Novel OrganoSilicone Fluoro-Free Anti-Graffiti Agents

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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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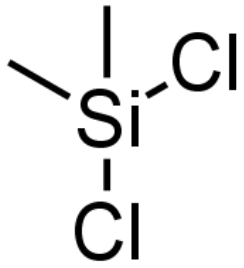
The Road from Silicon to Silicone

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

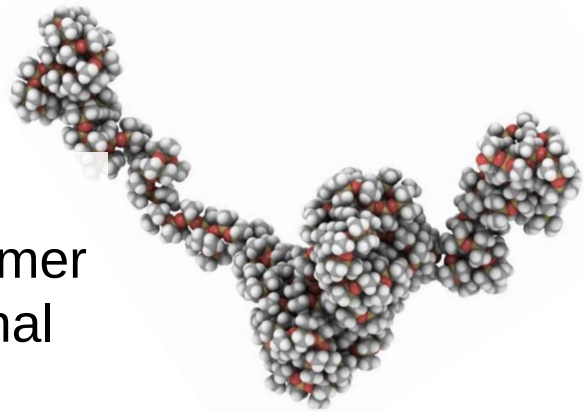
Catalysts:
From the Earth



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. It chemically degrades in the environment.

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Experimental Design and Methods:

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

Test Methods Utilized

- COF (Cheminstruments sled method)
- Gloss (gloss meter)
- Stain:
  - Two thick black marks and green marks are applied on the test panel with a Papermate permanent marker, Super Sharpie marker and Berol Liquid TIP marker. The degree of difficulty of marker to write on the coating and the degree of easiness to remove the marker from the coating are recorded. The rating is estimated by visual inspection.
  - Stain resistance is measured using hard rubbing by hand with paper towel for Marker removal dry and wet results.

Test Methods Utilized

- Mar resistance is measured using a Sutherland 2000 Ink Rub Tester with first 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 on coating. (Marker resistance with weighting factor = 0.4)
  - Degree of difficulty to remove black marks without damaging the coating, (Marker removal with weighting factor=0.4)
  - Mar and stain resistance according to the aforementioned procedure (Mar resistance with weighting factor = 0.2)
  - Visual inspection

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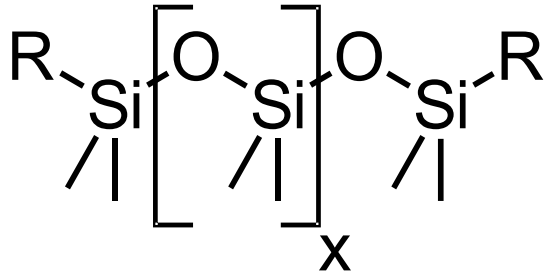
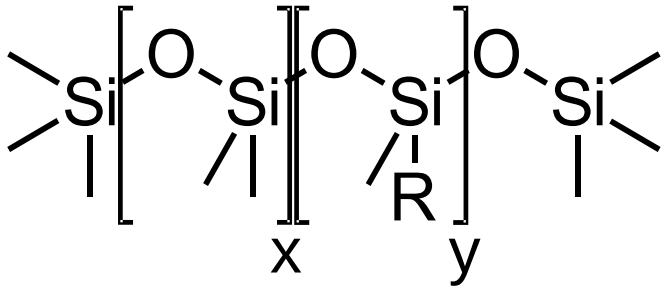
Organosilicones

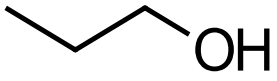


Linear

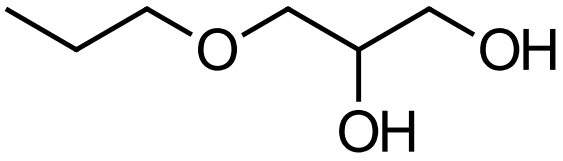


Pendant

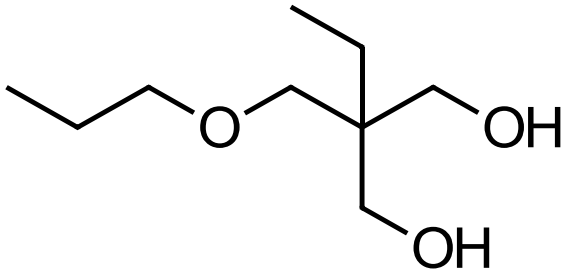
Type A: R=



Type B: R=



Type C: R=



Products 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	
Bayhydrol A145	54.55%	Desmophen A870 BA	31.84%
Surfynol 104 DPM	1.30%	Desmophen VPLS 2388	21.19%
Borchigel PW 25	0.19%	Dabco T-12 (Durastab LT-2)	0.05%
Water (Distilled)	23.23%	n-BA (used Tert Butyl Acetate)	5.72%
Subtotal	79.28%	PMA (Glycol Ether PM Acetate)	7.62%
Part B		EEP (Ester EEP)	9.14%
Desmodur I	9.32%		
Bayhydur VP LS 2150/1	7.24%	Part B	
Exxate 600	4.15%	Desmodur N-3390A BA/SN	24.45%

- #10 wire wound rod on Aluminum Q-panels.
- 110°C for 60 minutes to effect curing.
- Conditioned at ambient for a minimum of 24 hrs.

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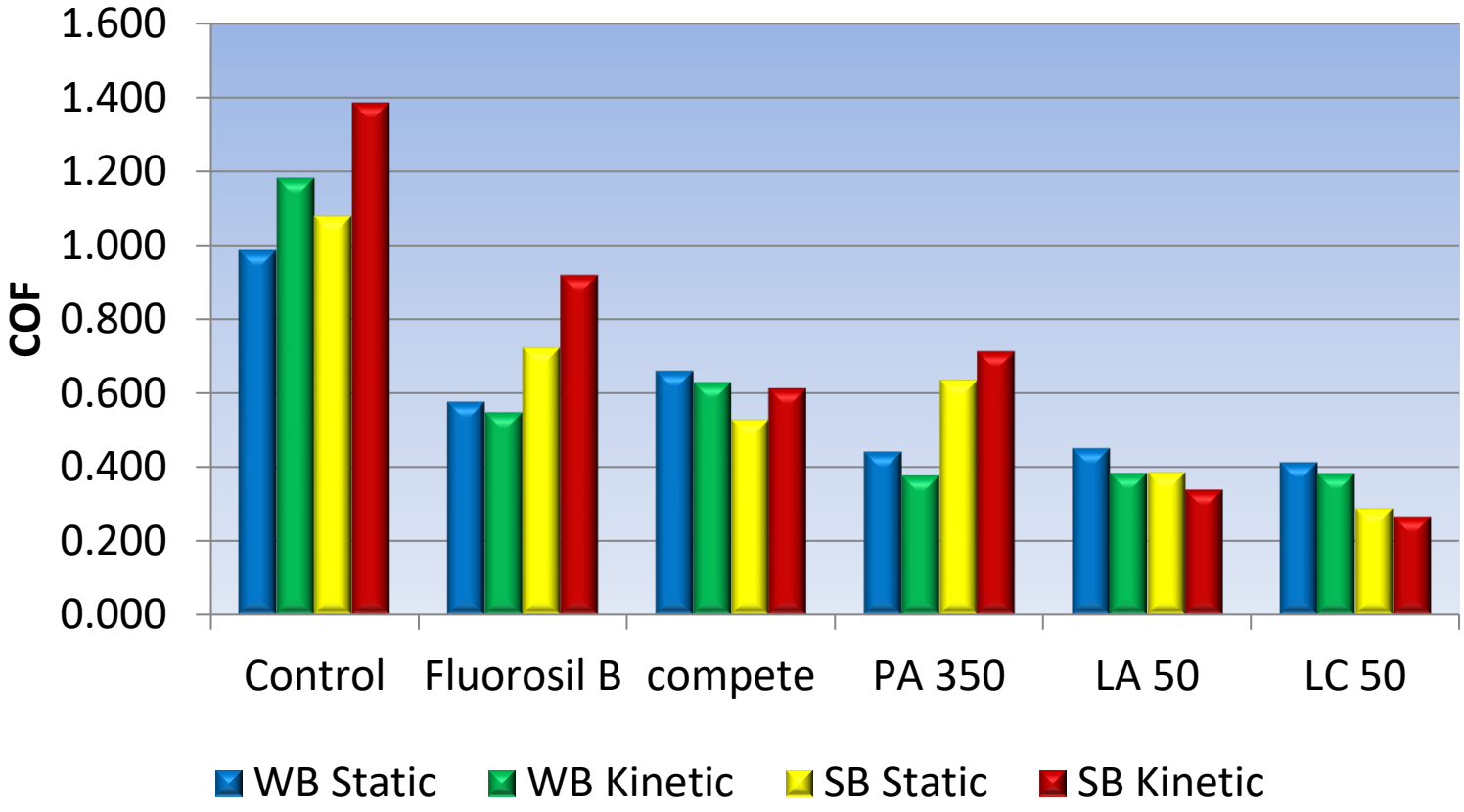
COF Reduction Screen



Type A and Type C are all better than both controls

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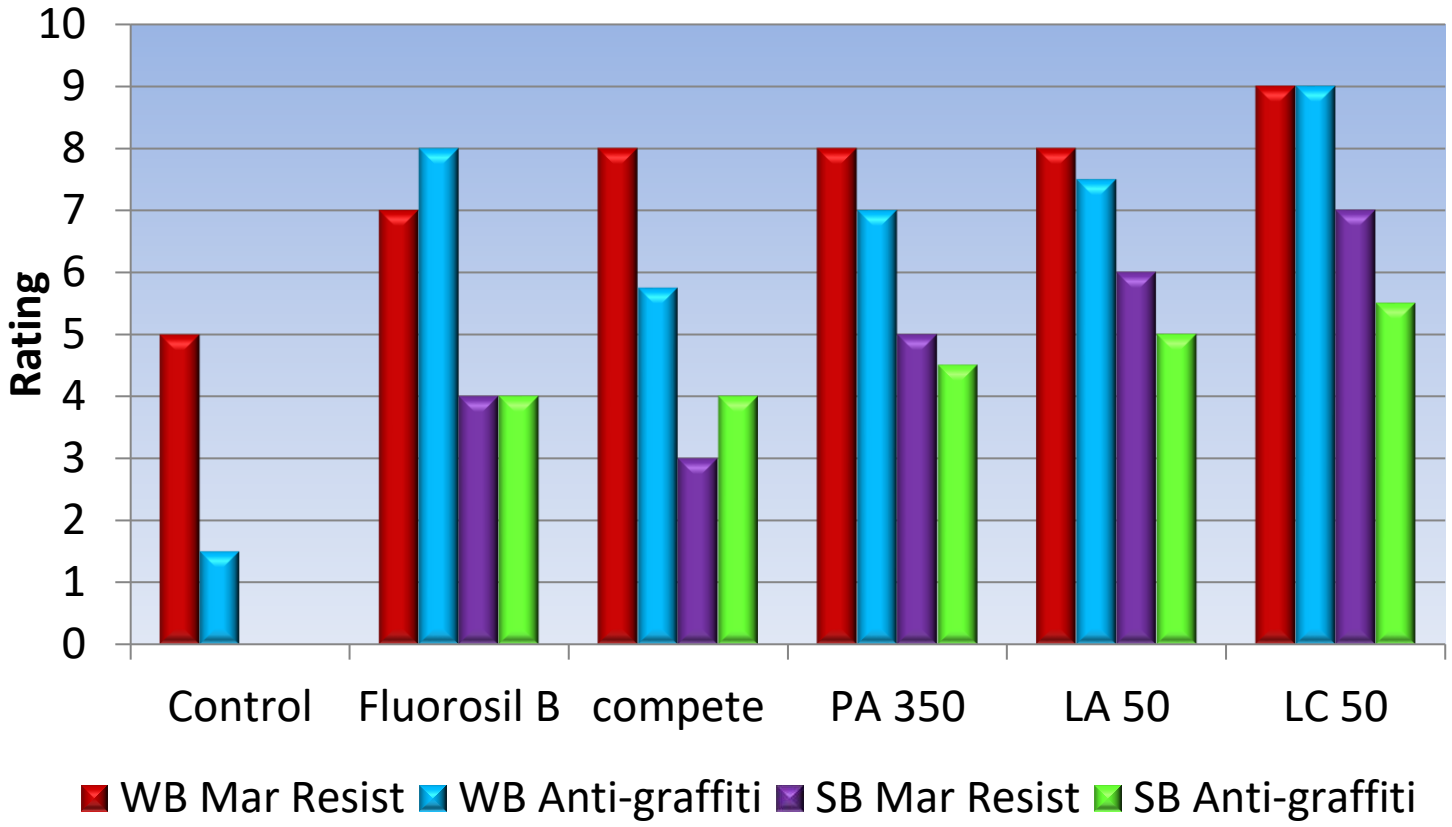
Resistance Screen



Type A and Type C are all better than both controls

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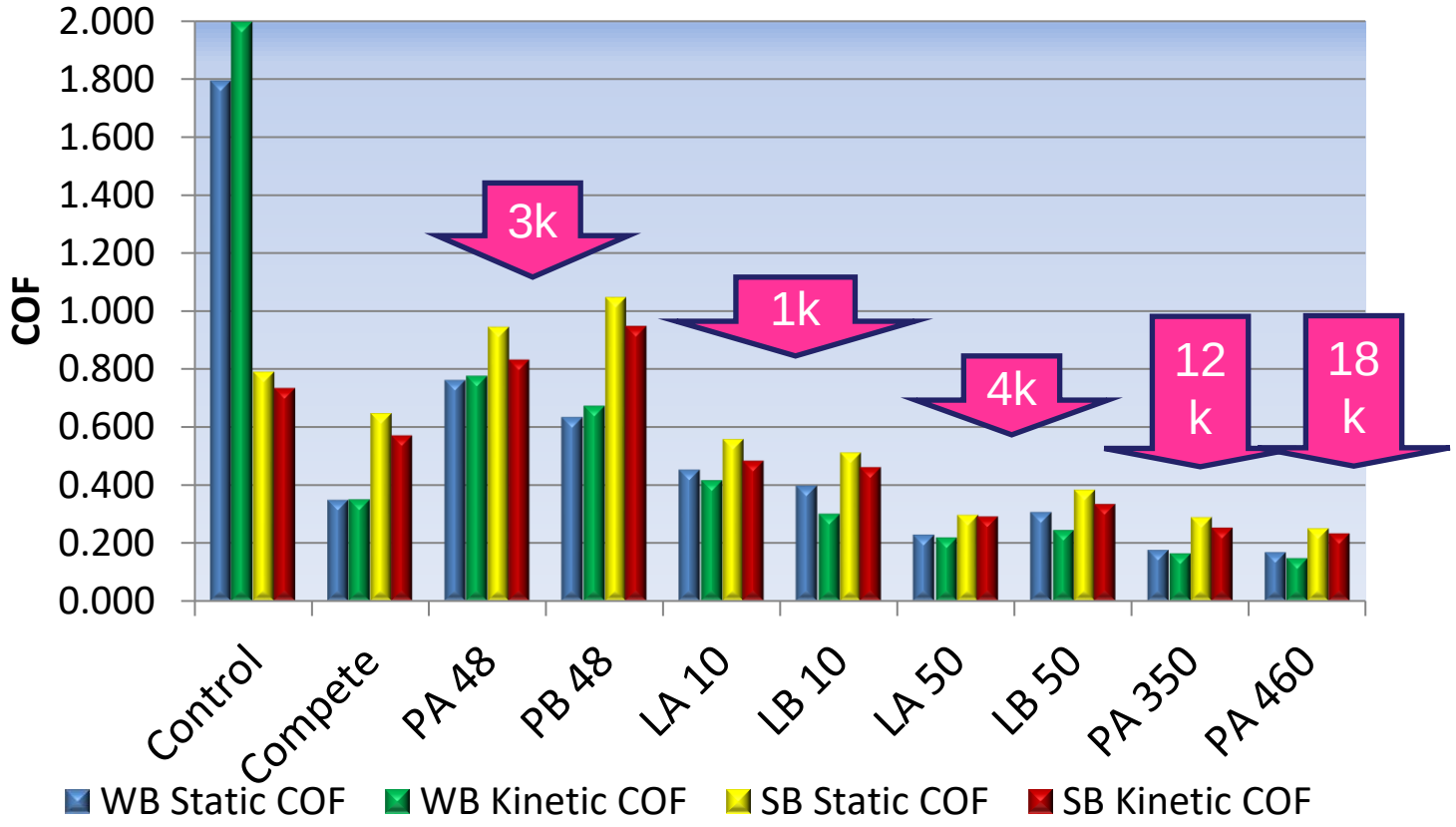
COF Reduction 1%



All are better than control

Pendant < Linear

LA 50 and higher MW are better than compete

Type A and Type B are similar

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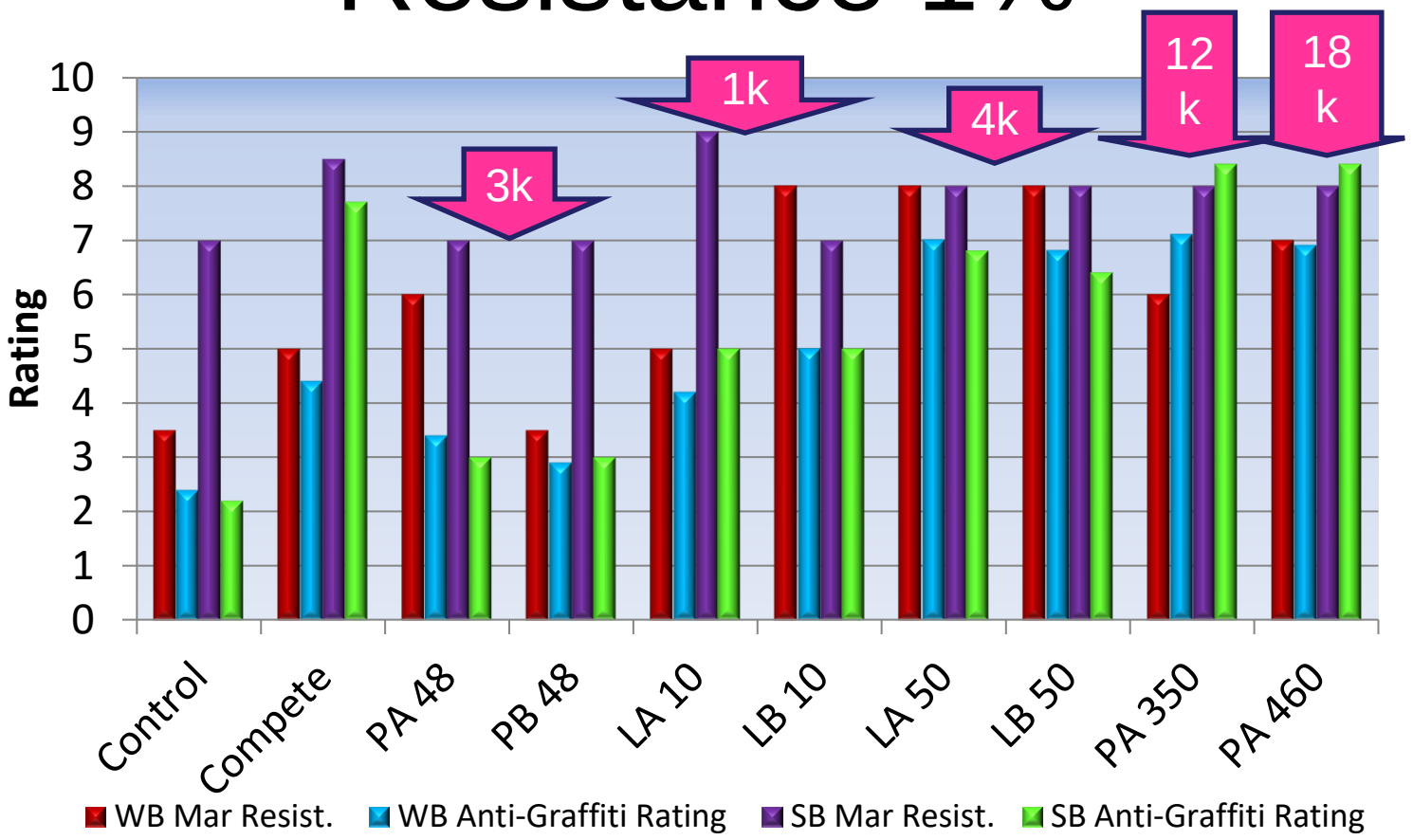
Resistance 1%



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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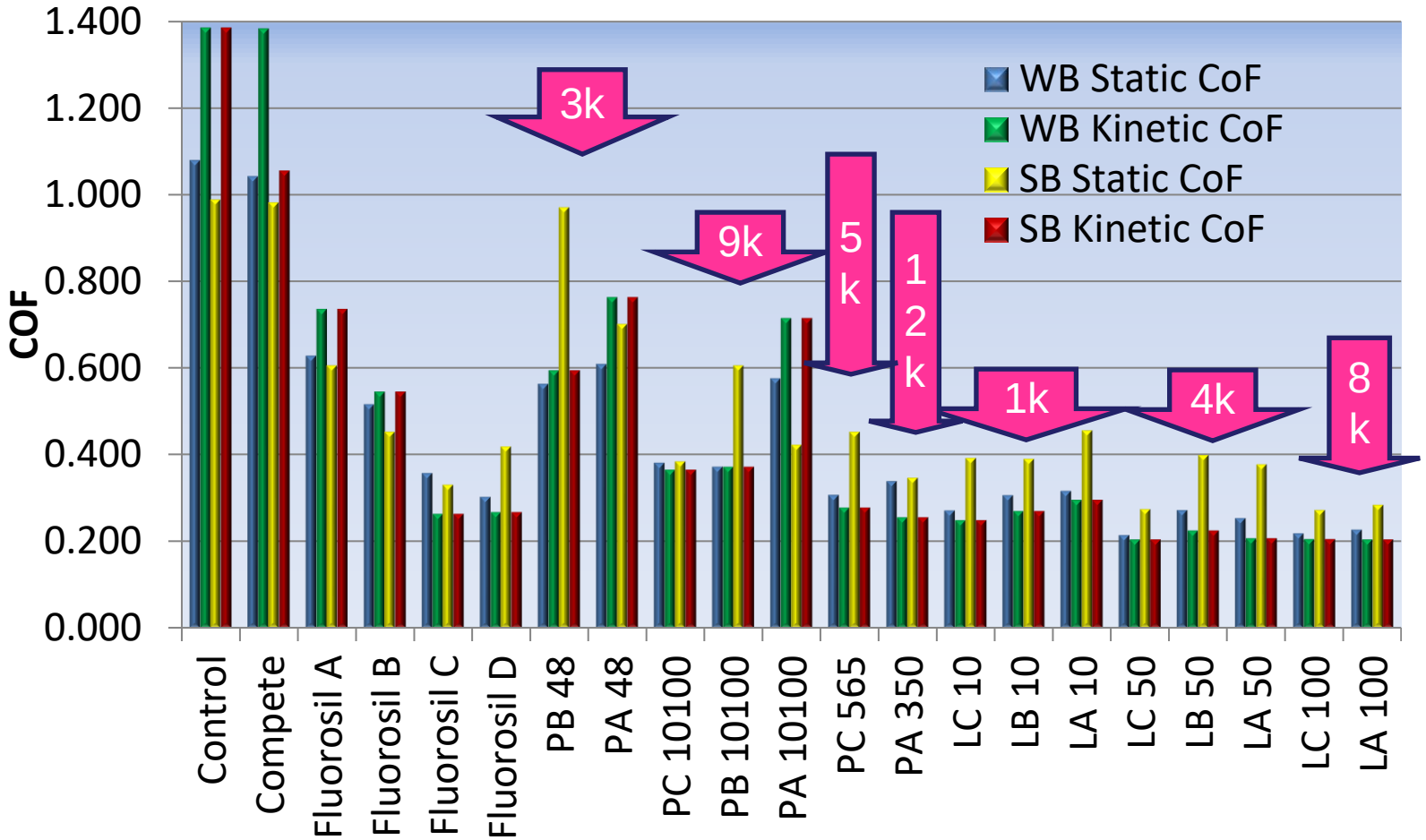
2% Additive COF



All are better than compete

Some are as good as best Fluorosil

Type C > Type A >~ Type B

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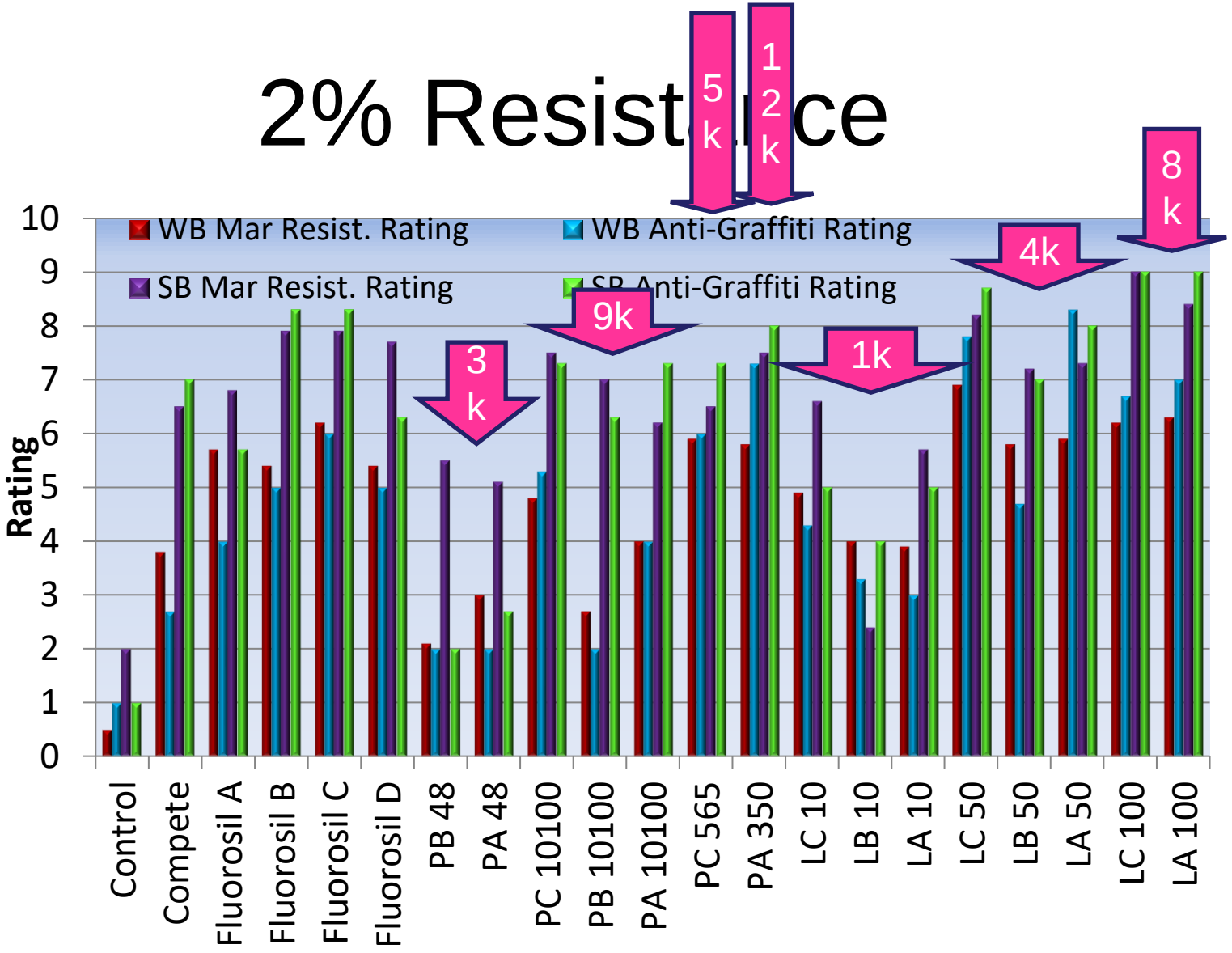
2% Resistance



Best silicones are linear and high MW

Types make a small difference

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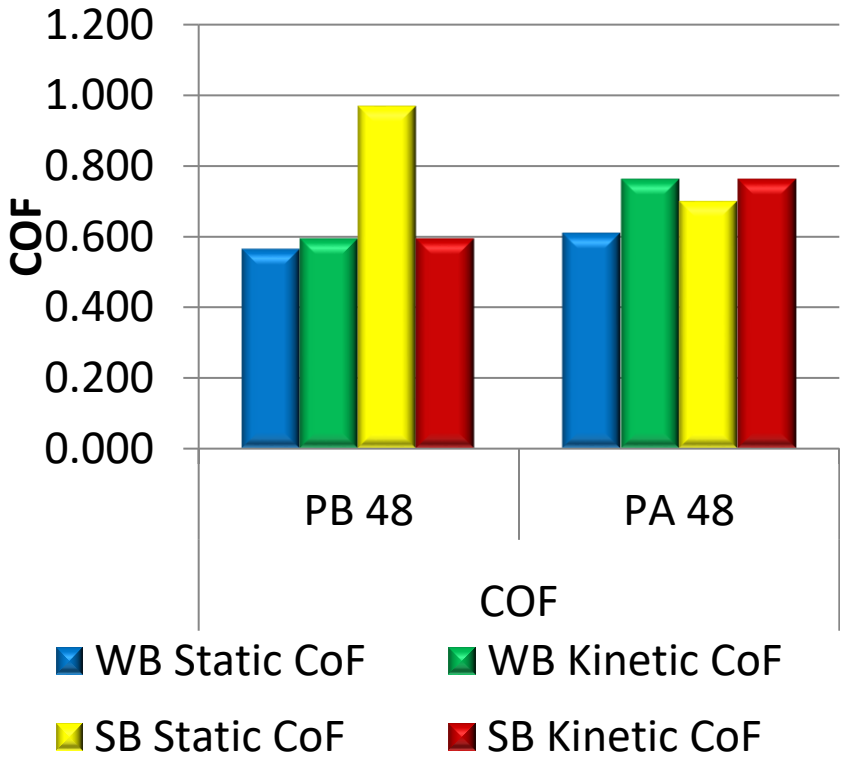
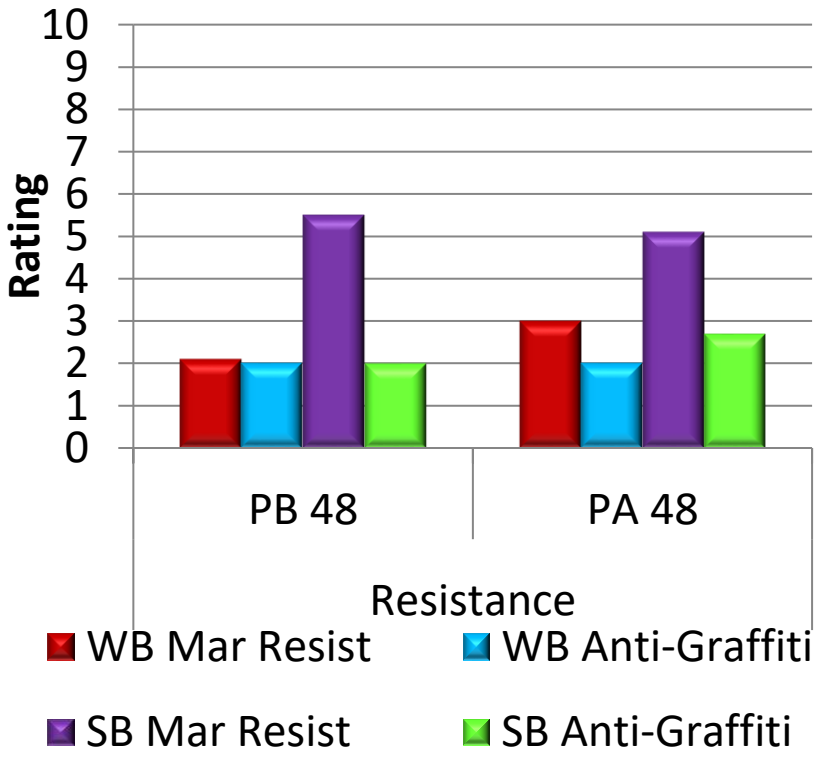
Details Pendant 3000 MW





PA 48 > PB 48

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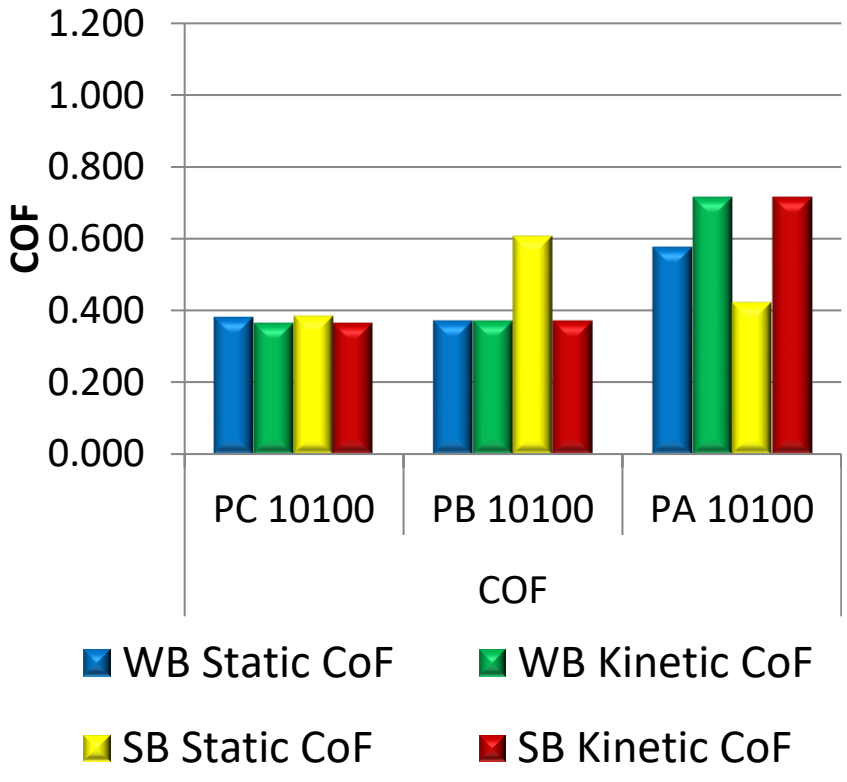
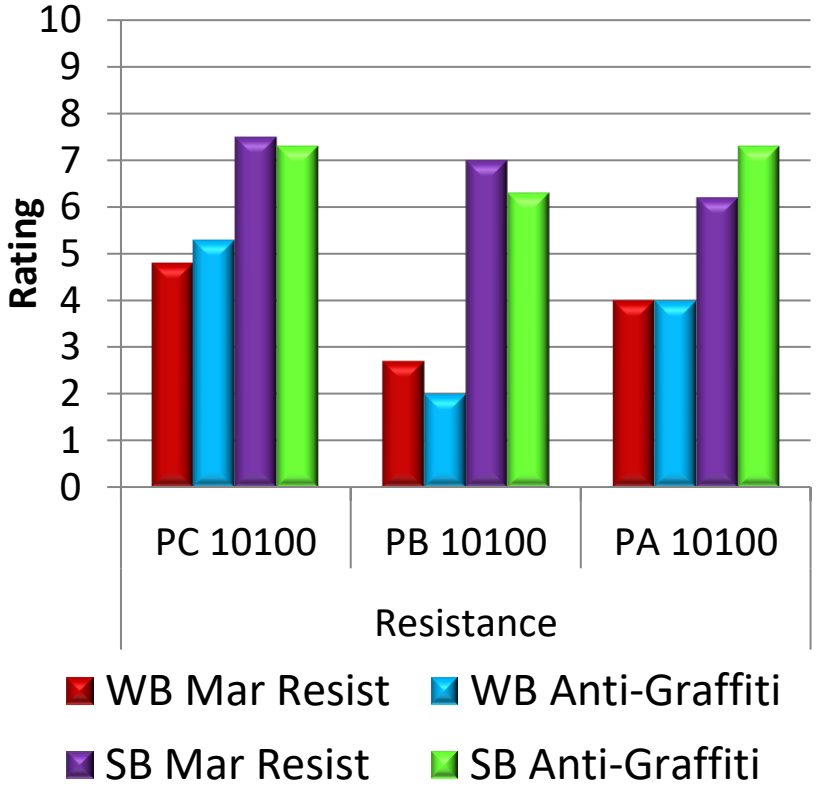
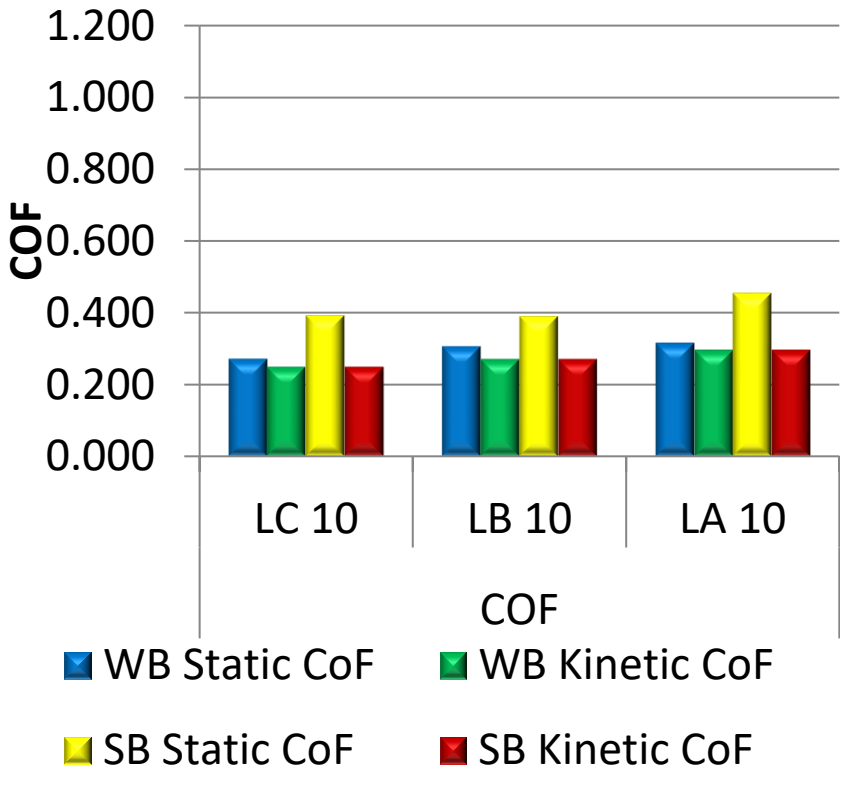
Details Pendant 9000 MW

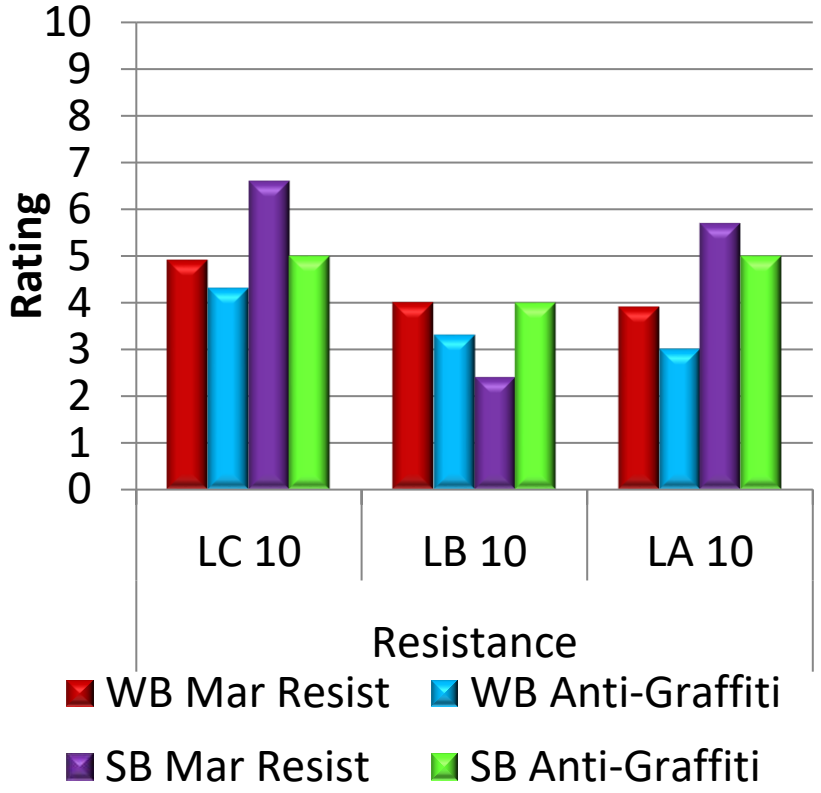




PC 101000 > PA 101000 > PB 101000

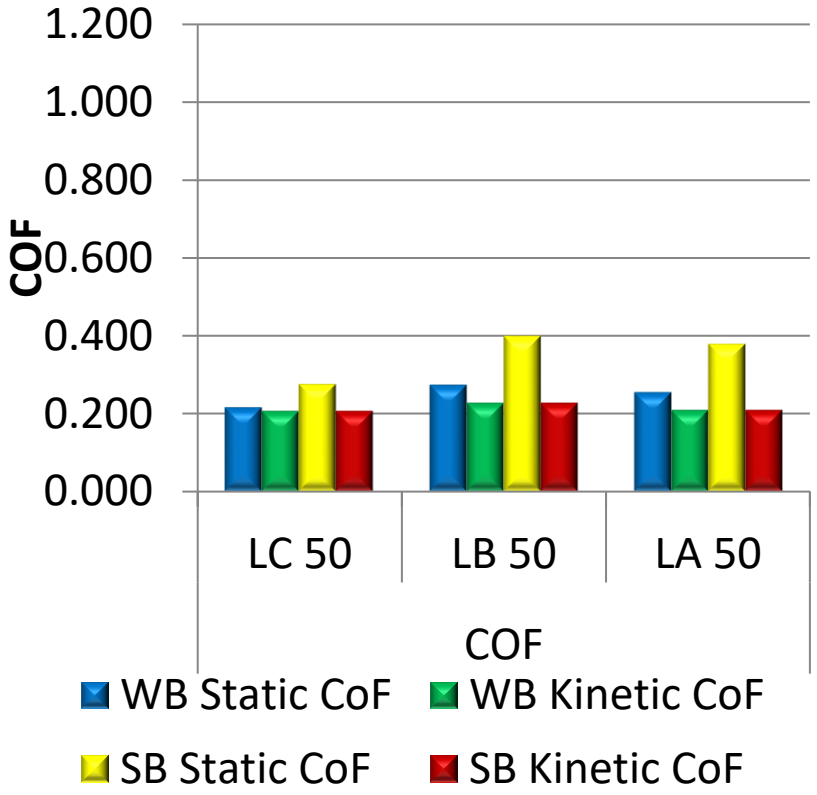
Details Linear 1000 MW

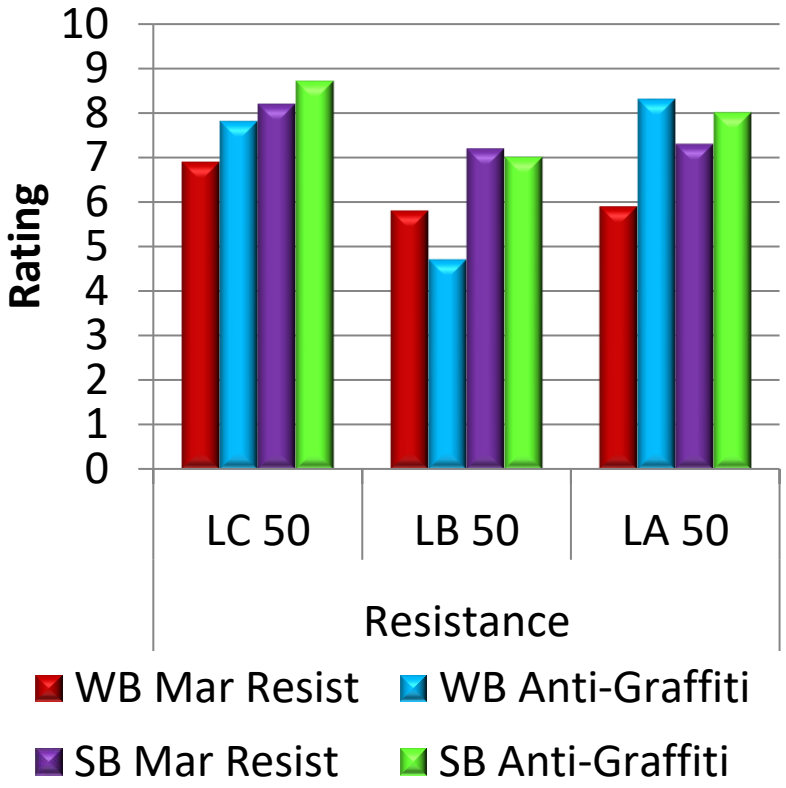




LC 10 > LA 10 ~ LB 10

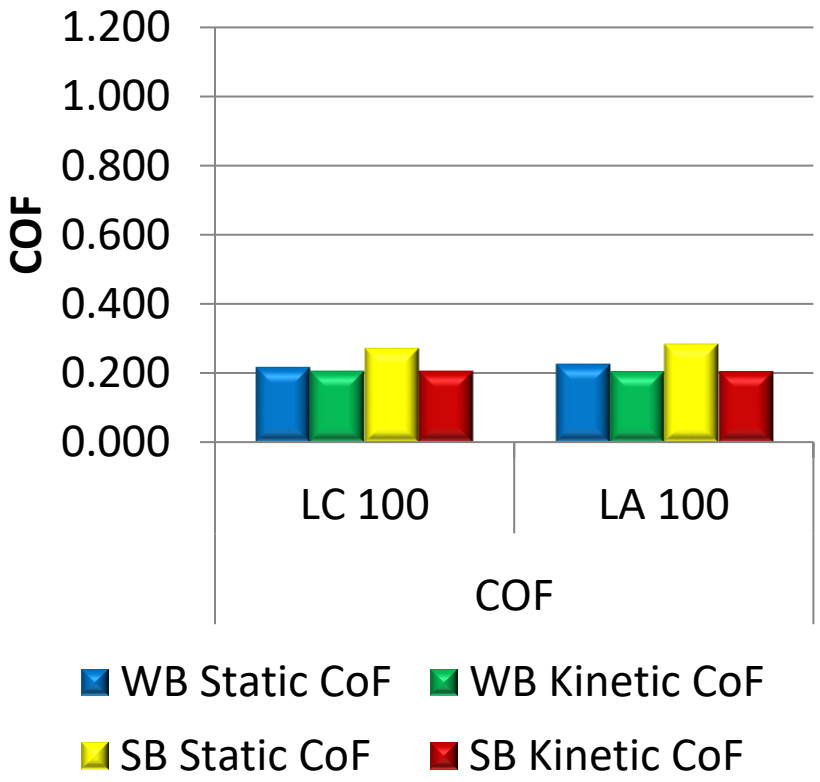
Details Linear 4000 MW

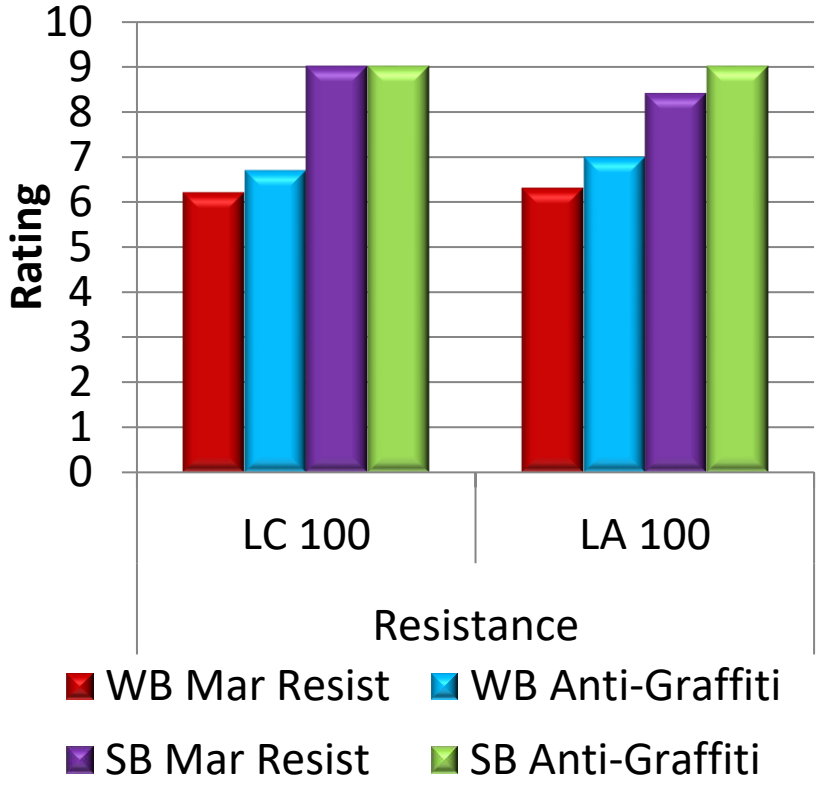




LC 50 > LA 50 > LB 50

Details Linear 8000 MW





LC 100 ~ LA 100

Conclusions

- Non-fluoro containing organomodified silicones can perform as good or better than fluoroalkyl silicones materials.
- Many are better than the commercially available silicone.
- Type B is not a strong player.
- The Type C family is much more interesting.
- The main variables in anti-stain performance were:
  - Linear silicones are better
  - Higher molecular weight gives better the performance.
  - Hydroxy alkyl chain

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Thank You

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