Fluoro-Free Anti-Graffiti Properties From A Novel OrganoSilicone

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Challenges from staining, fouling, graffiti, fingerprints, chemicals....

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Public Policy and Regulation Drivers for Innovation

- Today instant, fragmented communication and desire to lessen negative impact on the environment and society drive regulatory and market changes.

- Perception is the new reality.
  - Chemicals are often guilty until proven innocent
  - Market perception often more important than regulations. And it nearly always precedes regulatory mandate.

- Industry is pressured to stay ahead of the current hot topics with innovation and new product development.

Fluorine

Scrutiny, Pressure and *Ambiguity …*

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….

What are fluoropolymers and telomers and how are they used?

Fluoropolymers impart valuable properties, including fire resistance and oil, stain, grease, and water repellency. They are used to provide non-stick surfaces on cookware and waterproof, breathable membranes for clothing. They are employed in hundreds of other uses in almost all industry segments, including the aerospace, automotive, building/construction, chemical processing, electrical and electronics, semiconductor, and textile industries.

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

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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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Experimental Design and Methods

- Various silicones are evaluated for slip, COF, defects, mar resistance and stain resistance.
- Controls are fluoro-silicones and a commercial anti-graffiti additive
- The overall design used two systems:
  - *SB 2k Urethane*
  - *WB 2k Urethane*

Test Methods

- COF (Cheminstruments sled method)
- Gloss (gloss meter)
- Stain:
  - Marks with a Paper mate permanent marker, Super Sharpie marker or Berol Liquid TIP marker are applied on the test panel . The score is made by visual inspection, difficulty of writing and ease of removal.
  - A series of stains are also evaluated including coffee, red kool-aid, red wine, mustard, motor oil, iodine, $KMnO_4$
  - Stain resistance is measured via rubbing with paper towel for Marker removal

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Test Methods

- Mar resistance is measured using a Sutherland 2000 Ink Rub Tester first with a Nylon pad and then sand paper.
  - The rating is calculated based on the percentage change in gloss reading before and after the rubbing test, and rating from inspection.

- Anti-graffiti is rated based on the following parameters:
  - Degree of difficulty to put on black marks with permanent marker
  - Degree of difficulty to remove black marks without damaging the coating
  - Mar and stain resistance according to the aforementioned procedure

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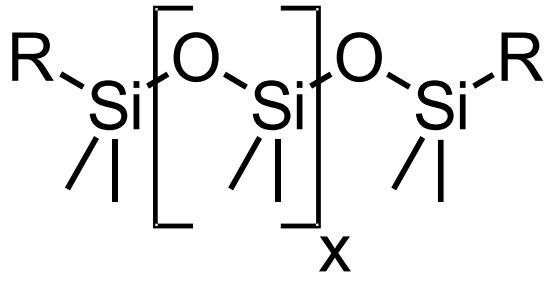
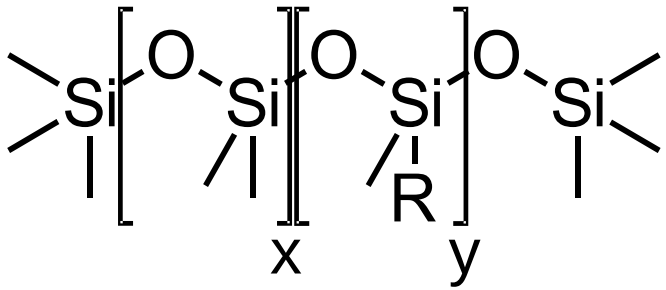
Organosilicones

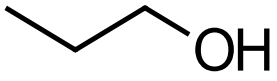


Linear

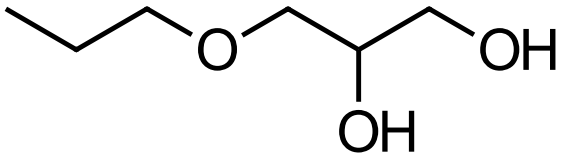


Pendant

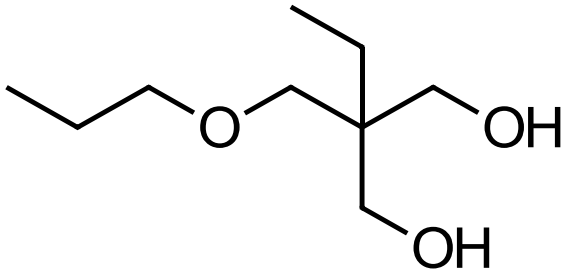
Type A: R=



Type B: R=



Type C: R=



Copolymers Tested

code	MW	Hydroxy Alkyl Type	Arch
LA 10	1000	A	Linear
LB 10	1000	B	Linear
LC 10	1000	C	Linear
LA 50	4000	A	Linear
LB 50	4000	B	Linear
LC 50	4000	C	Linear
LA 100	8000	A	Linear
LC 100	8000	C	Linear
PA 48	3000	A	Pendant
PB 48	3000	B	Pendant
PC 565	5000	C	Pendant
PA 10100	9000	A	Pendant
PB 10100	9000	B	Pendant
PC 10100	9000	C	Pendant
PA 350	12000	A	Pendant
PA 460	18000	A	Pendant

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Formulations

2K WB PU		2K SB PU	
Part A		Part A	
OH-functional polyacrylic dispersion	54.55%	Hydroxyl-bearing polyacrylate	31.84%
Acetylenic diol Surfactant	1.30%	Flexibilizing hydroxyl-bearing polyester	21.19%
Non-ionic polyurethane based thickener	0.19%	Tin Catalyst	0.05%
Water (Distilled)	23.23%	n-BA (used Tert Butyl Acetate)	5.72%
Subtotal	79.28%	PMA (Glycol Ether PM Acetate)	7.62%
		EEP (slow evaporating ether-ester solvent)	9.14%
Part B			
Isocyanate I	9.32%		
Isocyanate II	7.24%	Part B	
Oxygenated solvent	4.15%	Aliphatic Isocyanate	24.45%

- Coating applied with #10 wire wound rod onto Aluminum Q-panels
- Cure conditions were 110°C for 60 minutes
- Conditioned at ambient for a minimum of 24 hrs

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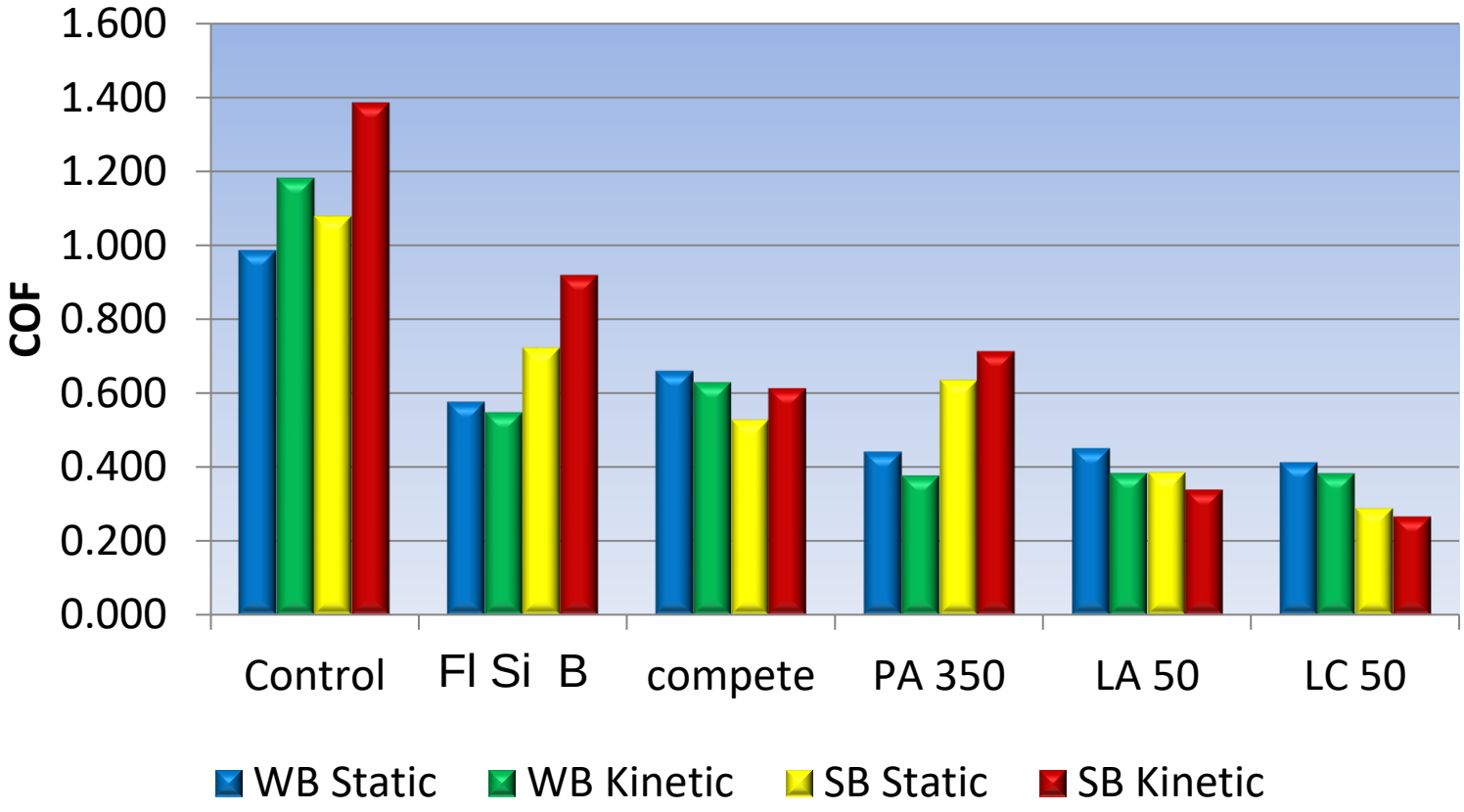
COF Reduction Screen



Type A and Type C are all better than both controls

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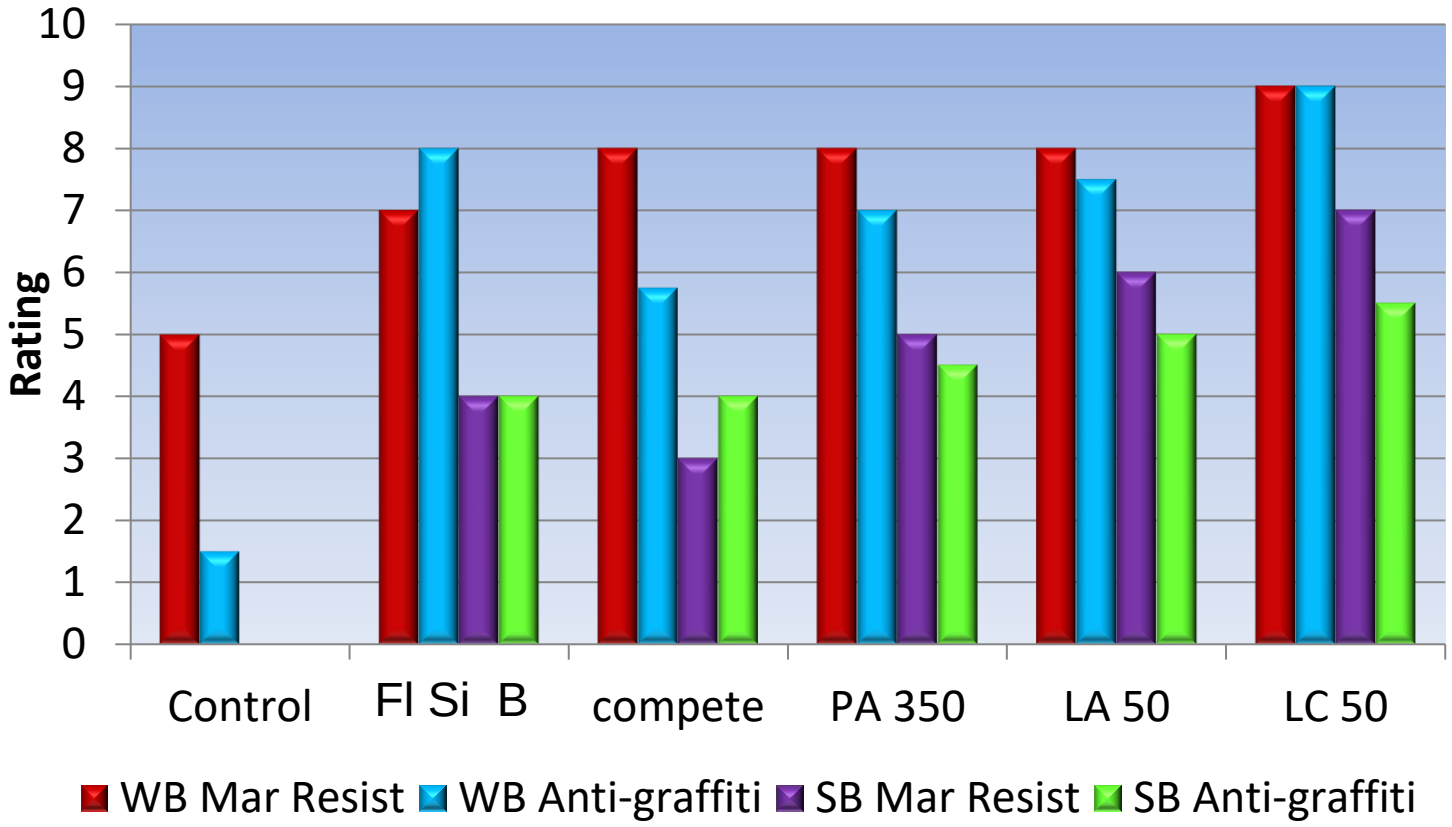
Resistance Screen



Type A and Type C are all better than both controls

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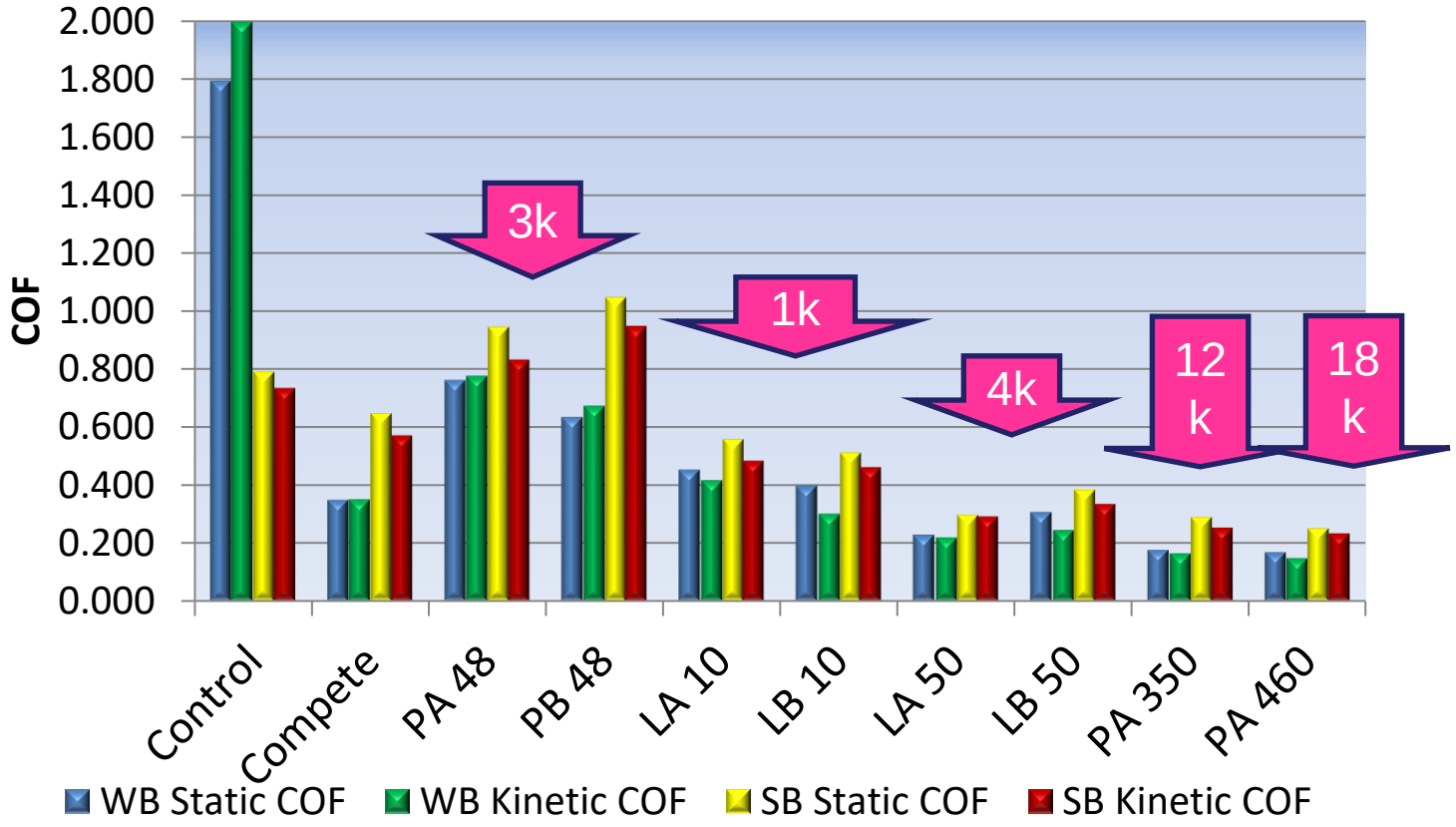
COF Reduction 1%



All are better than control

Pendant < Linear

LA 50 and higher MW are better than competitive

Type A and Type B are similar

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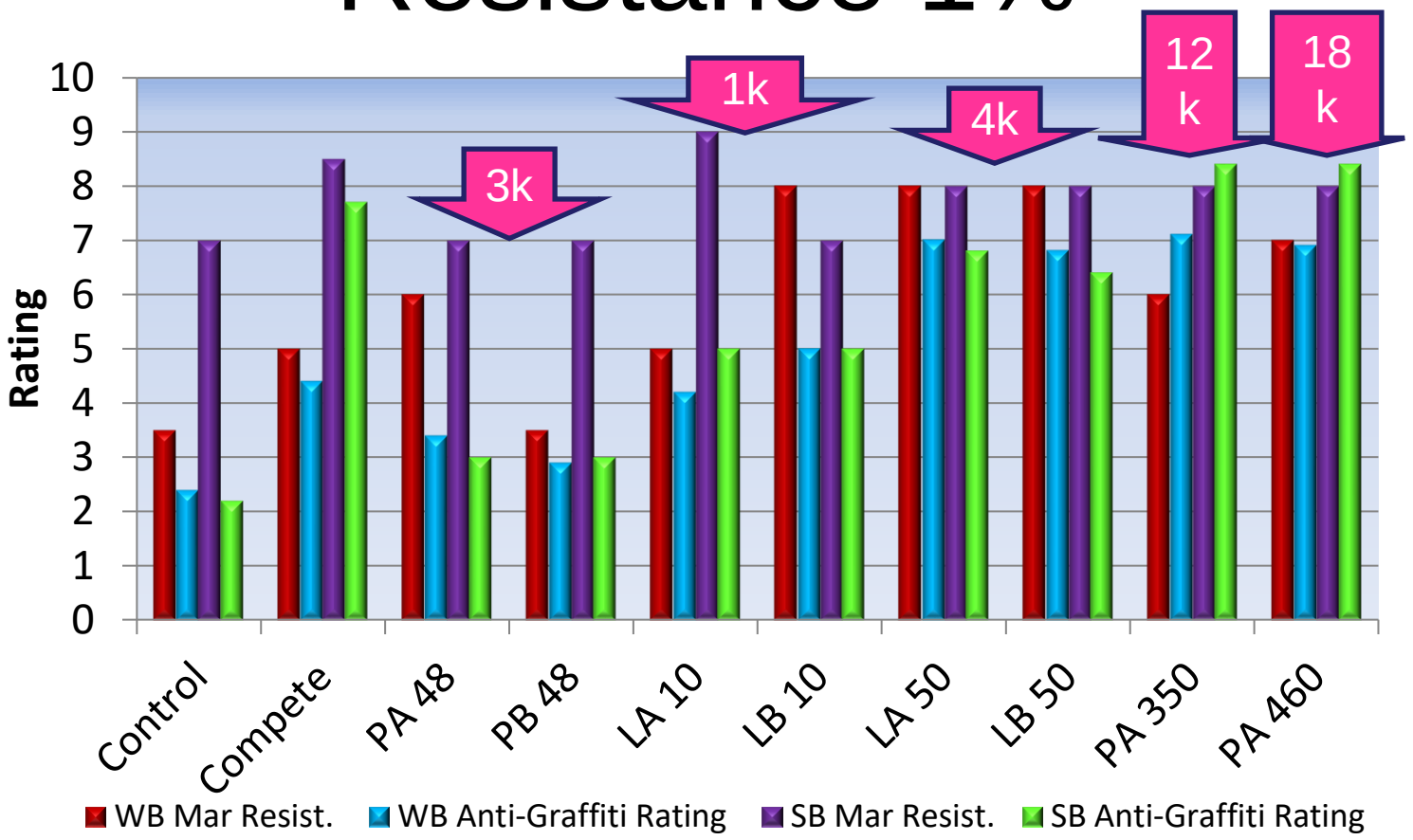
Resistance 1%



All are better than control

Pendant < Linear

LA 50 and higher MW are better than compete

Type A and Type B are similar

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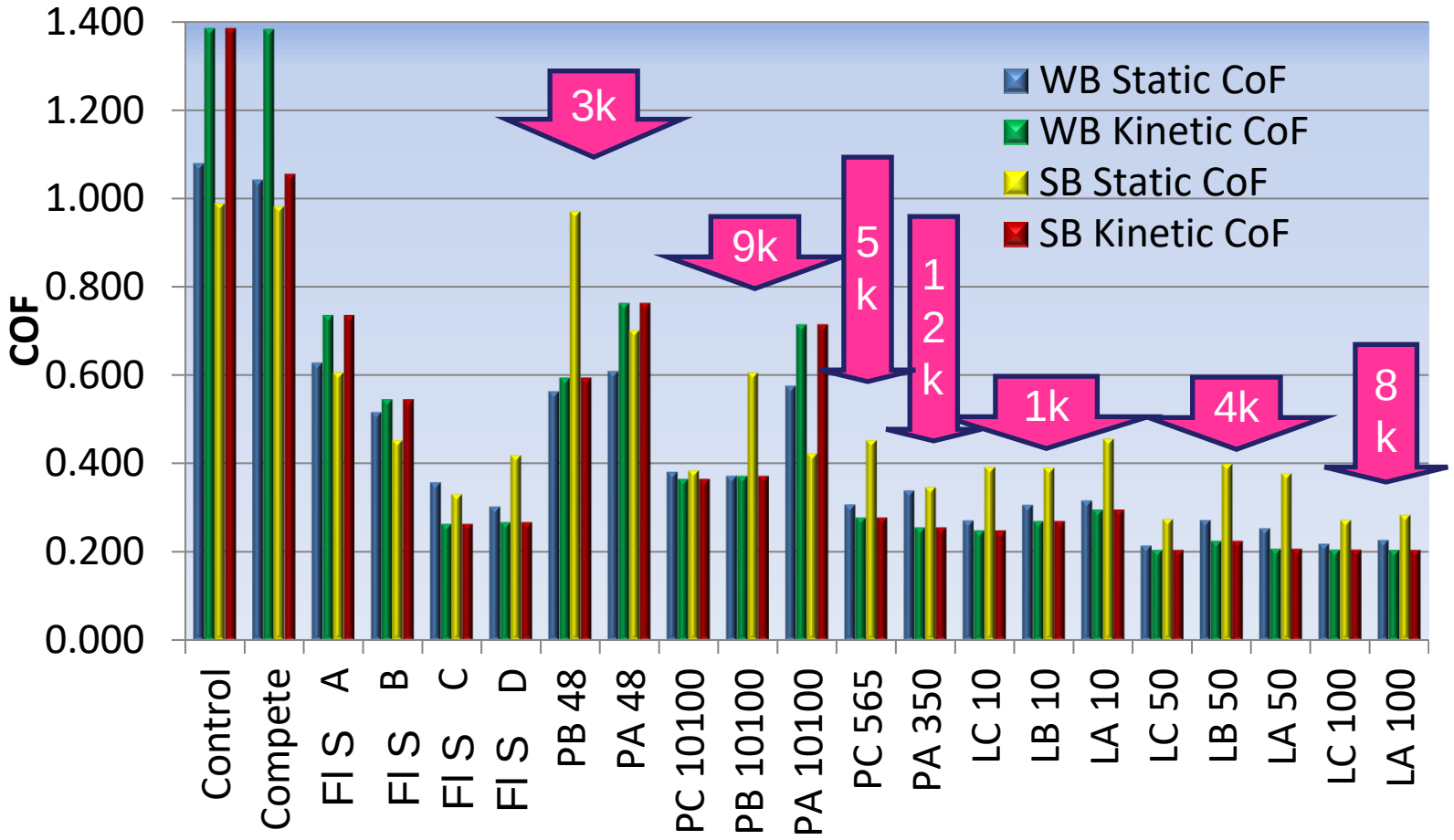
2% Additive COF



All are better than competitive

Some are as good as the best flouro silicone

Type C > Type A >~ Type B

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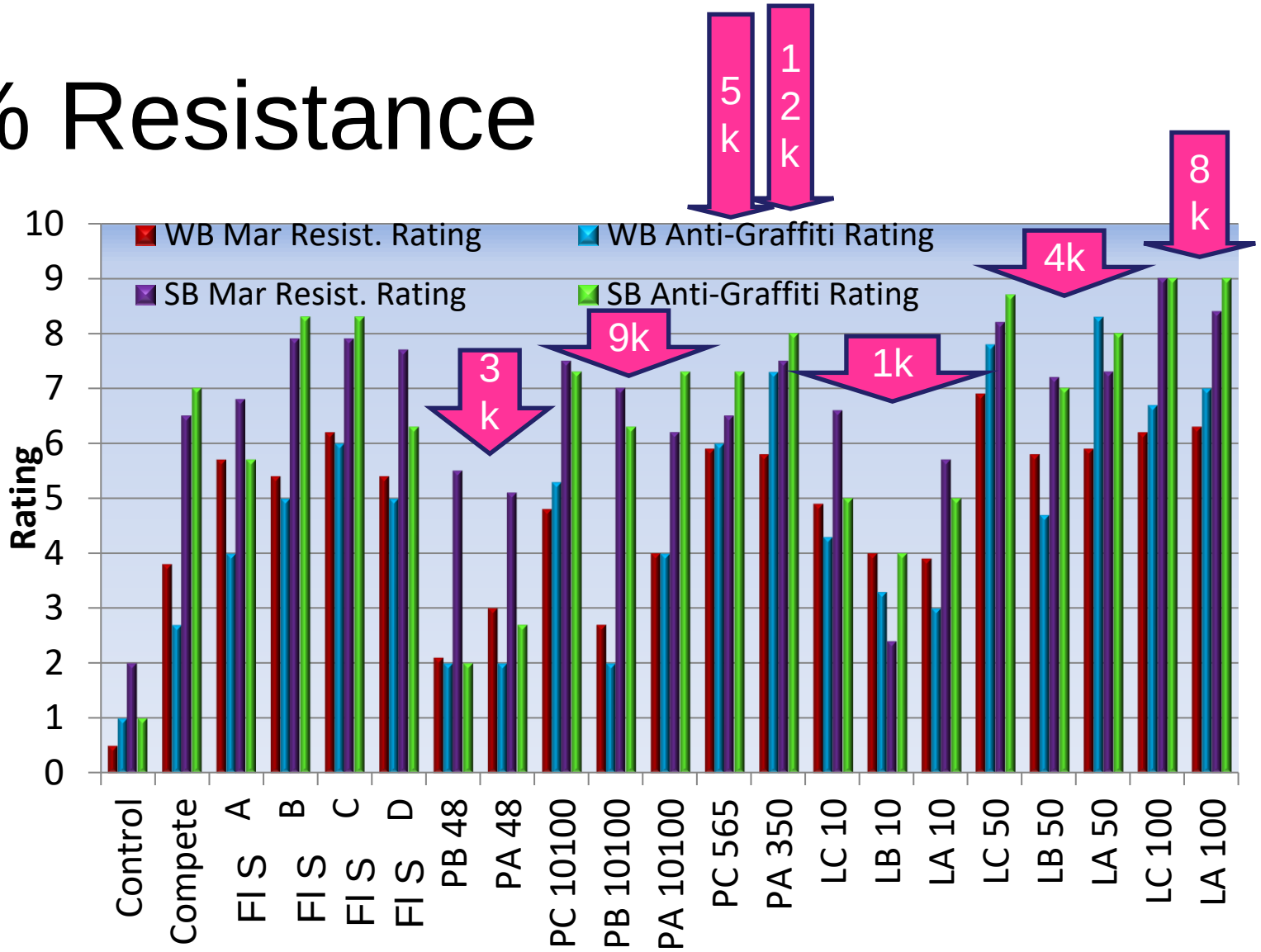
2% Resistance



Best silicones are linear and high MW
Types make a small difference

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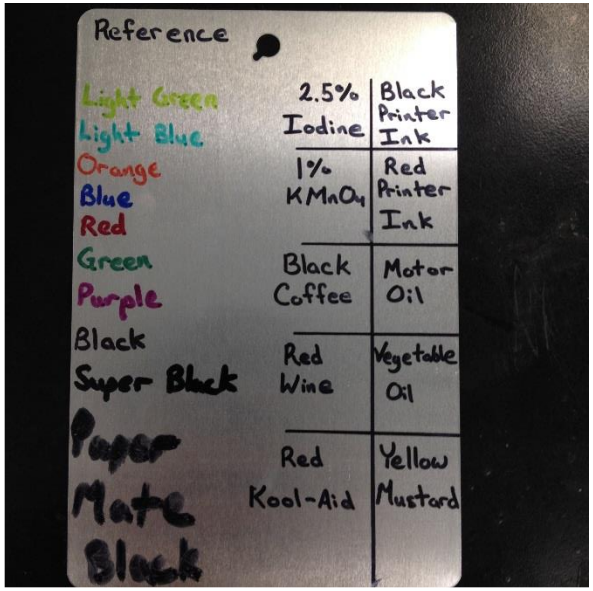
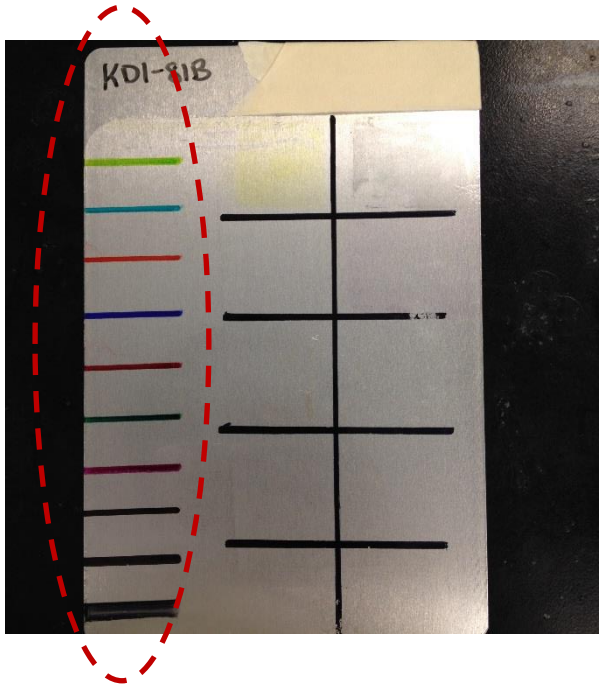
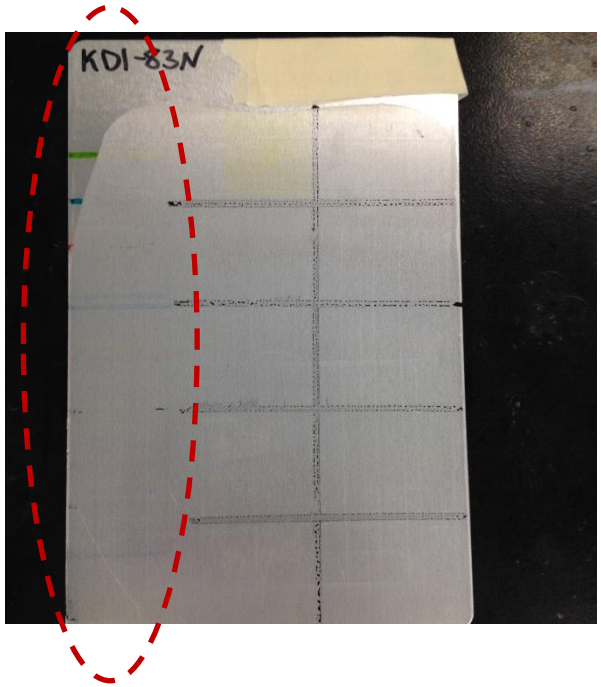
Examples of post-rub test panels



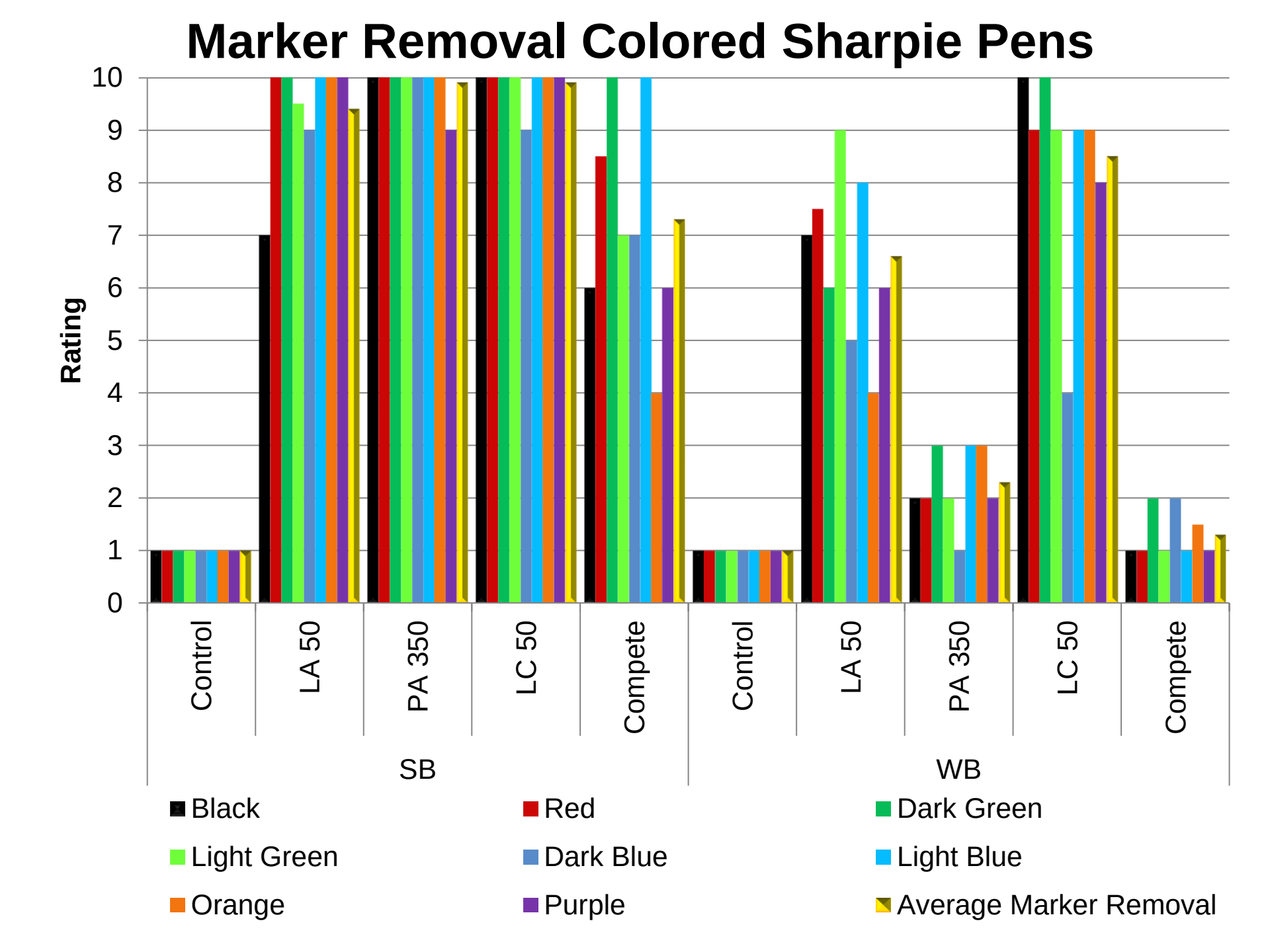
Reference Stain Panel

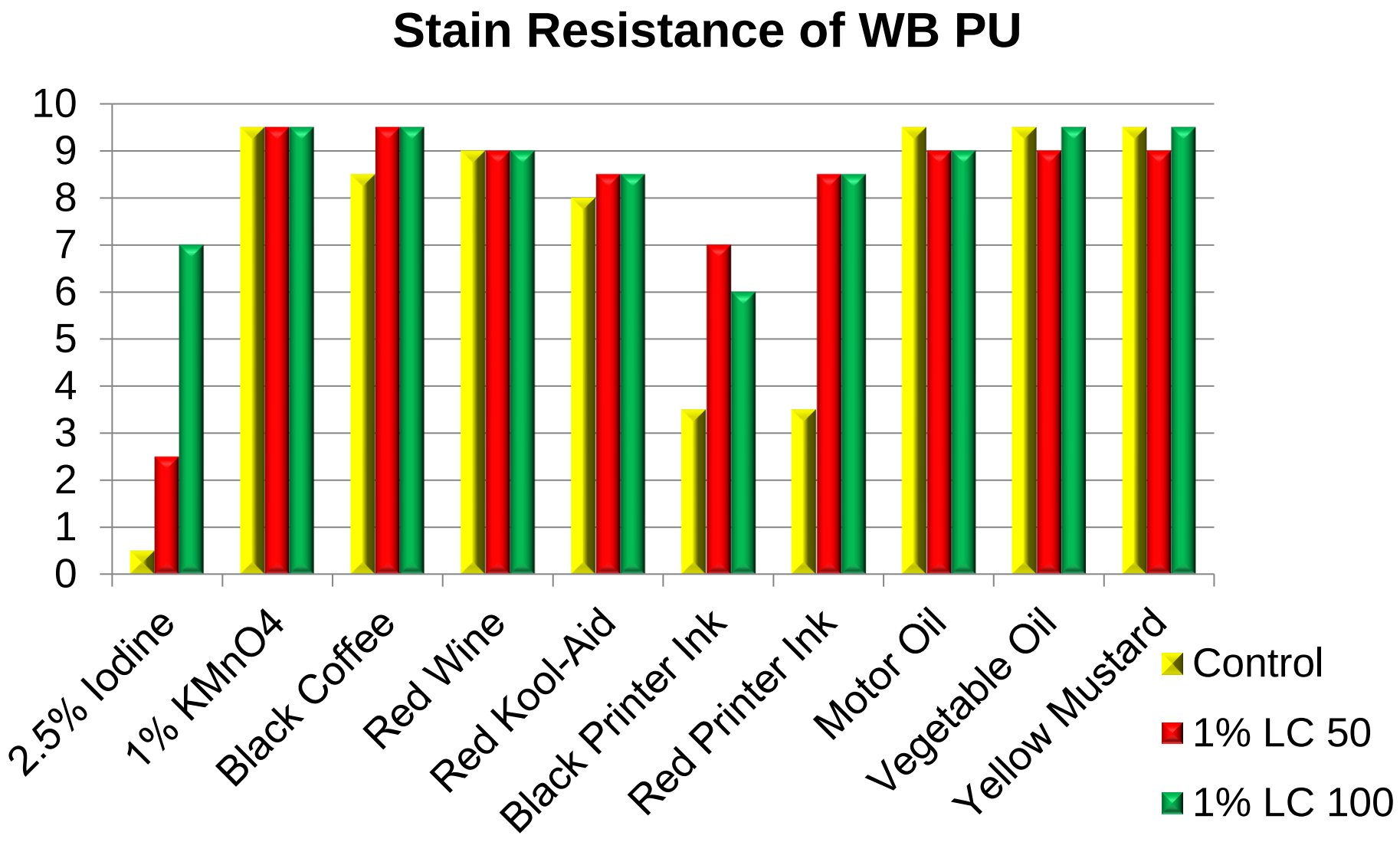


SB Control Stain Panel



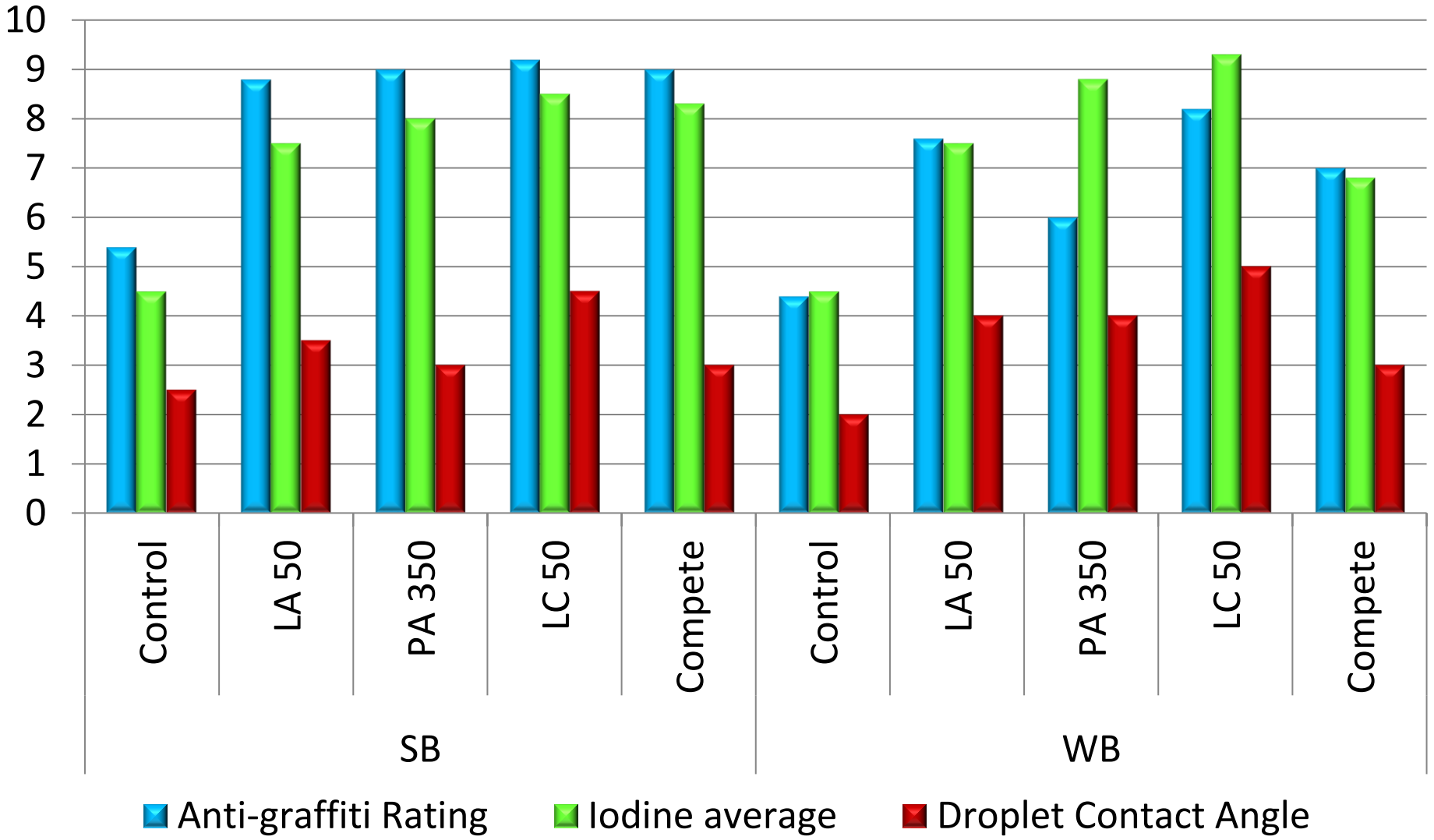
2% LC 100 SB Stain Panel


Marker Removal Colored Sharpie Pens
Rating
10
9
8
7
6
5
4
3
2
1
0
Control
LA 50
PA 350
LC 50
Compete
Control
LA 50
PA 350
LC 50
Compete
SB
WB
Black
Red
Dark Green
Light Green
Dark Blue
Light Blue
Orange
Purple
Average Marker Removal

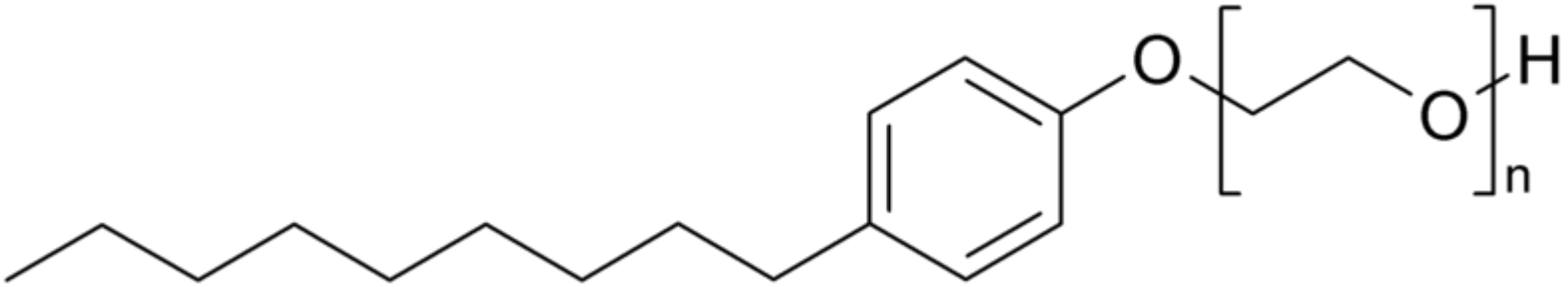


Where control is not high, additives increase resistance

Stain Resistance



Emulsifiers
(APEO- and EO-free surfactants)



- Most pressure is on Nonyl
- Lipophilic and Hydrophilic Balance
- Good emulsifying and dispersing properties
- Low toxicity but degradation products of concern
- Can we have APEO- and EO-free too?

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Examples of Emulsion Formulations

Ingredients	FC337B Wt %	FC337C Wt %	FC337H Wt %	FC337I Wt %	FC337J Wt %	FC337G Wt %
D.I. Water	65.2	65.2	65.2	65.2	65.2	65.2
Glycerine	5.0	5.0	5.0	5.0	5.0	5.0
MgSO4	2.0	2.0	2.0	2.0	2.0	2.0
Mineral Oil	11.20	11.20	11.20	11.20	11.20	11.20
Isoparaffin	7.60	7.60	7.60	7.60	7.60	7.60
PC 565	5.0	0	0	0	0	0
LC 50	0	5.0	0	0	0	0
PA 48	0	0	5.0	0	0	0
PB 48	0	0	0	5.0	0	0
LAO 5D	0	0		0	5.0	0
PCO 5D	0	0	0	0	0	5.0
Microcrystalline Wax	2.4	2.4	2.4	2.4	2.4	2.4
Macadamia Nut Oil	1.5	1.5	1.5	1.5	1.5	1.5
Citric Acid	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Total	100%	100%	100%	100%	100%	100%

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Example Copolymers Tested for anti-graffiti and emulsification

code	MW	Hydroxy Alkyl Type	Arch
LC 50	4000	C	Linear
LC 100	8000	C	Linear
PCO 5D	4700	C	Pendant w/ olefin
PA 48	3000	A	Pendant
PB 48	3000	B	Pendant
PC 565	5000	C	Pendant
LAO 5D	3000	A	Pendant w/ olefin
PB 48	3000	B	Pendant
PB 10100	9000	B	Pendant

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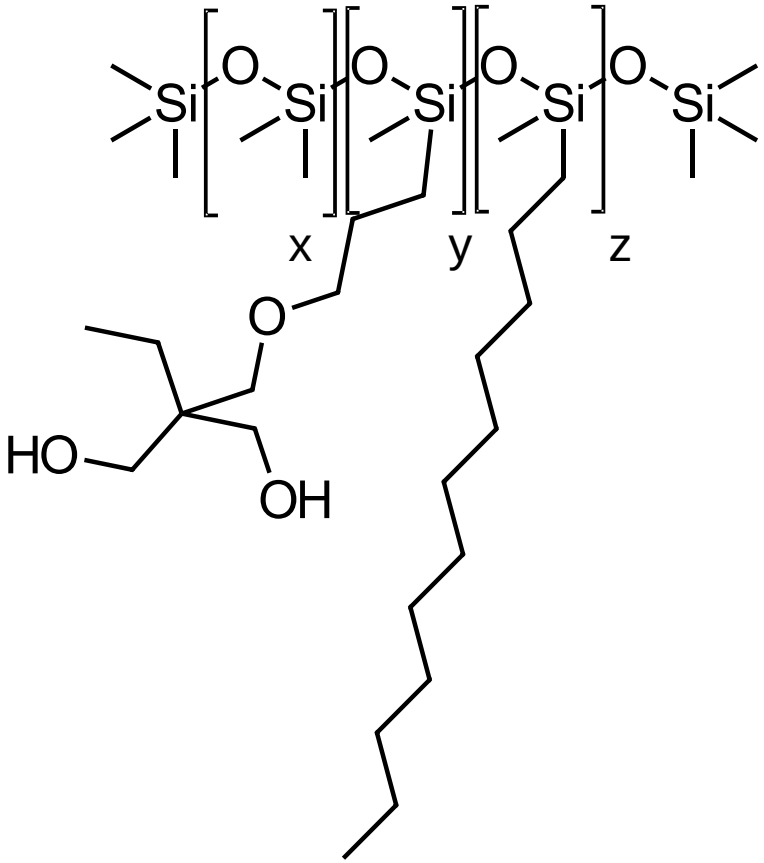
Type C with alkyl modification for emulsification
PCO series

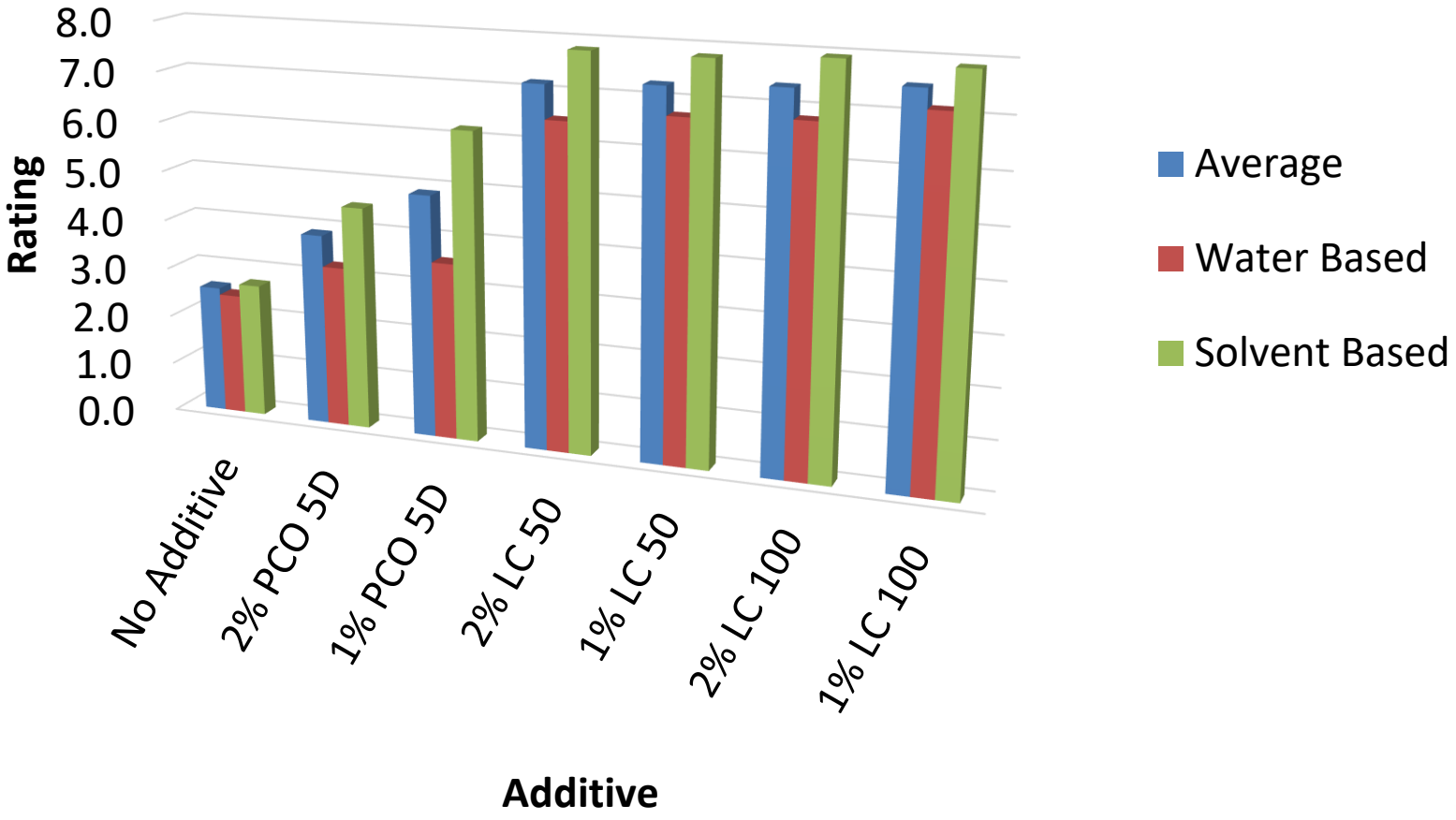


Emulsification properties poor without additional polymer modification and linear not as good as pendant.

Image comparing a W/O emulsion of FC337C containing PCO 5D and emulsion FC337G containing LC 50

Anti-graffiti Ratings

Olefin required to provide emulsification, but decreases anti-graffiti performance.



Conclusions

- Non-fluoro containing organomodified silicones can perform as good or better than fluoroalkyl silicones materials.
- Many are better than the commercially available anti-graffiti additive.
- The Type C family provided the best performance.
- The main variables in anti-stain performance were:
  - Hydroxy alkyl chain
  - Linear silicones are better
  - Higher molecular weight gives better the performance.
- EO/APEO free surfactant analogs of Type C:
  - Provided very good emulsification properties, but required addition of an olefin to provide stability.
  - Did not provide comparable anti-stain performance, likely due to the additional alkyl modification.

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Thank You

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