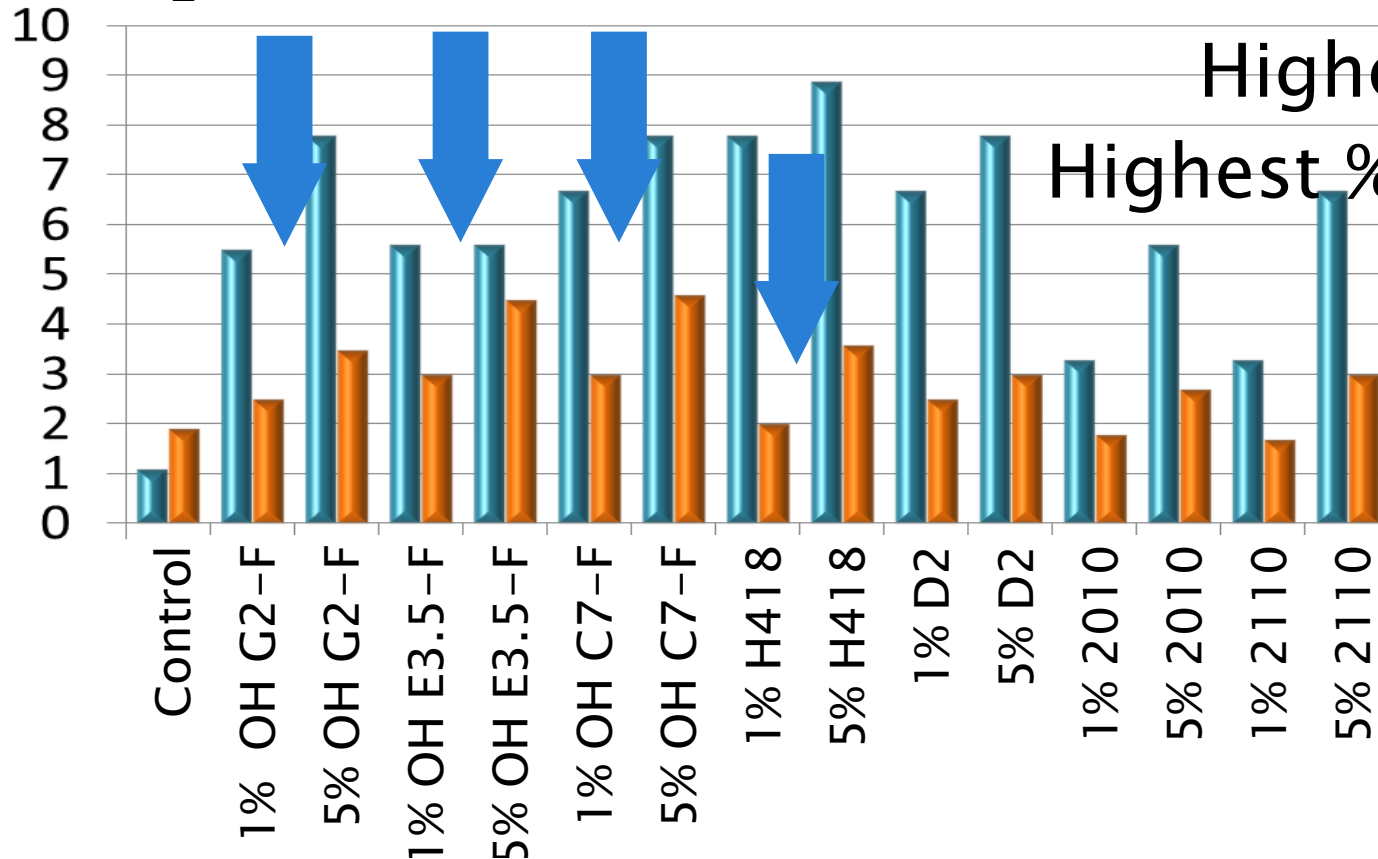


# Mar and Stain: post add

Highest  $CF_2$

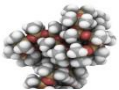
■ Mar Resistance

■ Stain Resistance



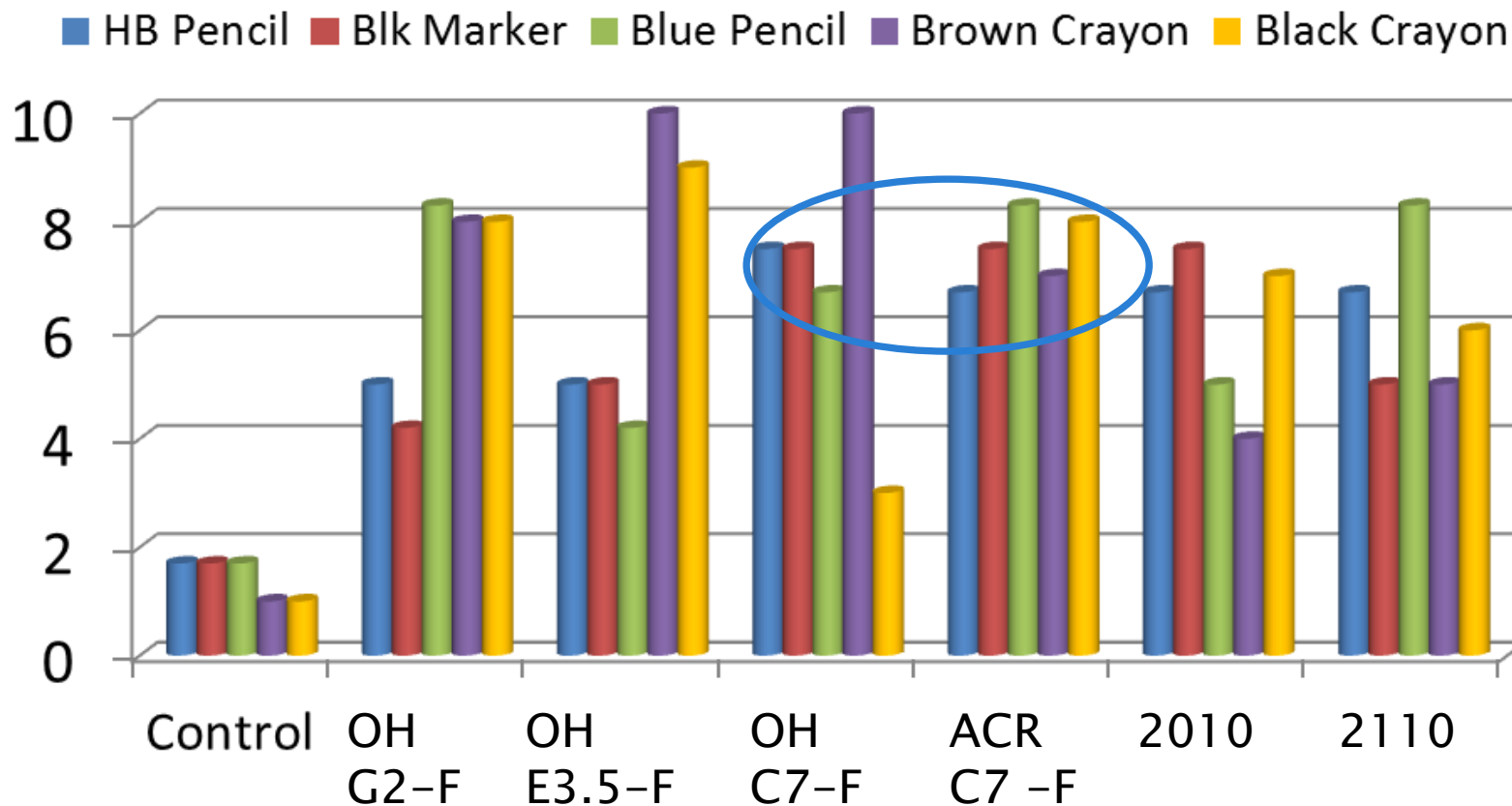
Highest % Sil

Highest %  $CH_2$

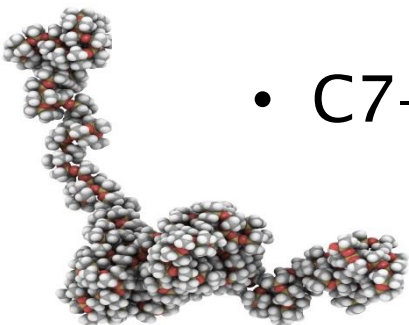


- All improve mar resistance/ more at 5%
- Both % $CF_2$  and %Sil help
- Lesser improvement in stain/ 5% better

# Stain Resist: SB Urethane

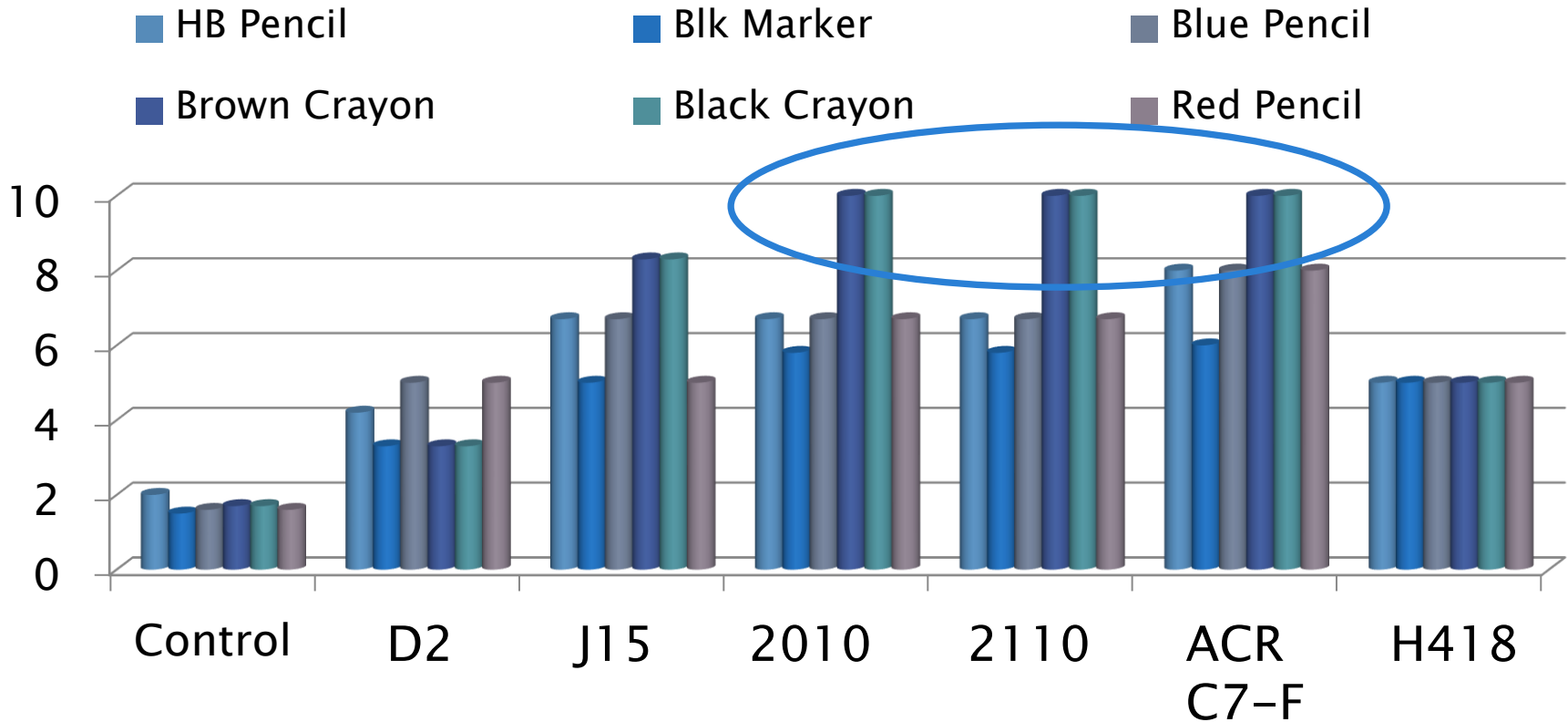


- C7-F structures again perform well

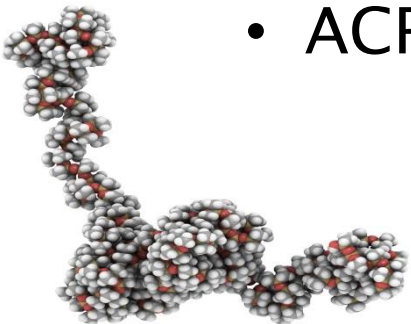




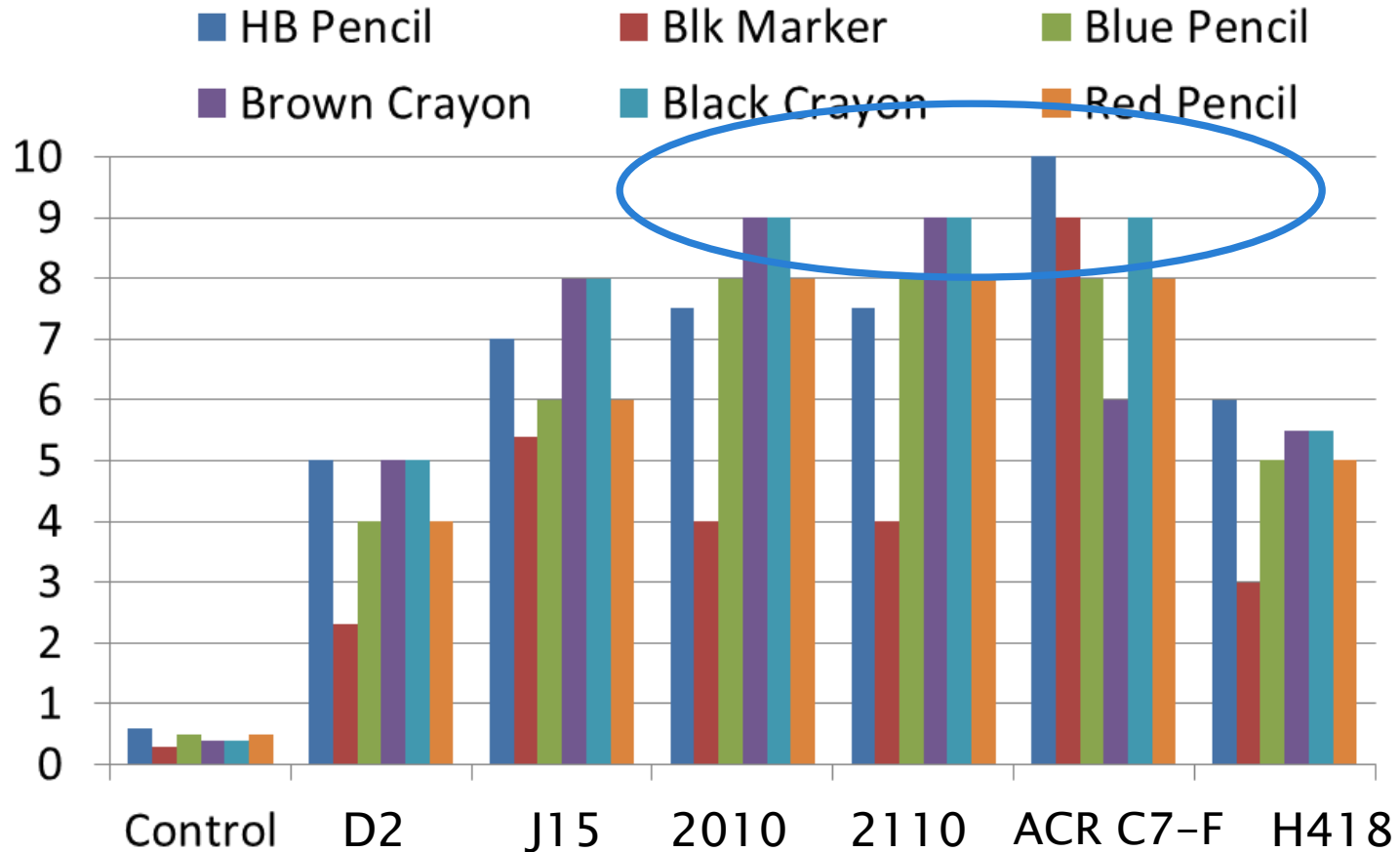
# Stain Resist: Urethane Acrylate



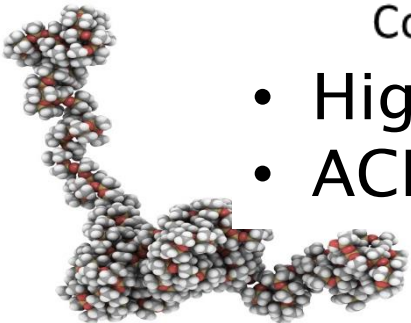
- ACR C7-F and FPEs are effective



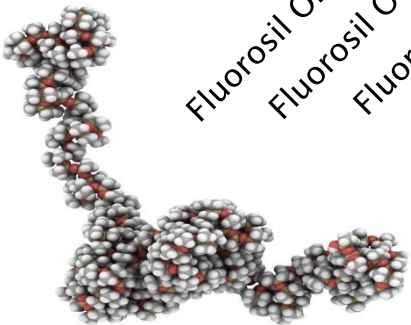
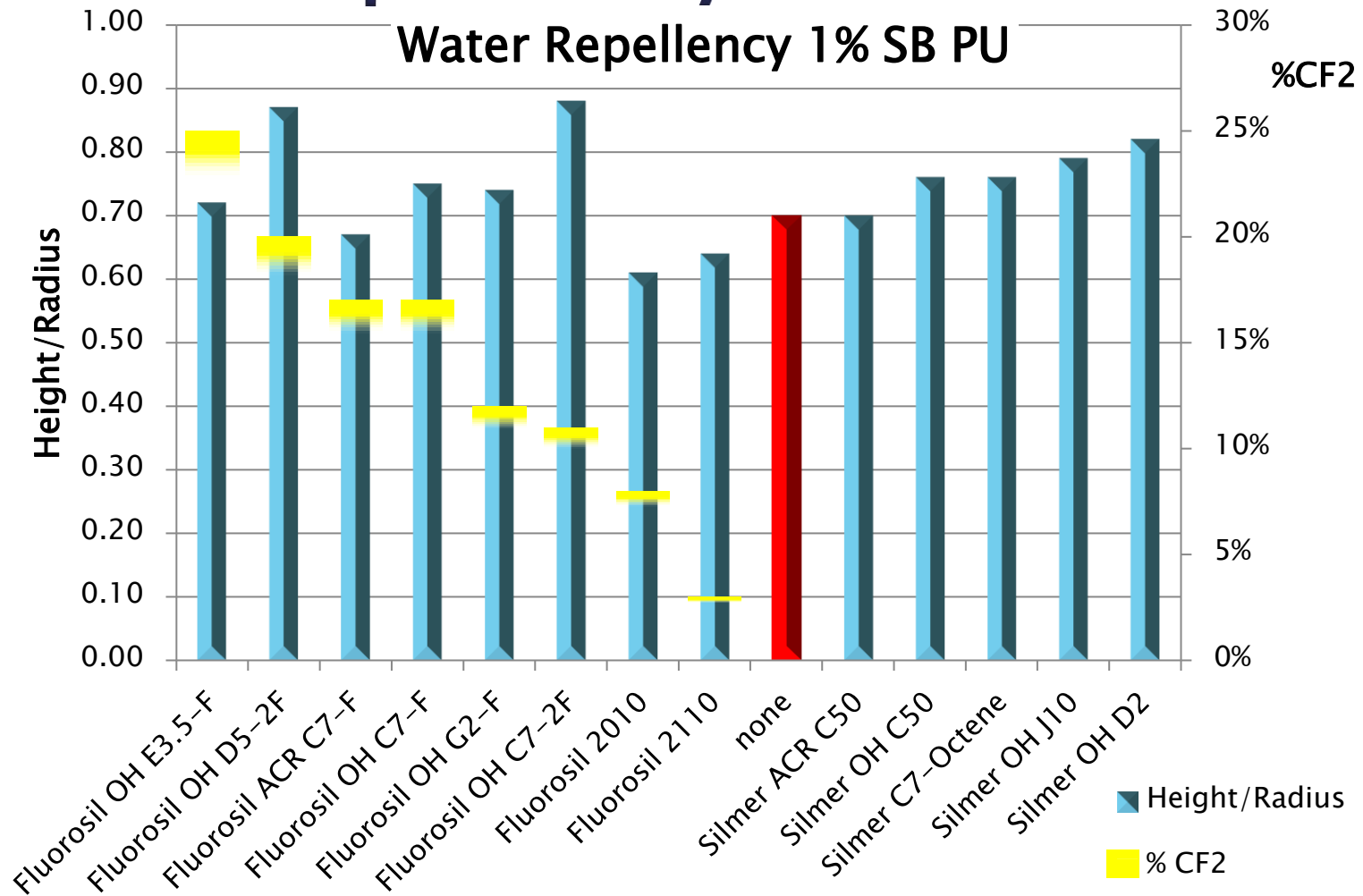
# Stain: UV Epoxy Acrylate



- Highest %CF<sub>2</sub> is least effective
- ACR C7-F and FPEs are effective



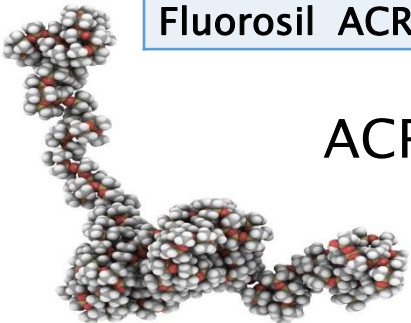
# Water Repellency: SB Urethane



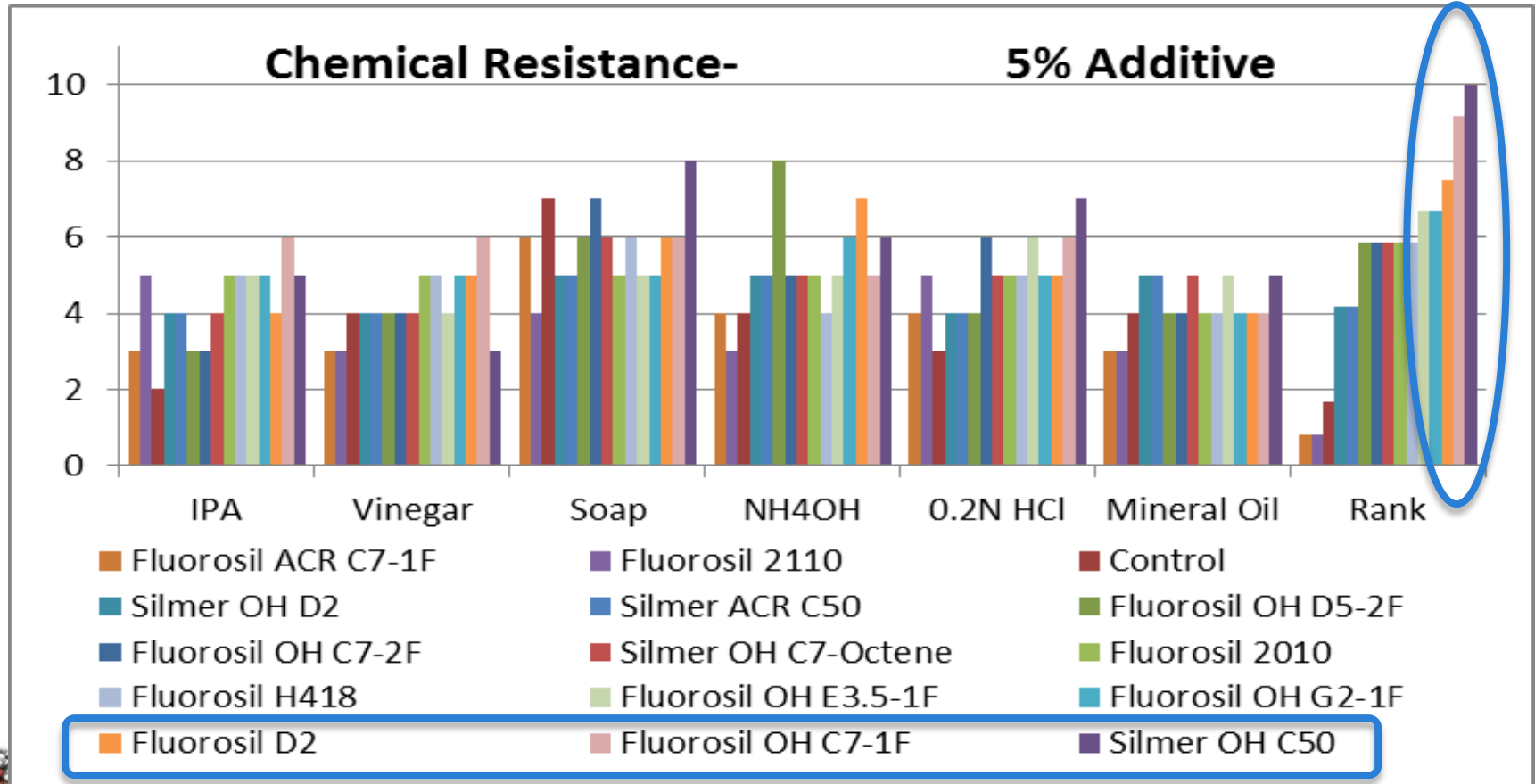
# Chemical Resistance: SB Urethane

Additive (1%)	IPA	Vinegar	Soap	NH <sub>4</sub> OH	HCl	Average	Normal-ized Rating
Fluorosil OH E3.5-F	5	2	3	2	2	2.8	1.0
Fluorosil 2110	6	1	4	3	2	3.2	2.0
Fluorosil OH C7-F	6	4	5	2	3	4	4.0
Silmer OH C7-Octene	6	2	4	6	4	4.4	5.3
Fluorosil 2010	7	3	5	1	6	4.4	5.3
Fluorosil OH G2-F	8	2	4	5	5	4.8	6.7
Silmer OH C50	8	3	4	5	5	5	7.3
Silmer ACR C50	7	7	6	3	2	5	7.3
Fluorosil OH C7-2F	6	5	5	5	4	5	7.3
Control	8	4	5	5	4	5.2	8.0
Silmer OH D2	8	2	7	6	5	5.6	9.3
Silmer OH J10	7	6	6	6	3	5.6	9.3
Fluorosil ACR C7-F	8	7	6	5	3	5.8	10.0

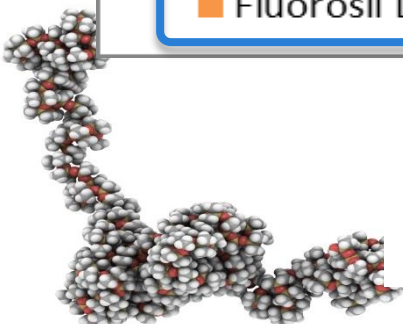
ACR C7-F and two AS types gave an improvement here



# Summary Chemical: Post add

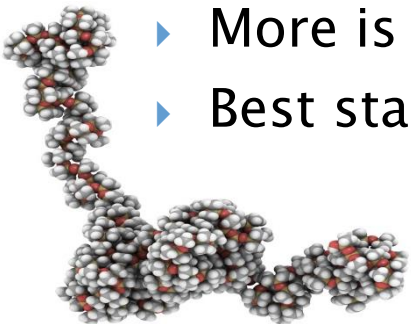


- Silmer OH C50, an AS type is best.
- OH C7-F and Fluorosil D2 are next best
- ACR C7-F is worst.



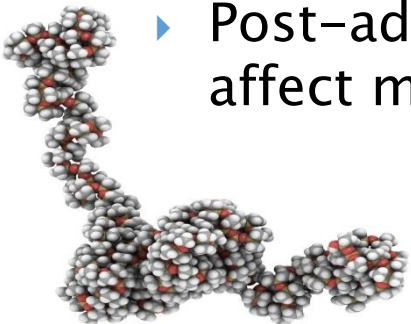
# Results

- ▶ All FAS additives improve COF, mar and stain resistance and to a lesser degree fingerprint.
- ▶ The FPE type are the most compatible. Surprisingly, they are also among the best for slip and mar resistance, but not fingerprint.
- ▶ The very incompatible FA types are not as effective as expected for slip and mar. Formulation may help this and the defects.
- ▶ OH C7-F is often the best for slip, mar and stain resistance.
- ▶ ACR C7-F is better than OH C7-F in Urethane and UV.
- ▶ J15, H418 and ACR C7-F give the best finger print resistance
- ▶ More is better for mar and stain.
- ▶ Best stain results are for waxy stains.



# Results

- ▶ H418 – which has a balance of % Si, %CF<sub>2</sub>, & %CH<sub>2</sub> – gives a very good balance of properties.
- ▶ Water repellency can be improved with high CF<sub>2</sub> or high silicone content additives.
- ▶ For chemical and water resistance performance varied more depending on the coating system and use level.
  - In some cases alkyl silicone copolymers were very good.
- ▶ Use levels needed were up to 5% and more is better in most cases.
- ▶ Increasing % CF<sub>2</sub> is often not the best in performance.
- ▶ Post-added FAS have little effect on slip and gloss but do affect mar and stain resistance.



# Recommendations

- ▶ Fluorosil 2010 and Fluorosil 2110. These are very good for all but fingerprint resistance
- ▶ Fluorosil ACR C7-F or Fluorosil OH C7-F are best overall including fingerprint resistance. They are not always compatible.
- ▶ Use levels are up to 5% and more is better in most cases.

