Regulatory Driven Innovation

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Abstract

- Regulation is often considered an obstacle to new product innovation.
- Yet history shows this is not the case – regulatory drivers trigger innovation like any other driver.
- Herein, we will summarize a few of the innovations we have made due to regulatory drivers.

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Reality of Public Policy and Regulation on Innovation

- Our desire to lessen negative impacts on our environment and society coupled with instant, fragmented communication drives regulatory and market changes.
- Perception is the new reality. Chemicals are guilty until proven innocent.
- Market perception is often more important than regulations and nearly always precedes regulatory mandates.
- Manufacturers scramble to stay ahead of the current hot topics with innovation and new product development.

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Regulatory Drivers for Silicones

1. The "Green" Trend
2. Emulsifiers/ Emulsions
   - Biocides
   - Sn-free
3. Solvents and Volatiles
4. PFOA and Fluoroalkyl materials

1. 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, it makes practical sense to use the available by-products rather than waste them.

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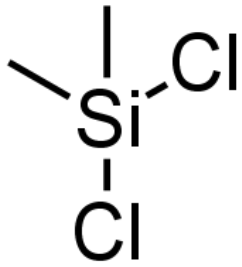
The Road from Silicon to Silicone

14
Si
28.0855

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

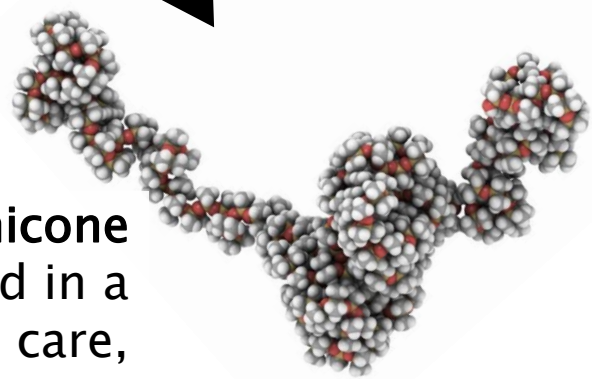
Catalysts:
From the Earth



Water:
Natural

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

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



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. Not bio-degradable, but chemically degrades in the environment and volatiles are non-HAPS.

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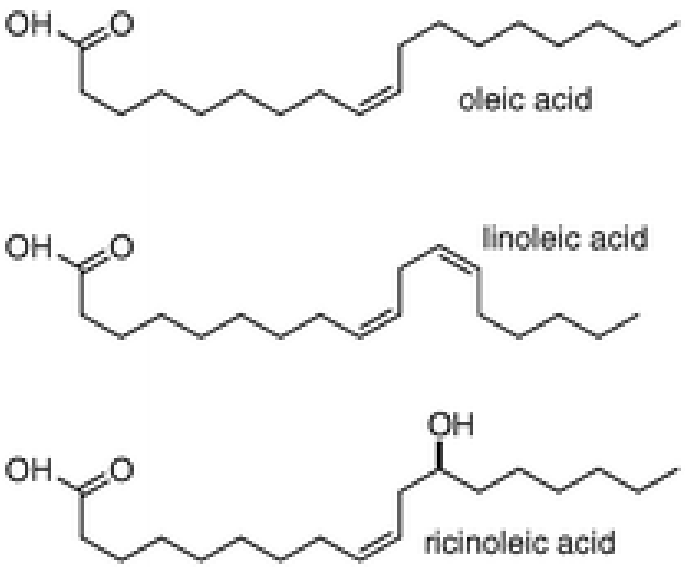
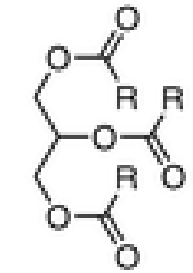
Green Trend

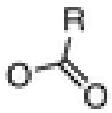
- Although there are few Green mandates, there is a market need for more natural products, and a mechanism for certification.
- Siltech has responded with natural products reacted onto silicones such as castor oil, aliphatic hydrocarbon and essential oils.
- Also, additive levels of some special silicones enable botanical oils to replace silicone oil.

Castor Oil Silicones





Castor oil



= ricinoleate, 87%
= oleate, 7%
= linoleate, 3%
= others, 3%

Silicone Castor Oil Polymer in Coatings: 1.7% additive in SB PU

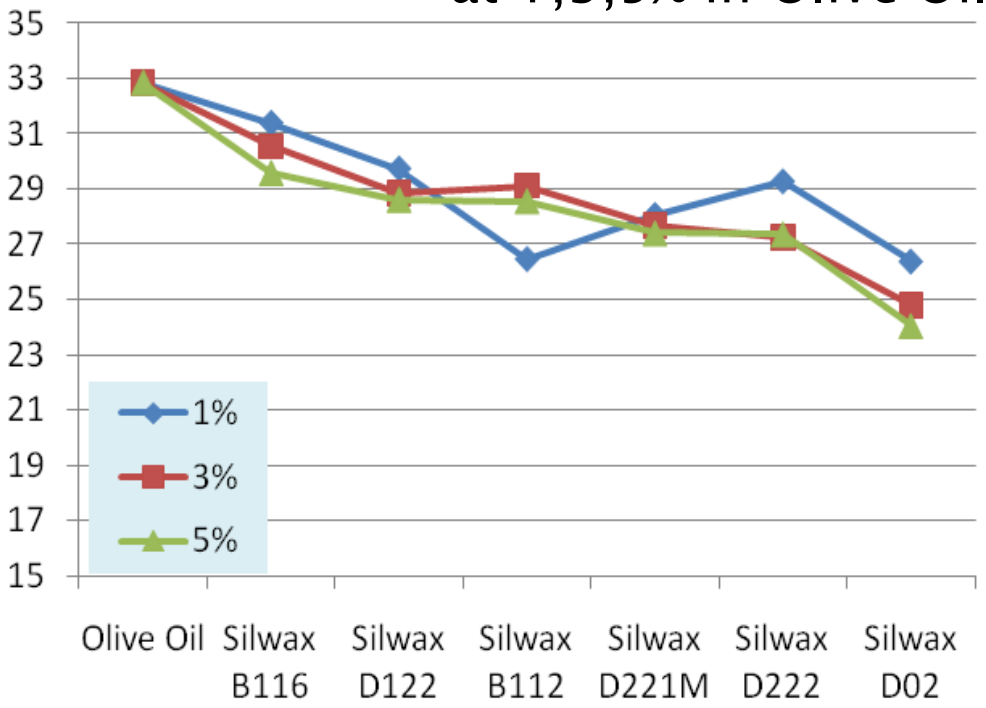
Type	Gloss	Static COF	Kinetic COF	Marker Resist.	Mar Resist.	Coating Appearance
Silmer ACR Di 50	92.2	0.405	0.384	7.500	7.5	Mild waves
Silmer OH Di 50	97.2	0.680	0.745	7.000	7.6	Mild waves
Silube CO Di 45	96.3	1.019	0.945	9.000	8.2	Smooth

Silicone Castor Oil

Natural oils can be “siliconized”

ST Reduction in Botanical Oils

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



ST reduction of solvents

	ST	w/0.5%	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-UP
motor oil	31.0	22.6	Silwax CR-5016

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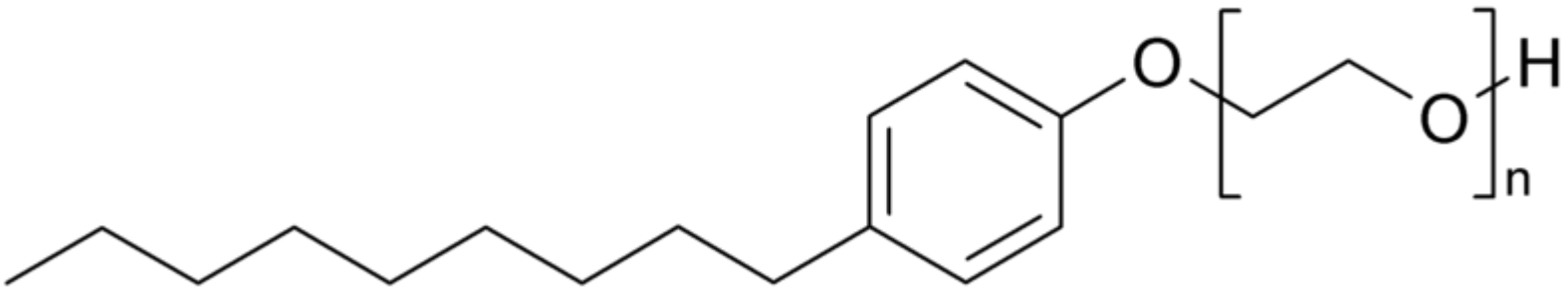
2. Emulsifiers (APEO- and EO-free surfactants)



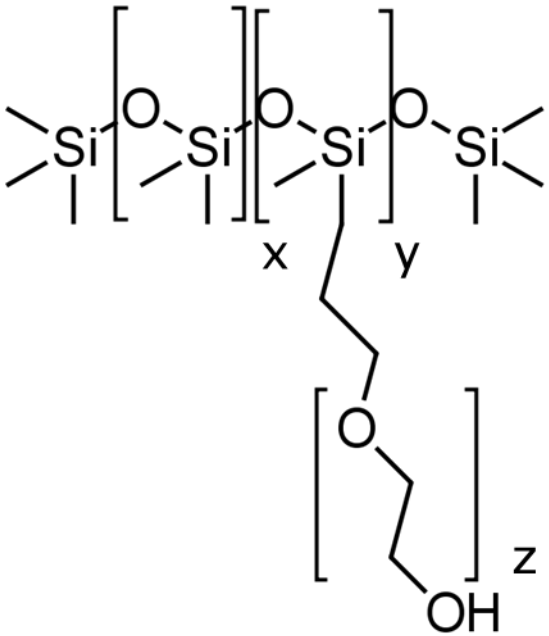
- Most pressure is on Nonyl Phenol Ethoxylate
  - Good emulsifying and dispersing properties
  - Low toxicity but degradation products are cited
- Not allowed in EU and Canada

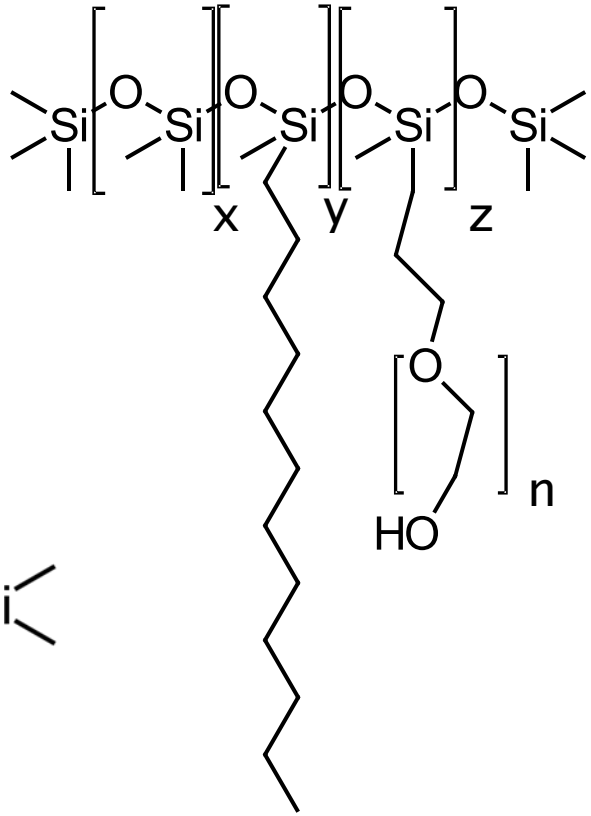
Emulsifiers: NPE Free

- EU and Canadian regulations have driven NPE free emulsions.
- Being a Canadian manufacturer, Siltech has never used NPE emulsifiers and rely on anionic surfactants, linear alcohol ethoxylates and/or silicone emulsifiers to stabilize our emulsions.

Silicone Emulsifiers

- But these have EO and allyl ethoxylates
- Many prefer to not have those components





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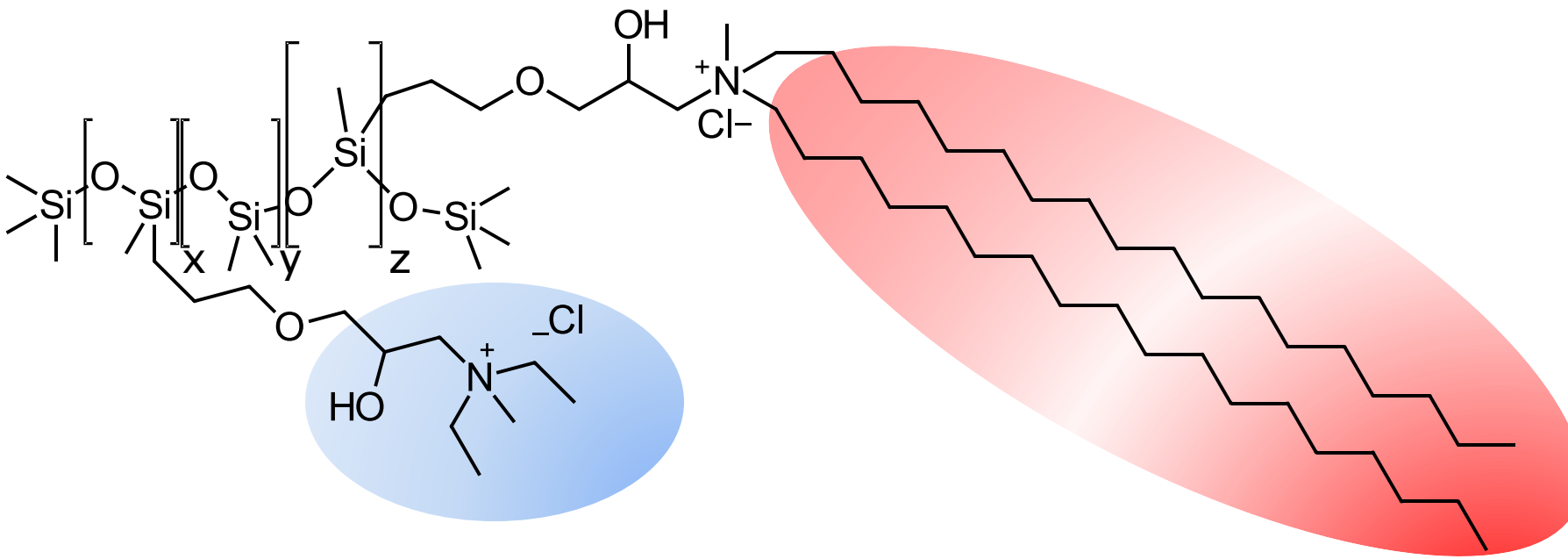
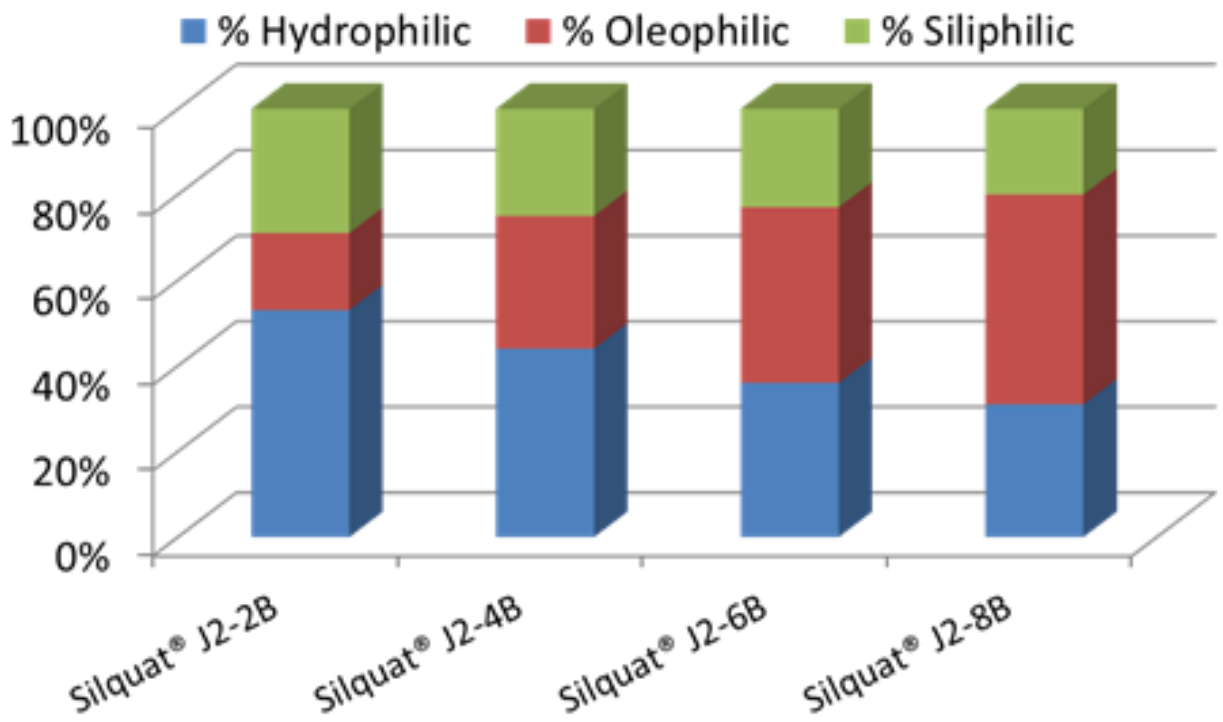
Silquat J2-xB EO Free Emulsifiers



Hydrophile

Lipophile

Silquat J2-xB series



Product	Emulsion Type	HLB	Viscosity
Silquat J2-2B	O/W	11	7000
Silquat J2-4B	O/W	9	7500
Silquat J2-6B	O/W	7	7500
Silquat J2-8B	O/W	5	6700

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Biocide Aversion

- Biocides are implicated in a variety of human maladies and some have been regulated, particularly parabens in the EU.
- Siltech uses pH and other alternatives when possible and constantly assesses the available biocide options for our emulsion products.
- The Silquat J2-xB products may multi-task as a biocide

Tin-free emulsions

- EU concerns and regulations against tin (Sn) catalysts commonly used in many reactive silicone emulsions and other condensation reacted silicones.
- Siltech is actively looking at titanium, zirconium and other catalysts as well as systems that don't need to be catalyzed.
- Siltech C-4435 and C-4445 are the latest tin-free offerings

3. Solvents and Volatiles

- CARB regulations led the way for current volatile organic compounds regulations.
- 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
High Solids Alkyd Resin	39.53%	42.75%
Glycol Ether/Solvent Mix	**28.35%**	**22.51%**
Special Black 4A	13.95%	15.09%
Filler Blend	16.61%	17.96%
Siltech Additives	0%	0 or 0.5%
Anti-settling Agent	S.Q.	S.Q.
Dispersing Agent	S.Q.	S.Q.
Dryer blend	S.Q.	S.Q.
Stabilizer	S.Q.	S.Q.
Anti-skinning Agent	S.Q.	S.Q.
VOC	**315 g/l**	**259 g/l**
Solid	**60%**	**65%**

	Results
Appear.	Higher solids has more defects; additives improve it to better than high solids control
S.T.	Returned to or below high solids control
Visc.	Returned to high solids control
Flow	Improved directionally but not to control
Gloss	Higher solids control is better
Abr. Resist.	Lost in higher solids; regained and more with additives

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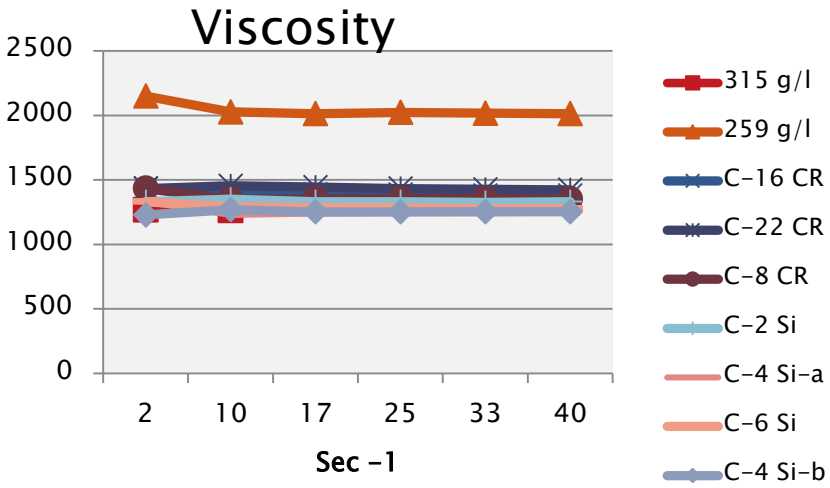
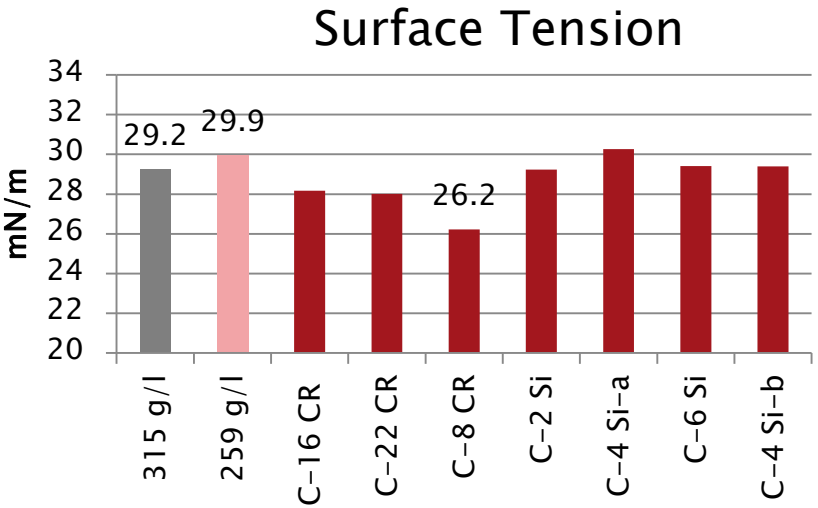
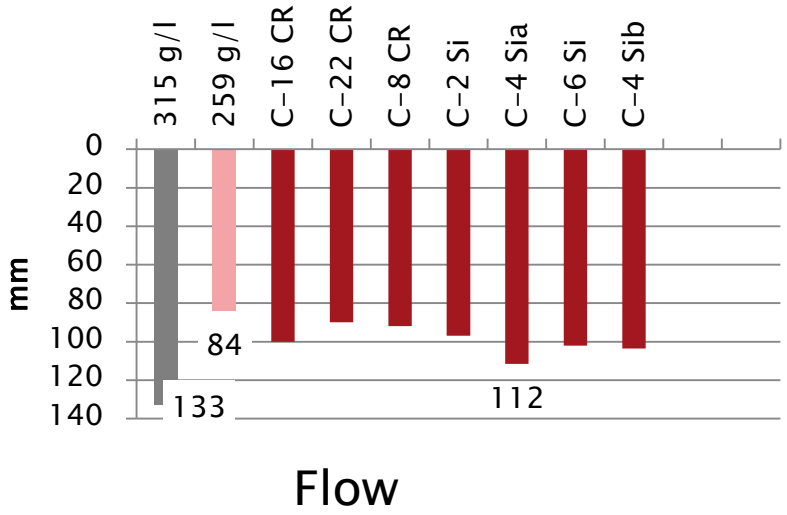
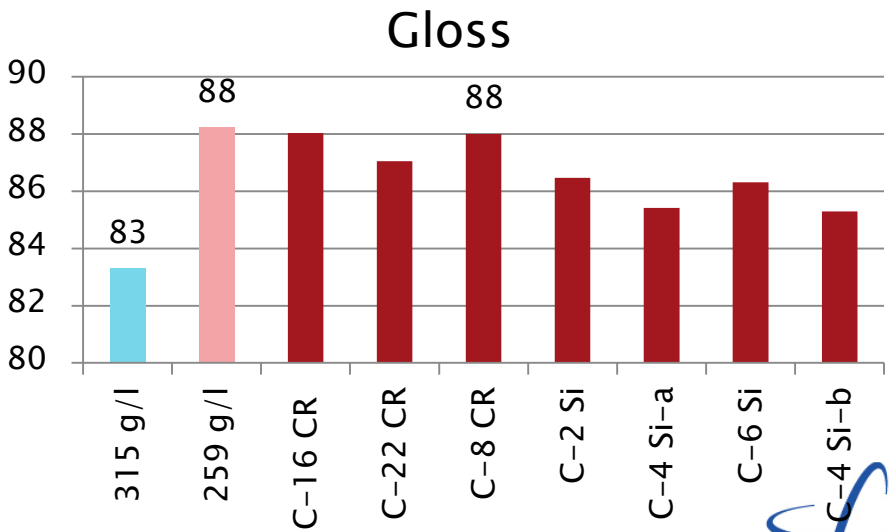
Properties with alkyl silicones









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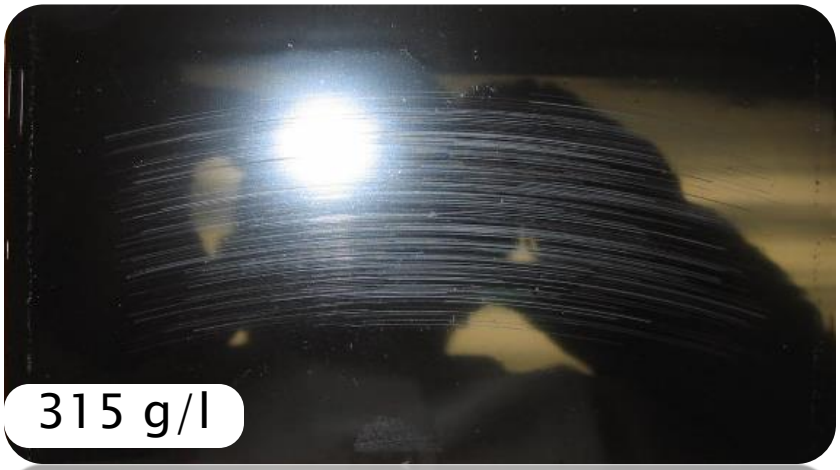
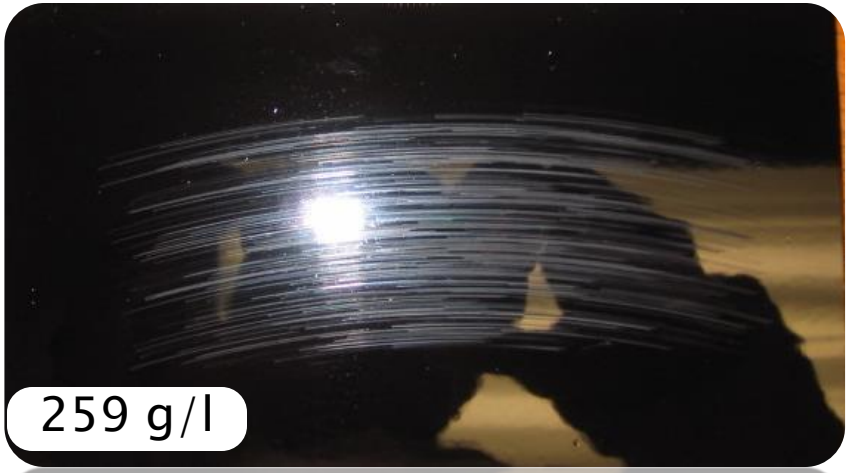
Black Enamel

Visual





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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.
- Extensive toxicological and environmental testing has been completed
  - In 2013, with all of the data in, FDA again allowed silicone gel implants.

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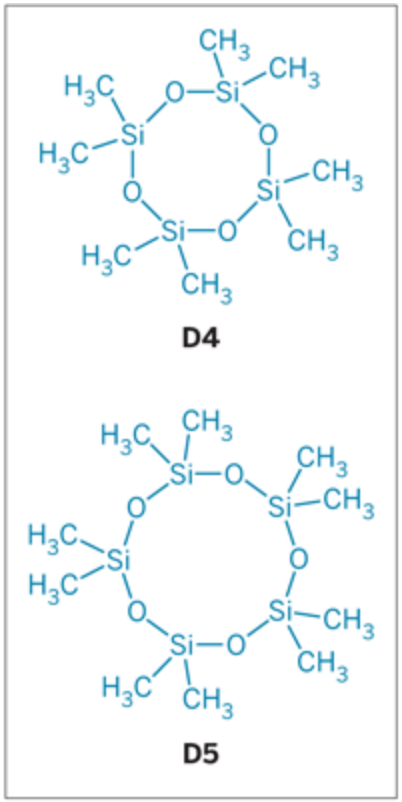
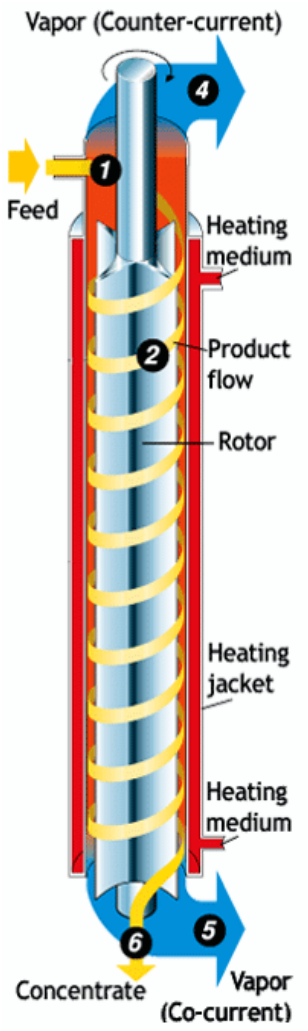
Volatile Cyclic Siloxanes

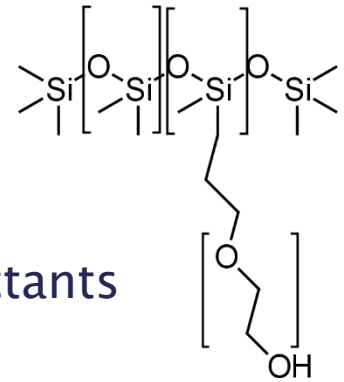
- Some early results led to concern over volatile silicones D_4/D_5
  - Personal Care Industry
  - Canada and Norway
- Although few current regulations require this, Siltech has responded to the market need for low VS content silicones.
- Silicones are non-HAPs



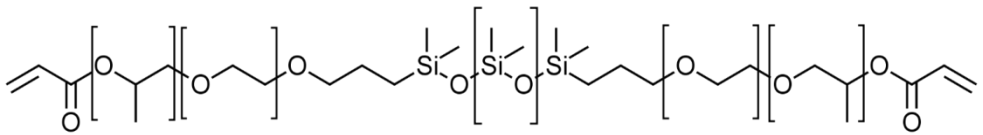
Volatile Cyclic Siloxanes

WFE





Silicone surfactants



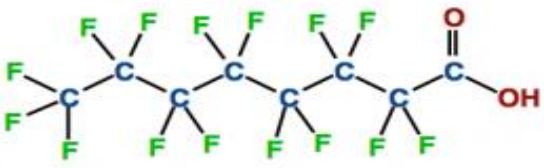
Silicone di-acrylates

We can remove D_4 and D_5 to less than 0.1%

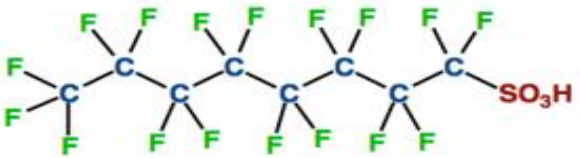
4. Fluoroalkyl

What are the concerns related to PFOA?

PFOA is very persistent in the environment and has been found at very low levels both in the environment and in the blood of the general U.S. population. Studies indicate that PFOA can cause developmental and other adverse effects in laboratory animals. PFOA also appears to remain in the human body for a long time. All of these factors….



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

(Source: http://epa.gov/oppt/pfoa/pubs/faq.html#concerns)

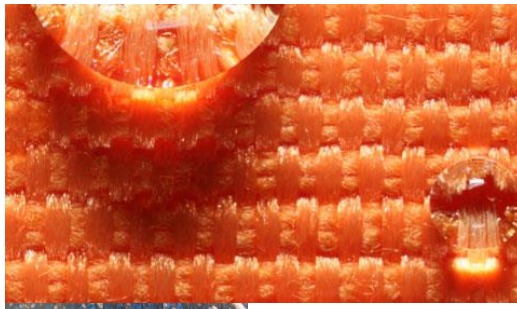
Fluoropolymers

Anti-
Fingerprint

Strategies for managing concerns and regulatory change

- Reduce length of fluorine chain
- Substitute fluorocarbons

Lipophobic
Hydrophobic



Anti-
Graffiti

Anti-
Stain

Anti-
Fouling

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Non-PFOS stain resistance

- US EPA consent order to replace PFOS based products spurs renewed focus on our Fluorosil $C_5H_4F_7$ 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.
- Latest approach: Silmer OHT products have no Fluoroalkyl.

Silicone and Fluoropolymers

Silicone	Fluoropolymer
✓ Low surface energy	✓ Very low surface energy
✓ Very good water resistance	✓ Good water resistance
✓ Marginal oil resistance–swelling	✓ Very good oil resistance
✓ Good chemical resistance	✓ Very good chemical resistance
✓ Very good thermal flexibility	✓ Marginal thermal flexibility
✓ Low abrasion resistance	✓ Low abrasion resistance
✓ High cost ($10/lb.)	✓ Very high cost ($80/lb.)
✓ Effective at low use levels	✓ Effective at low use levels

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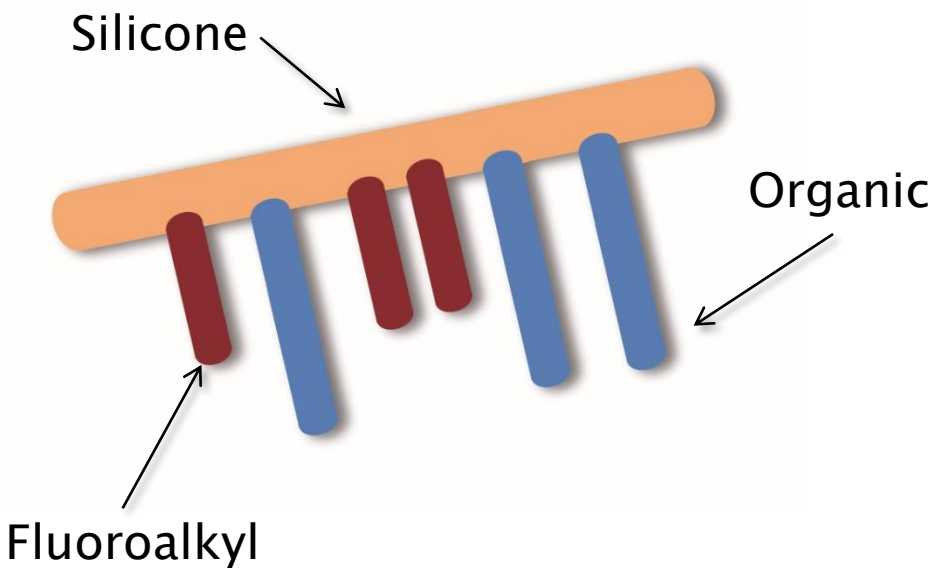
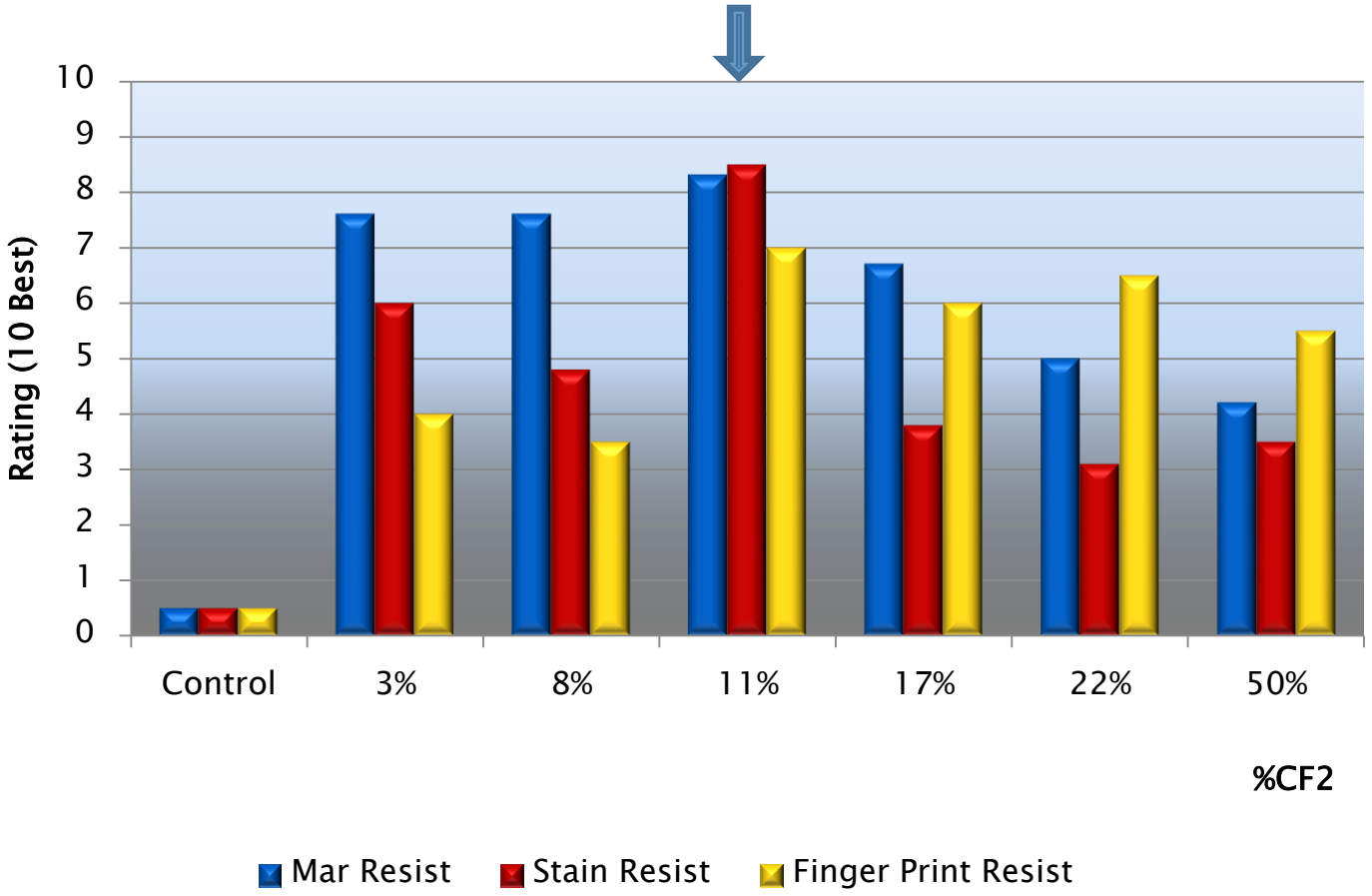
Fluoroalkyl Silicone Variants



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

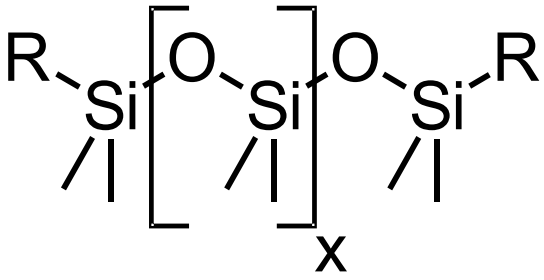
By varying the number, length and type of fluoroalkyl and/or organic substituents covalently bound to the silicone we can control properties.

Substitution of Fluorocarbons

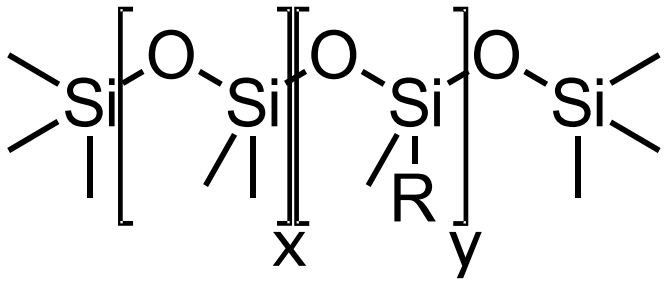


Reduce total F +

Fluoro-free Organosilicones

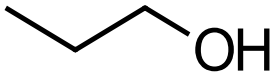


Linear

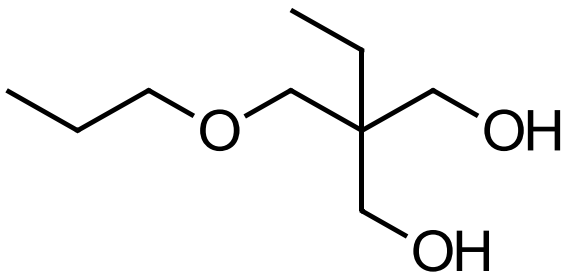


Pendant

Type A: R=



Type C: R=



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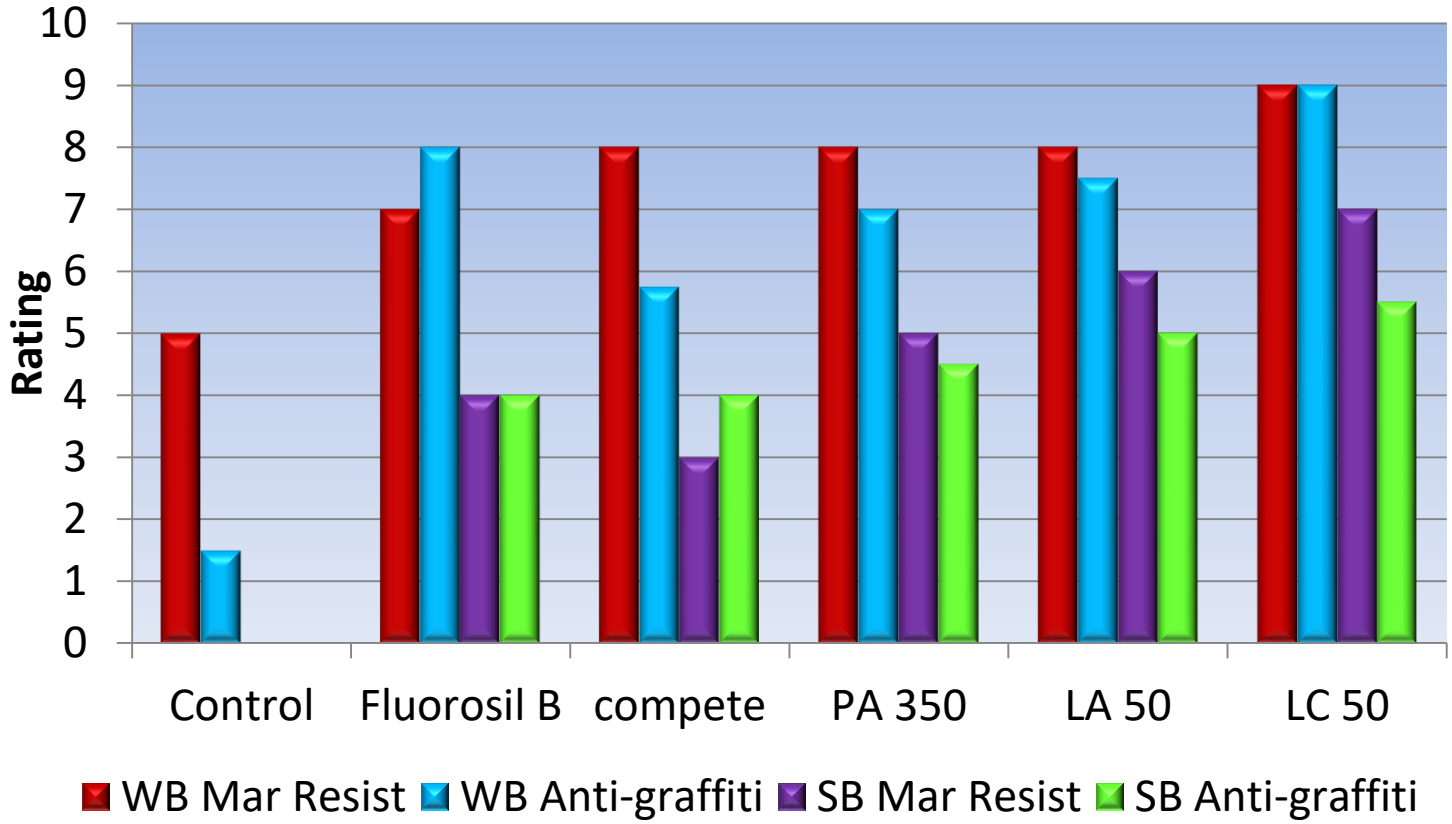
Resistance Screen



Type A and Type C are all better than both controls

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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.

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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 (D_4/D_5) 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.

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