Fluorosilicone Addition in Coating Films- impact on physical properties and application testing

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

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Comparison of selected properties of Silicone and Fluoropolymers

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.)
✓ Often effective at low use levels	✓ Often effective at low use levels

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Experimental Design and Methods:

- The overall design used five systems:
  - *SB Urethane*
  - *Urethane acrylate*
  - *Epoxy acrylate*
  - *Cationic UV cured epoxy silicone*
  - *Commercial Paint (post addition)*
- Various silicones are evaluated for slip, COF, defects and mar, stain, and fingerprint and chemical resistance.

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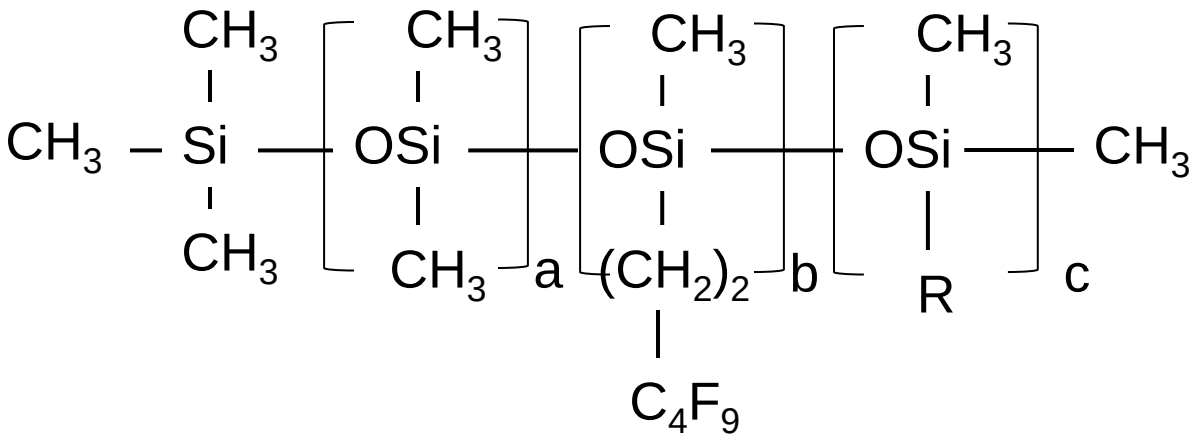
Test methods utilized

- 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)

Copolymer Variations



	c	b	R
FPE	>0	>0	$(CH_2)_3(OC_2H_4)_d(OC_3H_6)_e$ OH
FS	0	>0	n/a
AF	>0	>0	$C_nH_{(2n)}$ R' (R = acrylate, etc.)
AS	>0	0	$C_nH_{(2n)}$ R' (R = acrylate, etc.)

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Example details on copolymer design

	Wt % Silicone	Wt % CF_2	Wt % organic	Reactive Site	Water Miscible	MW	Type
2010	38%	7%	55%	OH	1%	3000	fluoroalkyl polyether silicone
2110	33%	3%	64%	OH	10%	7000	
D2	56%	44%	0%	no	no	2000	fluoroalkyl silicone
J15	86%	14%	0%	no	no	14000	
OH G2-F	57%	41%	2%	OH	no	3000	alkyl, fluoroalkyl silicone
OH C7-F	81%	17%	2%	OH	no	2000	
ACR OH C7-F	81%	17%	2%	ACR	no	2000	
H418	63%	16%	21%	no	no	5000	
OH C50	98%	0%	2%	OH	no	12000	alkyl silicone
OH J10	92%	0%	8%	OH	no	8000	

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System I: SB Urethane

Part A:	Wt%
Hydroxyl-functional polyacrylate resin	46.5%
Hydroxyl- polyester	31.0%
Silicone Additive	1.0%
catalyst	0.1%
n-BA	5.5%
PMA	7.2%
EEP	8.7%

Part B:	
aliphatic polyisocyanate resin based on HDI	A/B = 73.3/26.7

Preparation:

- 5 min after mixing, 1 mL drawn down on aluminum with a #10 rod.
- heated to 110°C for 1 hour
- Conditioned in ambient for two hours before testing.

Film Properties I: 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

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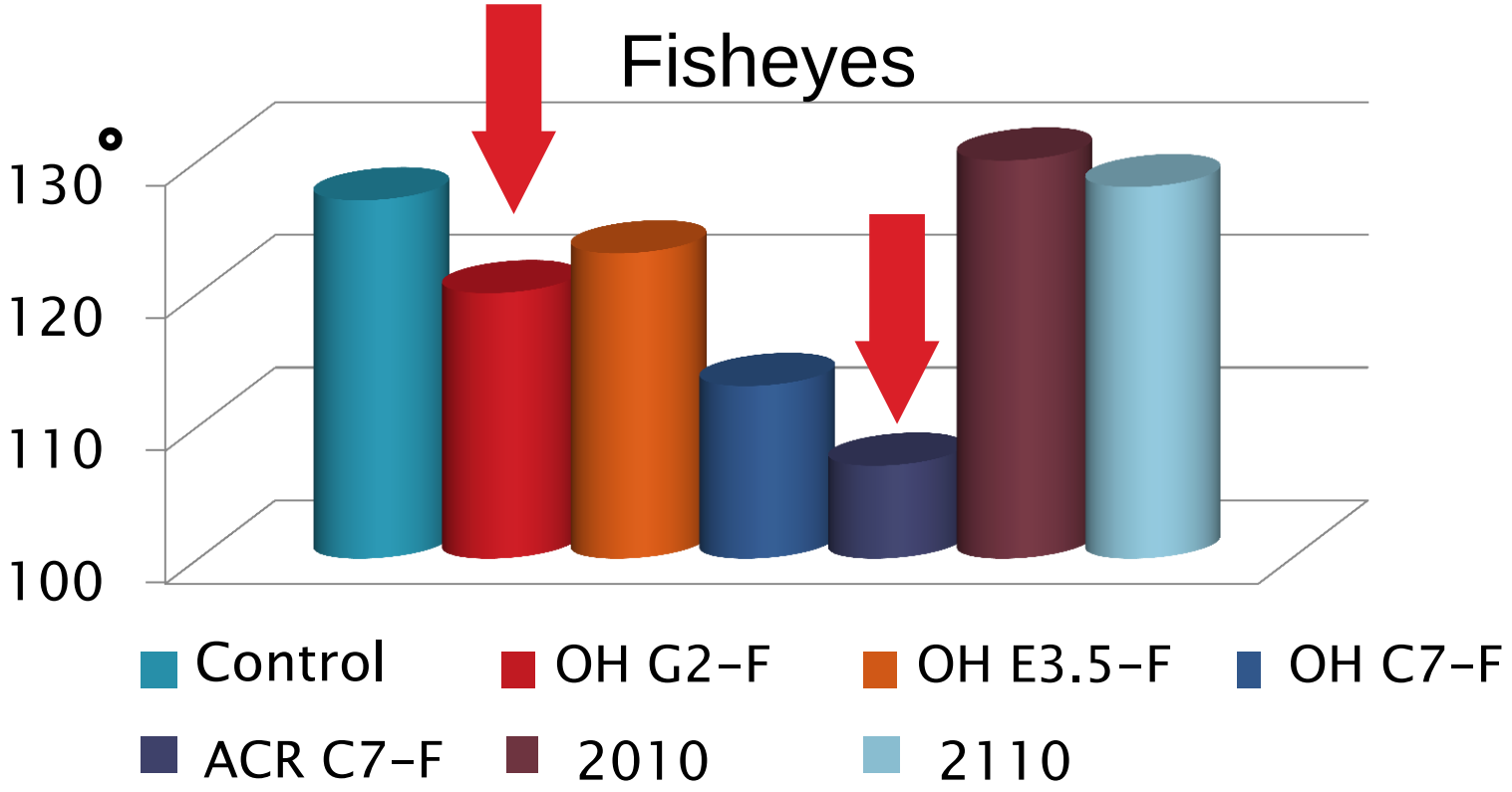
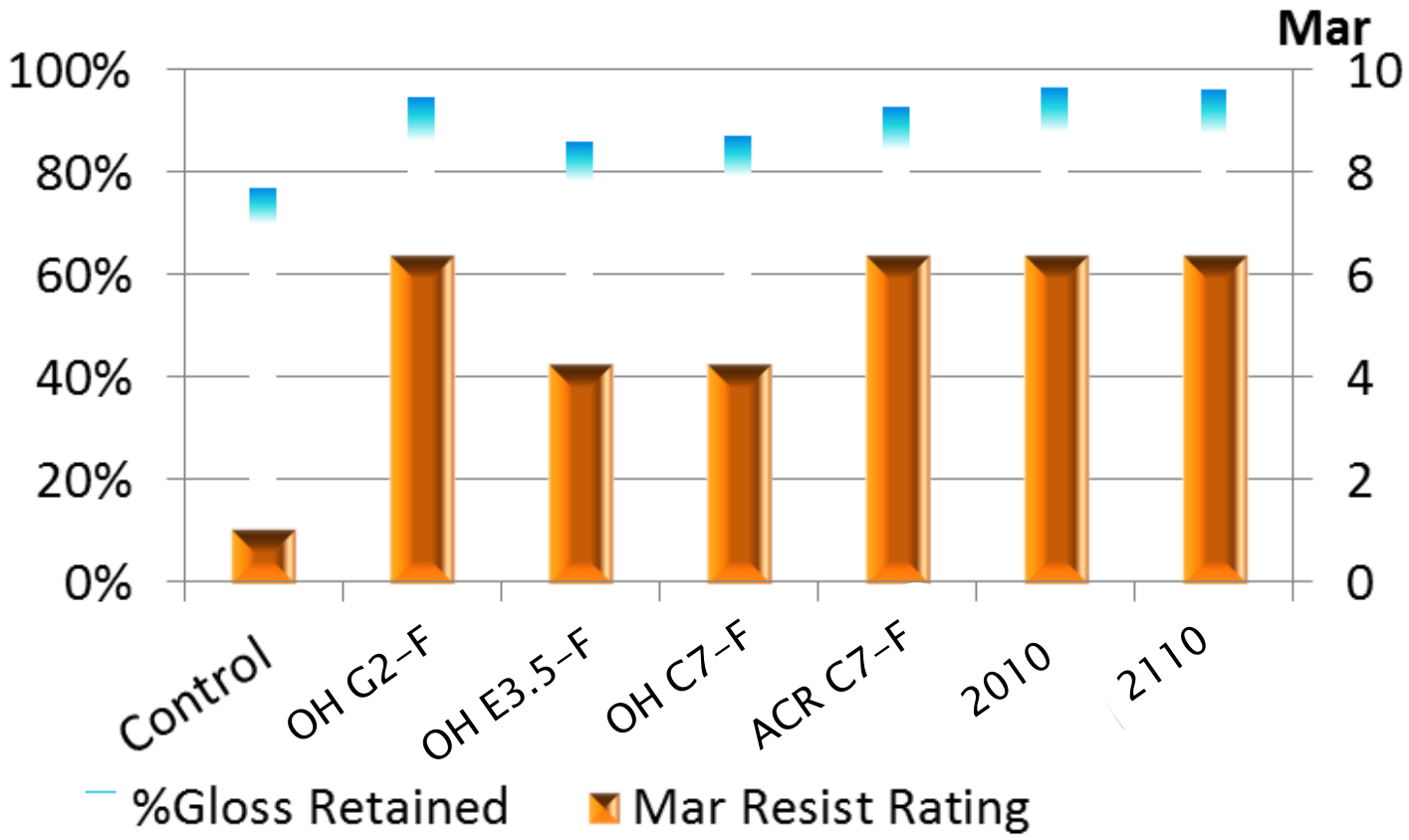
Gloss I: SB Urethane



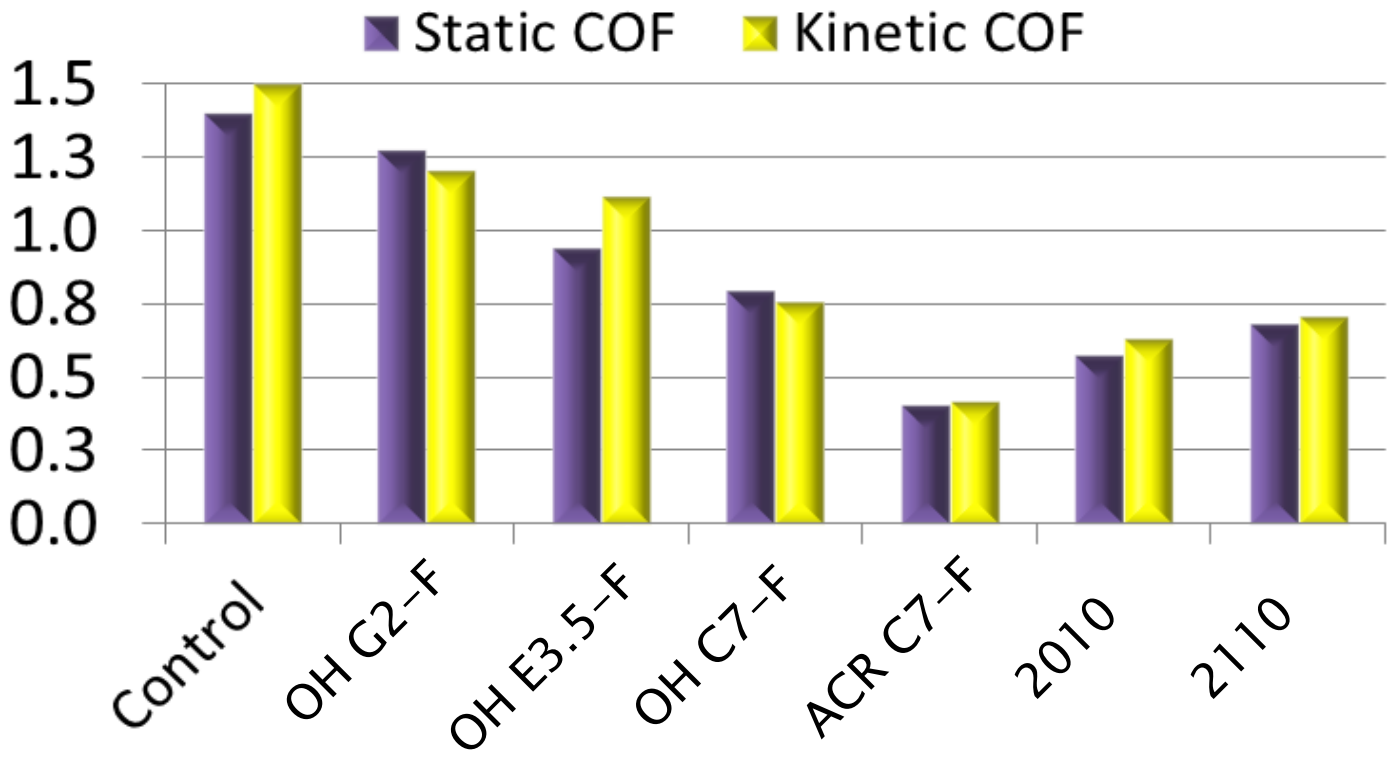
- FPE are most miscible, improve gloss
- FA type decrease gloss cause defects

Mar Resist I: SB Urethane



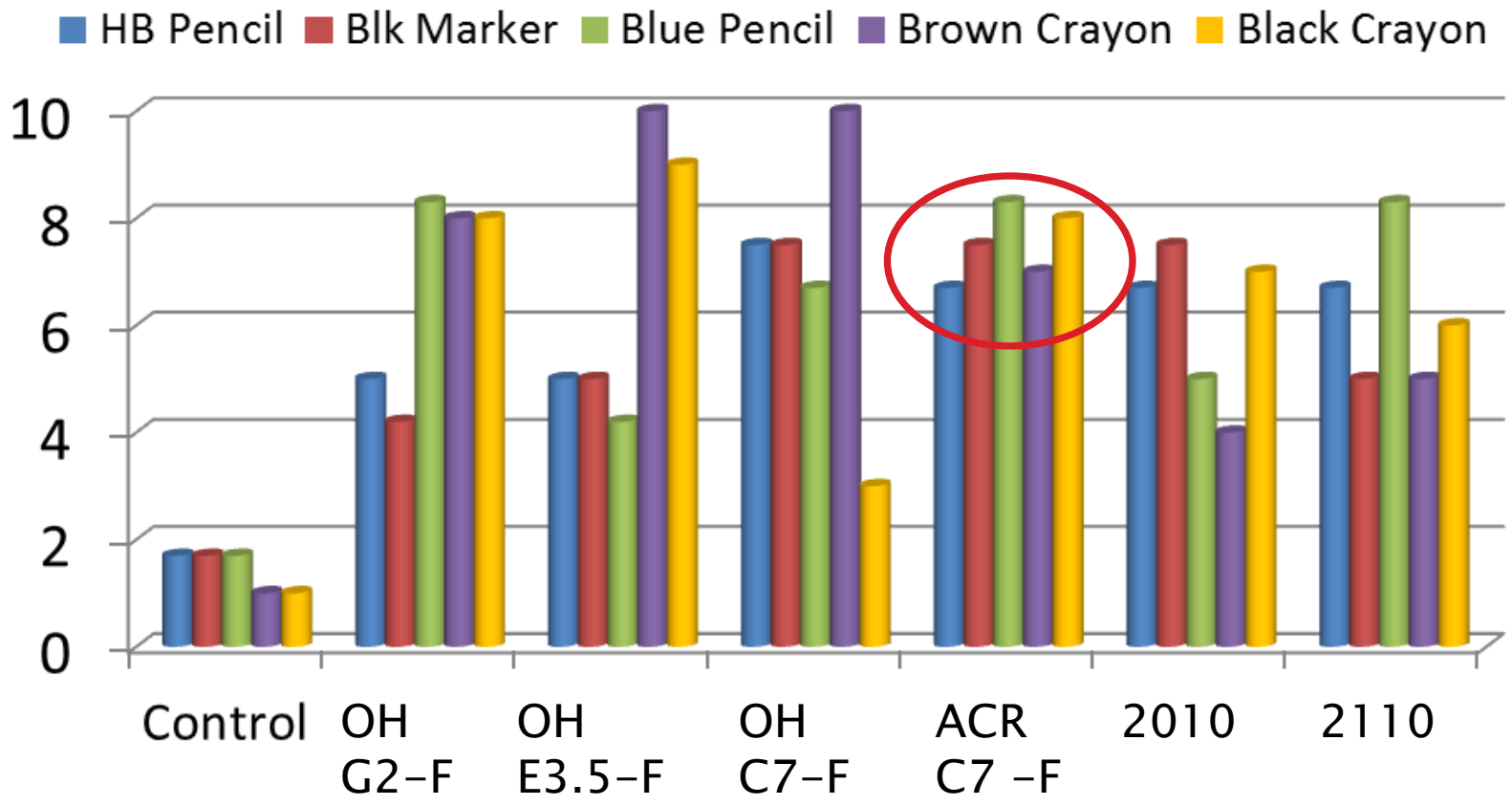
- All improve mar resistance

COF Reduction I: SB Urethane



- All improve COF
- More with > wt% silicone

Stain Resist I: SB Urethane



- OH C7-F and ACR C7-F perform well

Chemical resistance in SB Urethane

Additive (1%)	IPA	Vinegar	Soap	NH_4OH	HCl	Average	Overall Rating*
OH C7-1F	6	4	5	2	3	4	4.00
OH E3.5-1F	5	2	3	2	2	2.8	1.00
OH G2-1F	8	2	4	5	5	4.8	6.67
OH C7-2F	6	5	5	5	4	5	7.33
D5-2F	5	3	4	4	3	3.8	3.33
OH C50	8	3	4	5	5	5	7.33
OH D2	8	2	7	6	5	5.6	9.33
OH J10	7	6	6	6	3	5.6	9.33
Control	8	4	5	5	4	5.2	8.00
ACR C7-1F	8	7	6	5	3	5.8	10.00
ACR C50	7	7	6	3	2	5	7.33
OH C7-Octene	6	2	4	6	4	4.4	5.33
2010	7	3	5	1	6	4.4	5.33
2110	6	1	4	3	2	3.2	2.00

Low addition rate (1%) did not provide much chemical resistance

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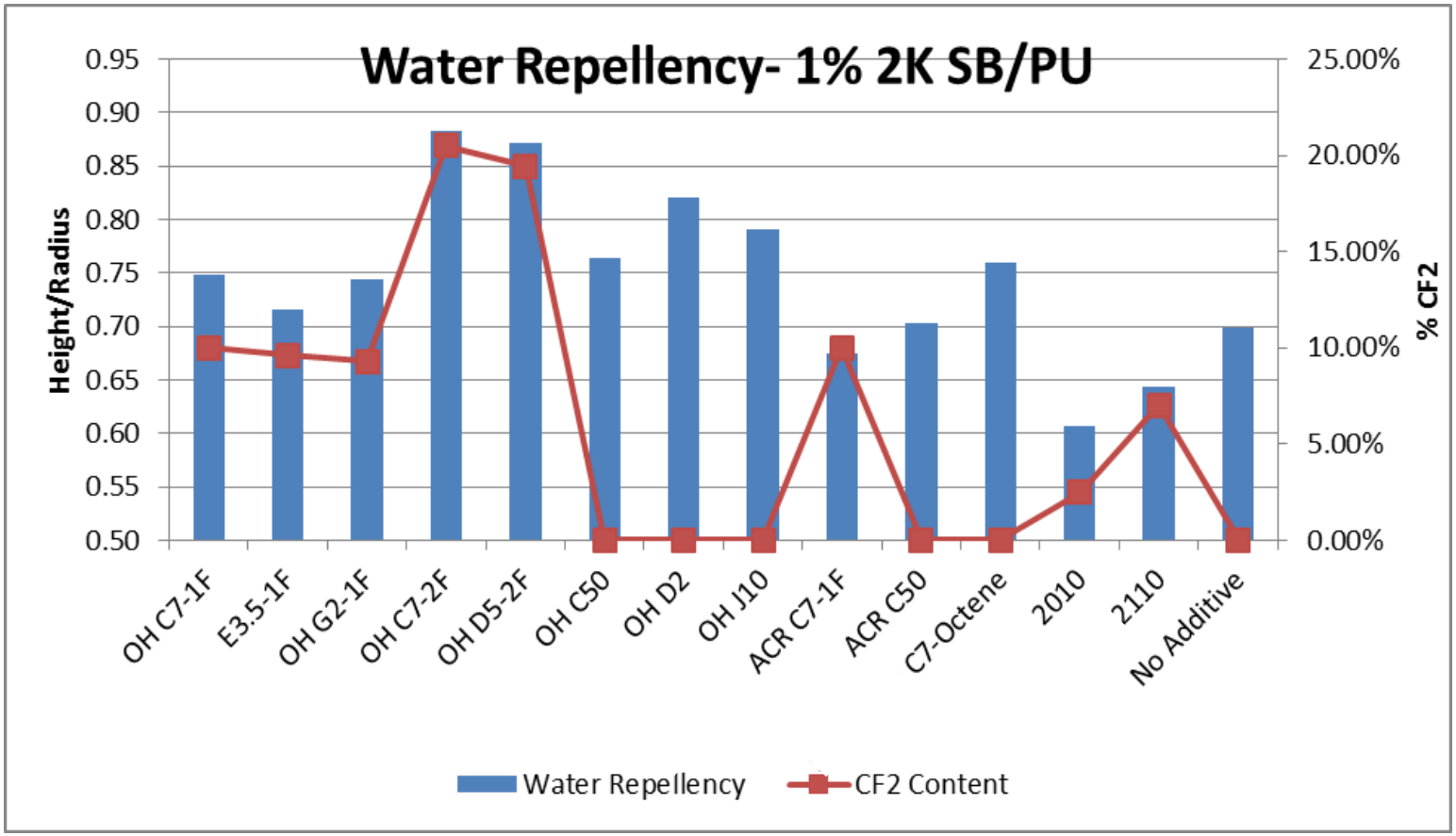
Water repellency as a function of Fluoro (%CF2) content



Series I – SB Urethane

- Based on gloss and defects the FPE type are most compatible. They are also among the best for slip and mar resistance.
- The very incompatible FA types are not as effective as expected for slip and mar.
- ACR C7-F is very good for stain, COF, and Mar, even over OH C7-F
- Chemical resistance was only marginally improved and often even reduced in this system.
- Water repellency can be improved with high flouro content but even without fluoro.

System II: Urethane acrylate

Component	Wt%
Aliphatic urethane acrylate oligomer	74.26%
Di-trimethylolpropane tetraacrylate	4.95%
Photoinitiator	4.95%
Silicone additive	0.99%
Butyl Acetate	3.71%
Toluene	3.71%
Methyl Isobutyl Ketone	4.46%
Methyl Ethyl Ketone	2.97%

Preparation:

- 0.5 ml is drawn on white Leneta Chart paper with a #5 rod
- Cured for 1 hour using 15 watt UVP at a distance of 3"

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Film Properties II: Urethane

	60° Gloss	Stain Resist	Mar Resist	Static COF	Kinetic COF	Finger Print Resist	Surface Appearance
Control	93.2	1.7	1.0	1.99	2.18	0.5	Some craters
D2	54.6	4.0	6.0	0.93	0.93	4.5	Patches
J15	76.5	6.7	5.8	1.37	1.26	6.0	Patches
2010	92.4	7.6	5.9	1.25	1.56	2.0	Smooth
2110	92.9	7.6	6.8	1.31	1.34	2.0	Smooth
ACR C7-F	68.3	8.3	8.2	0.58	0.56	5.5	Smooth
H418	79.5	5.0	7.2	0.78	0.76	5.0	Wavy

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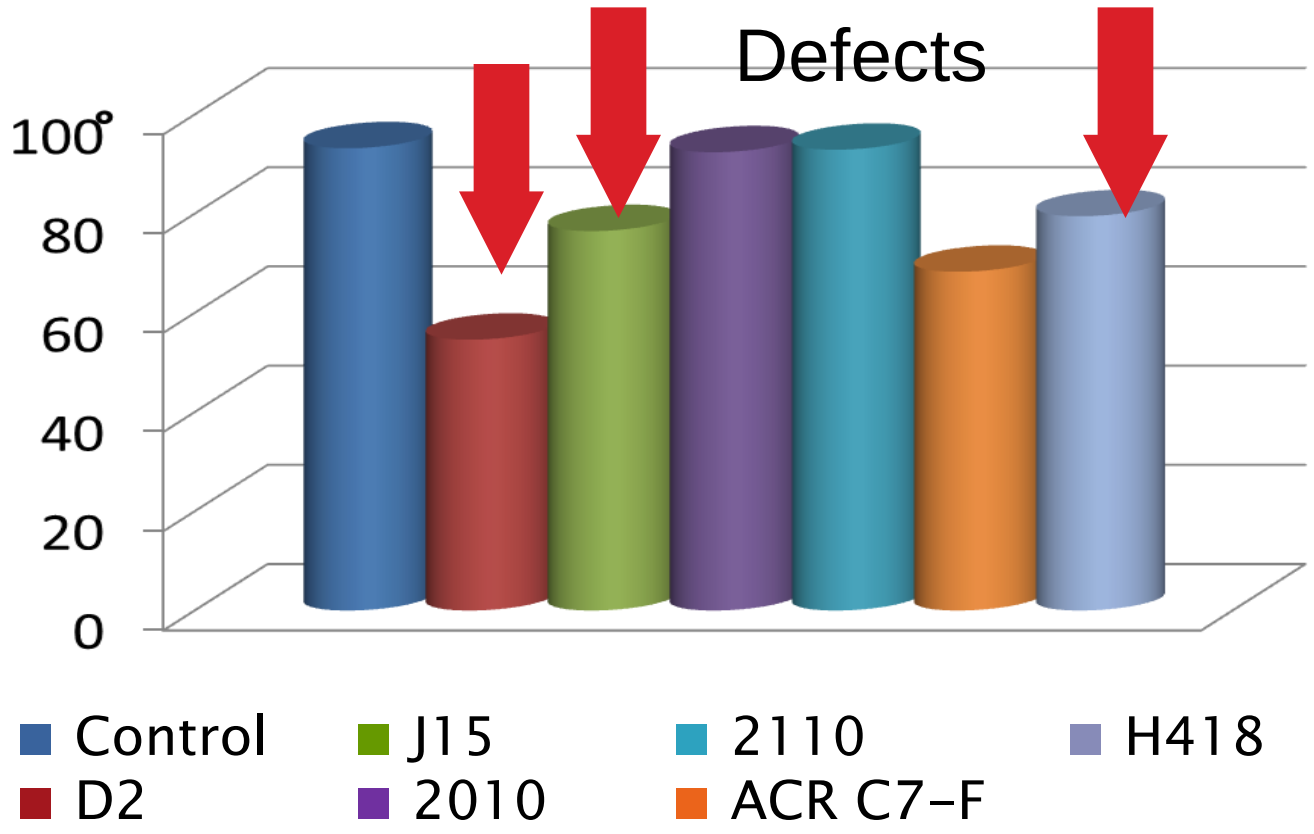
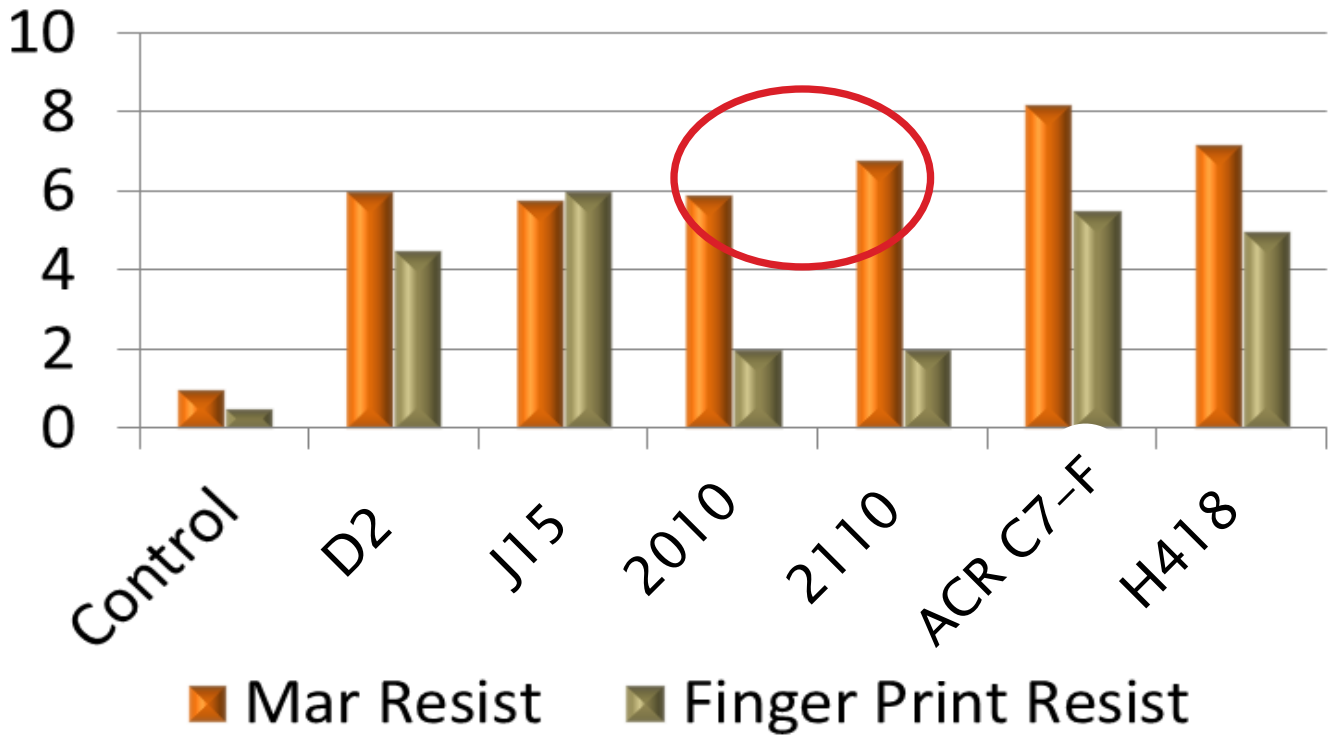
Gloss II: Urethane Acrylate



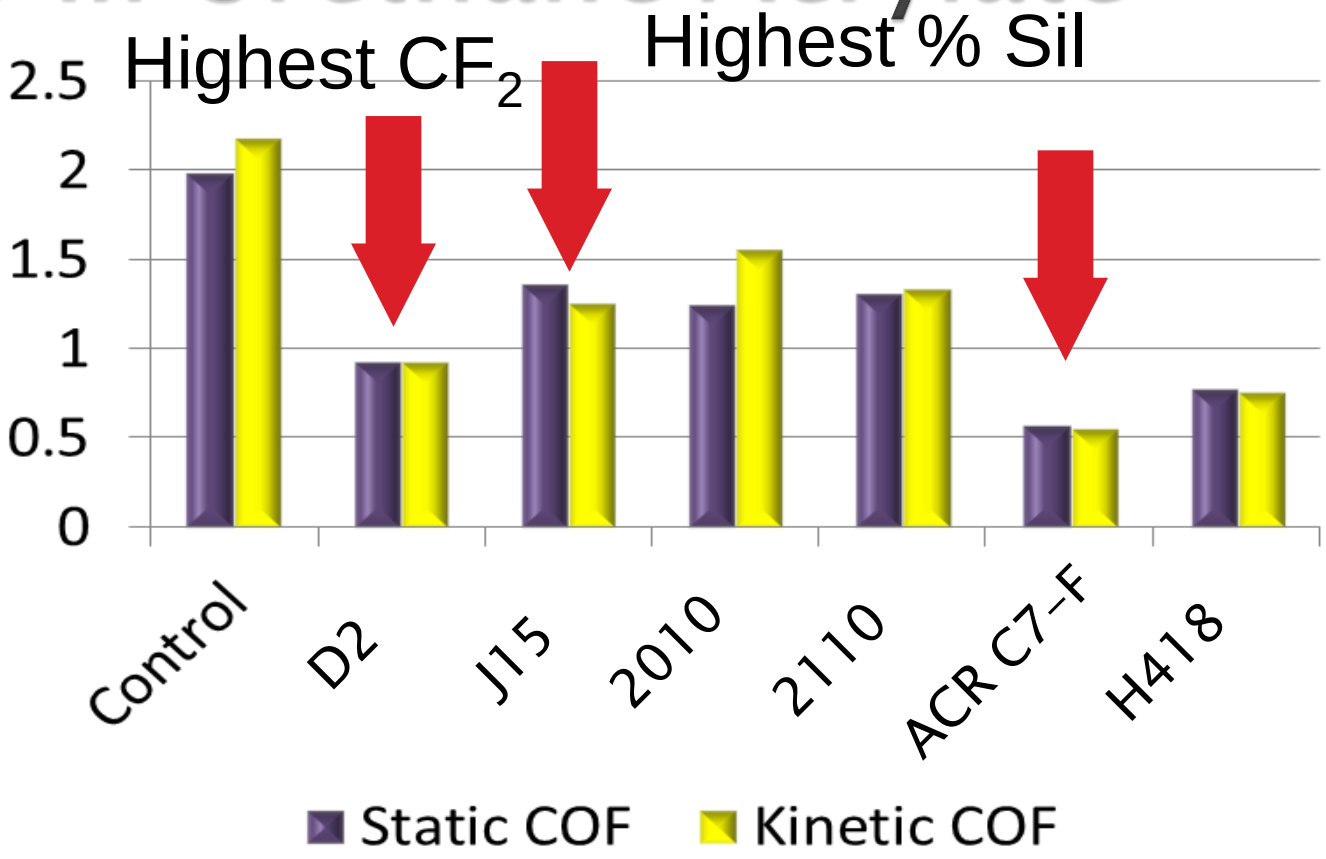
- FPE are most miscible, keep gloss
- FA and FS types decrease gloss

Mar/ Finger Print II: Urethane



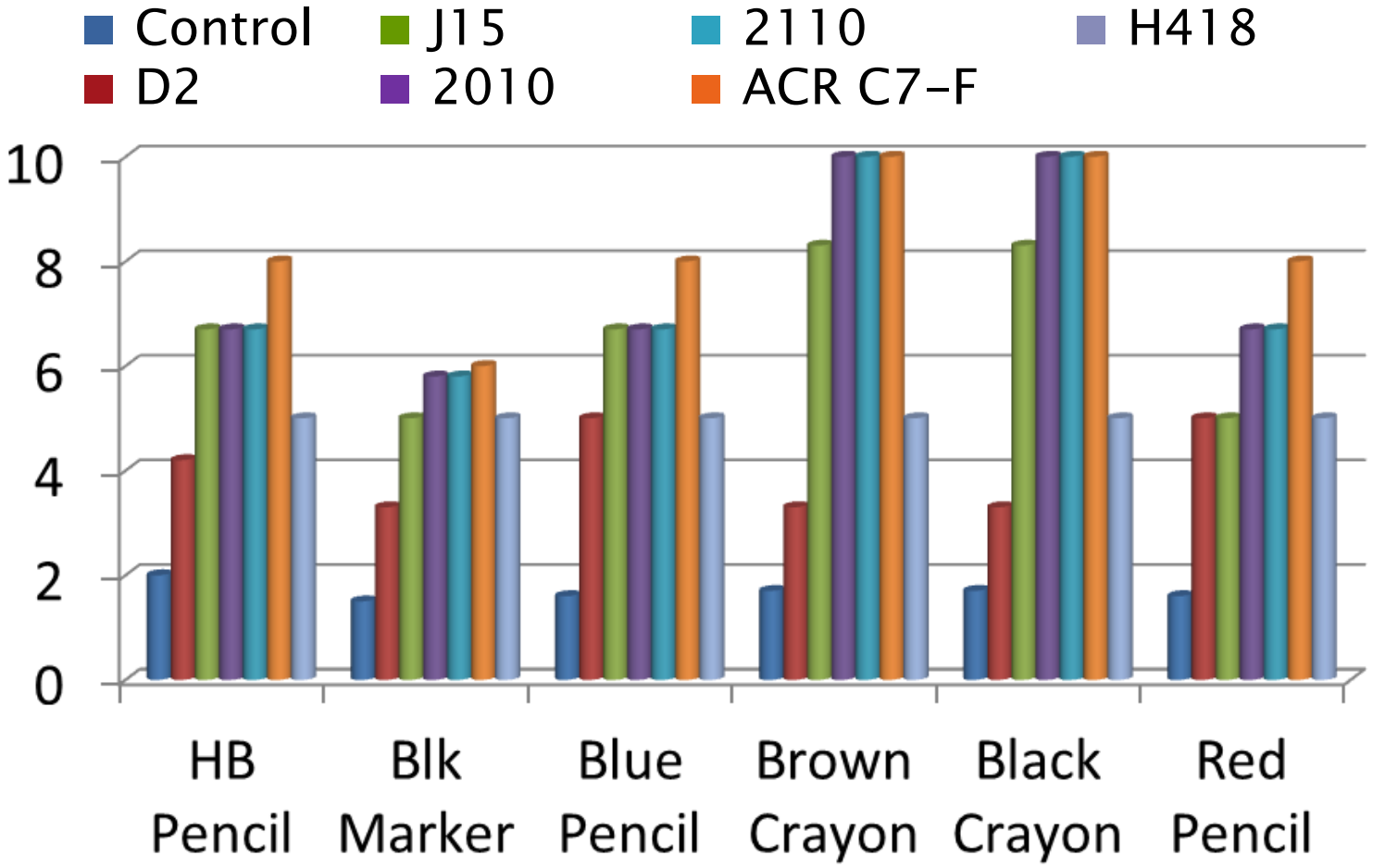
- All improve mar resistance
- All improve anti-finger print

Slip II: Urethane Acrylate



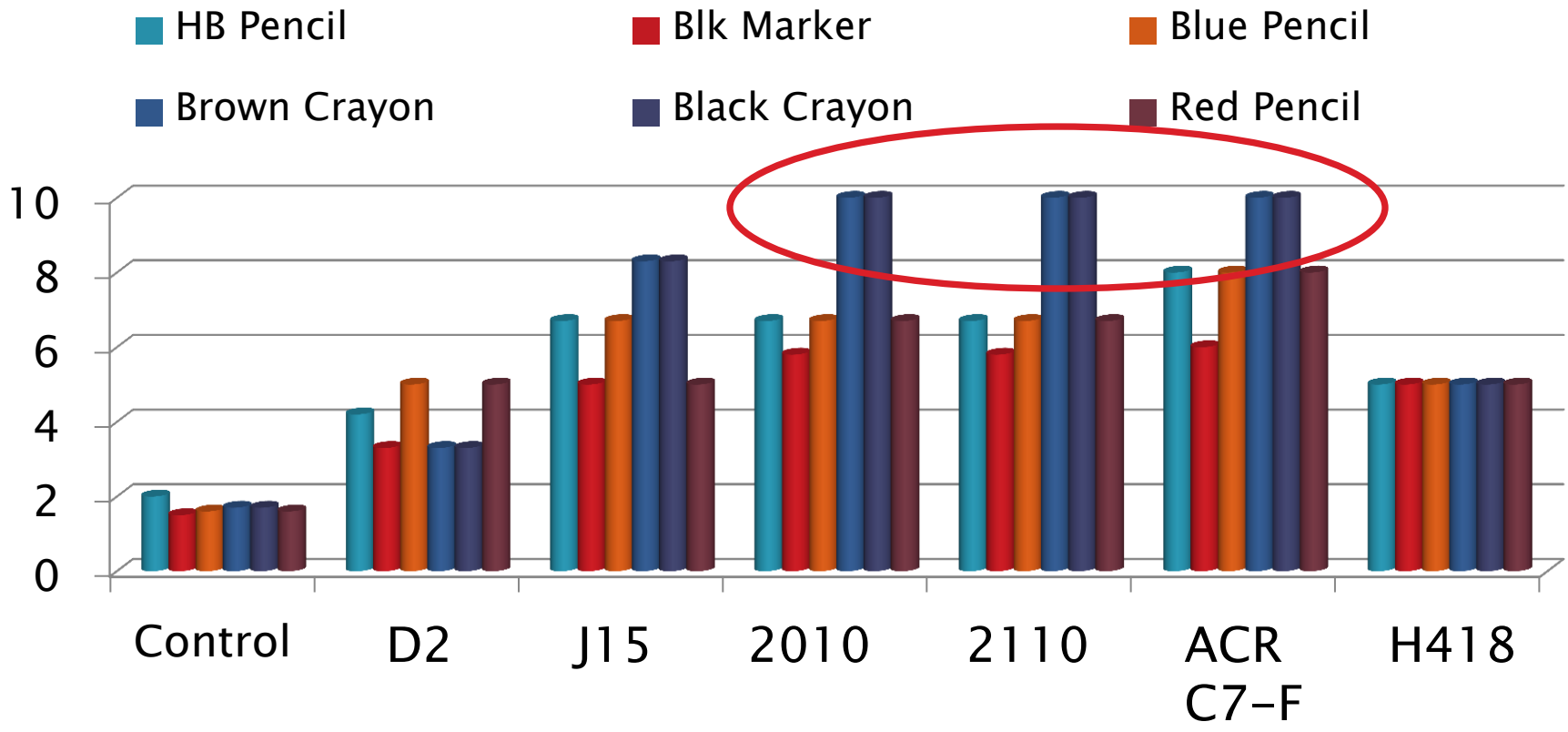
- All improve COF
- More with > wt% CF_2

Stain Resist II: Urethane Acrylate



- Crayons are effectively blocked by several

Stain Resist II: Urethane Acrylate



- ACR C7-F and FPEs are effective

Results System II Urethane

- All FAS additives improve COF, mar and stain resistance and to a lesser degree fingerprint.
- FPE are the only compatible FASs and give good slip, mar and anti stain, but weak fingerprint resist.
- ACR C7-F, 2010 and 2110 give relatively high ratings for gloss, mar and stain resistance.
- J15, H418 and ACR C7-F give the best finger print resistance
- H418 – which has a balance of % Sil, %CF2, & %CH2 – gives a very good balance of properties.
- Best stain results are for crayons.

System III: Epoxy Acrylate

Component	Wt%
Epoxy Acrylate UV Resin	66.0%
FAS additive	1.0%
Butyl Acetate	8.25%
Toluene	8.25%
Methyl Isobutyl Ketone	9.9%
Methyl Ethyl Ketone	6.6%

Preparation:

- Drawn down on a Leneta paper using a wire-wound rod #10.
- Cured for at least 1 hour in a 10 mW/cm^2 UV box.

Film Properties III: Epoxy Acrylate

	60° Gloss	Stain Resistance	Mar Resistance	Static COF	Kinetic COF	Finger Print Resistance	Appearance
Control	89.0	0.5	0.5	2.78	2.80	0.5	Pinholes
D2	85.5	4.2	3.5	2.32	2.06	5.5	Patches
H418	91.2	5.0	3.1	1.88	1.80	6.5	Matte
J15	90.8	6.7	3.8	1.96	1.61	6.0	Patches
2010	92.7	7.6	4.8	2.08	2.33	3.5	Smooth
2110	92.7	7.6	6.0	2.26	2.76	4.0	Smooth
ACR C7-F	88.3	8.3	8.5	0.52	0.51	7.0	Smooth

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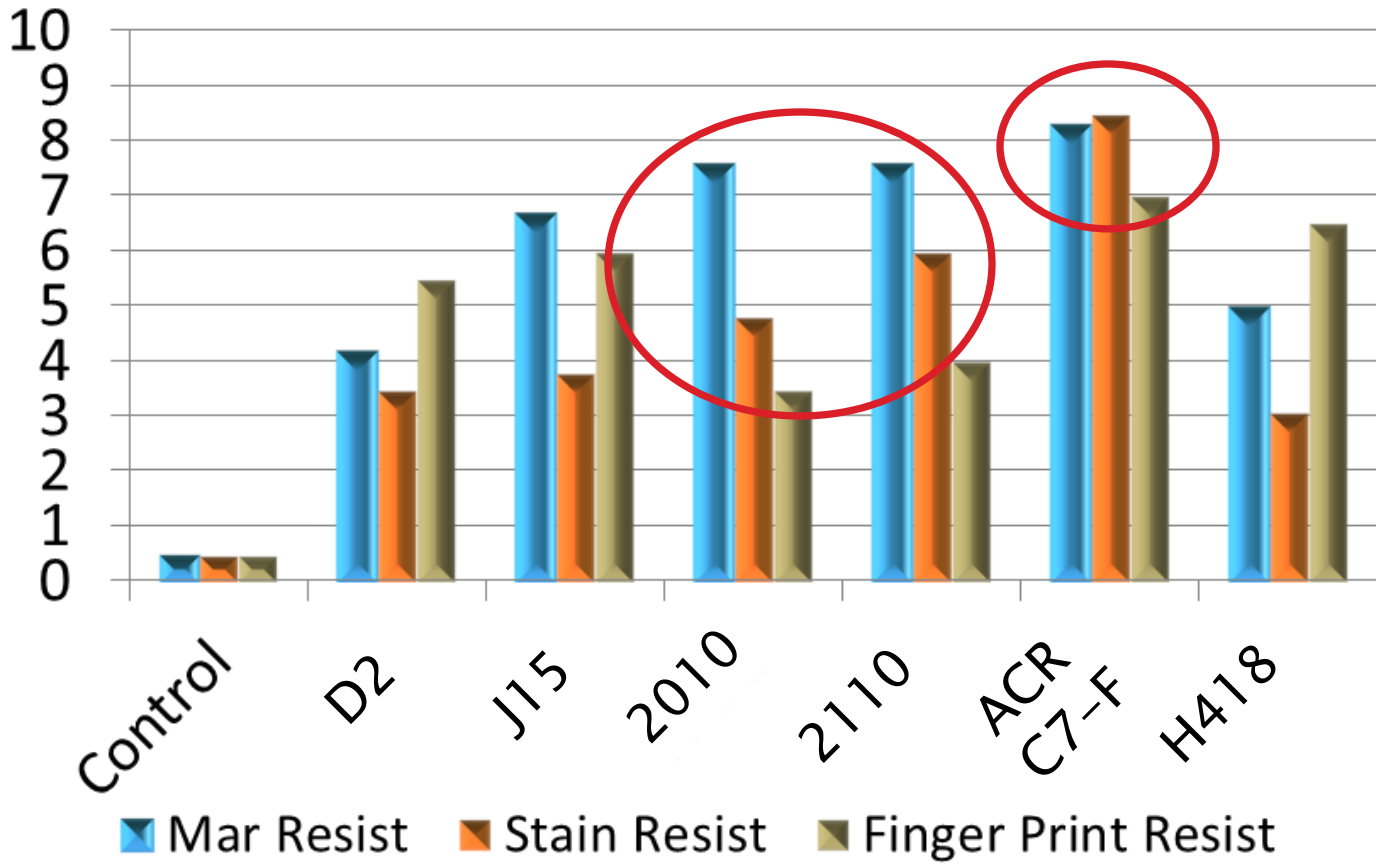
Mar, Stain, Print III: Epoxy Acrylate



- All improved, more with %sil
- FPEs weak on fingerprint
- ACR C7-F strong on all

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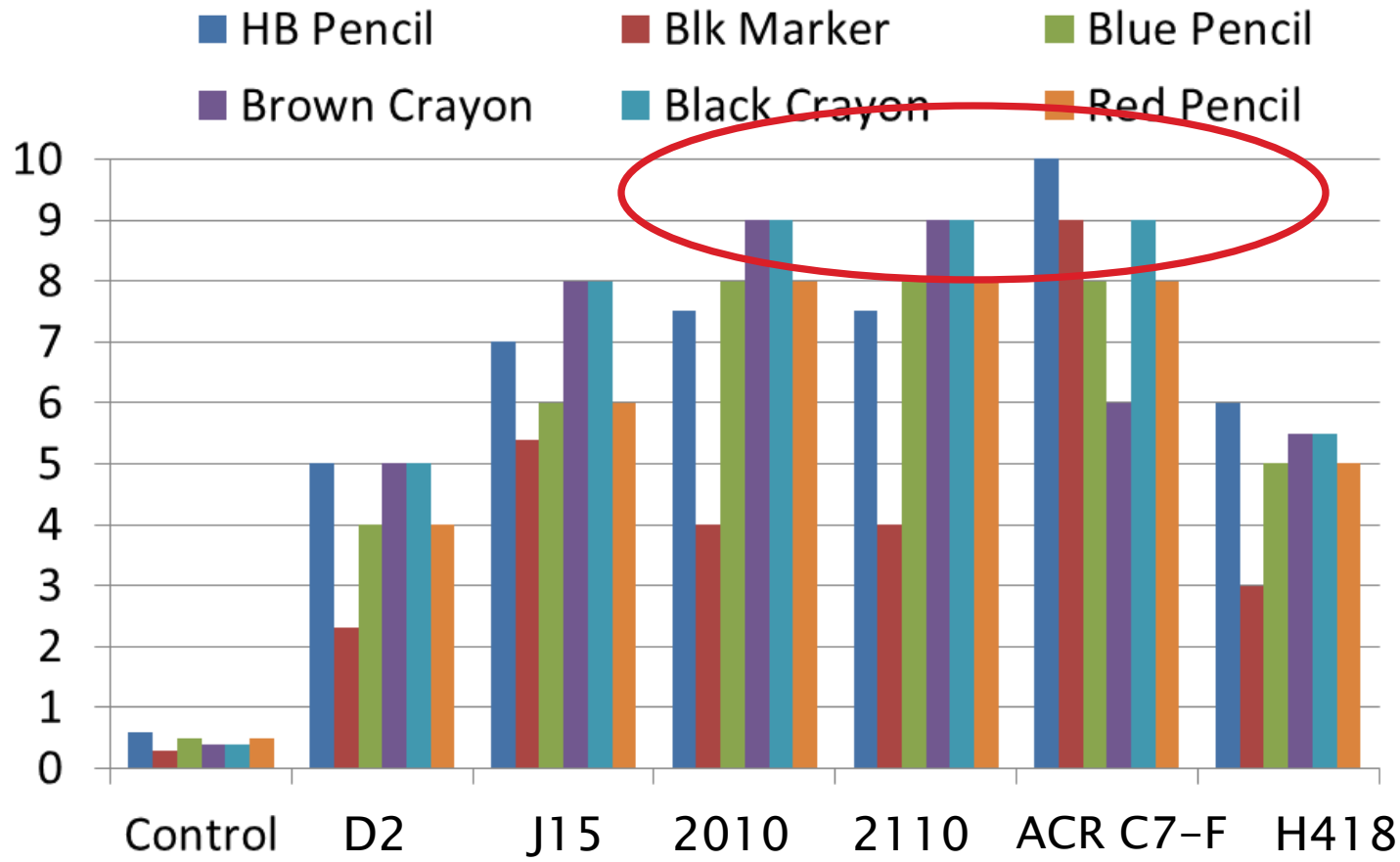
Stain III: Epoxy Acrylate



- Highest %CF_2 is least effective
- ACR C7-F and FPEs are effective

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Results System III: Epoxy Acrylate

- All FAS additives improve COF, mar and stain resistance and to a lesser degree fingerprint resist.
- FPE are the only compatible FASs and give good slip, mar and anti stain, but weak finger print resist
- ACR C7-F, 2010 & 2110 again give relatively high ratings for gloss, mar and stain resistance.
- Best results are for crayons
- J15, H418 & ACR C7-F give the best fingerprint resist.
- H418 – which has a balance of % Sil, $\%CF_2$, & $\%CH_2$ – again gives a very good balance of properties.

System IV: Cationic Silicone Resin

A silicone epoxy resin based cationic UV epoxy cured system uses a cycloaliphatic epoxy silicone with the relevant percentage of FAS (0.2%, 0.5%, 1%, 3%, 5%) added, along with 0.5% of a cationic catalyst for UV curing. Formulations were as follows:

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
D2	.2%	.5%	1%	3%	5%															
OH C7-F						.2%	.5%	1%	3%	5%										
OH G2-F											.2%	.5%	1%	3%	5%					
OH E3.5-F																.2%	.5%	1%	3%	5%

- Drawn down on Leneta paper with a wire-wound rod #10.
- Cured with a 10 mW/cm2 UV box for 1 hour
- Kept at room temperature for one day

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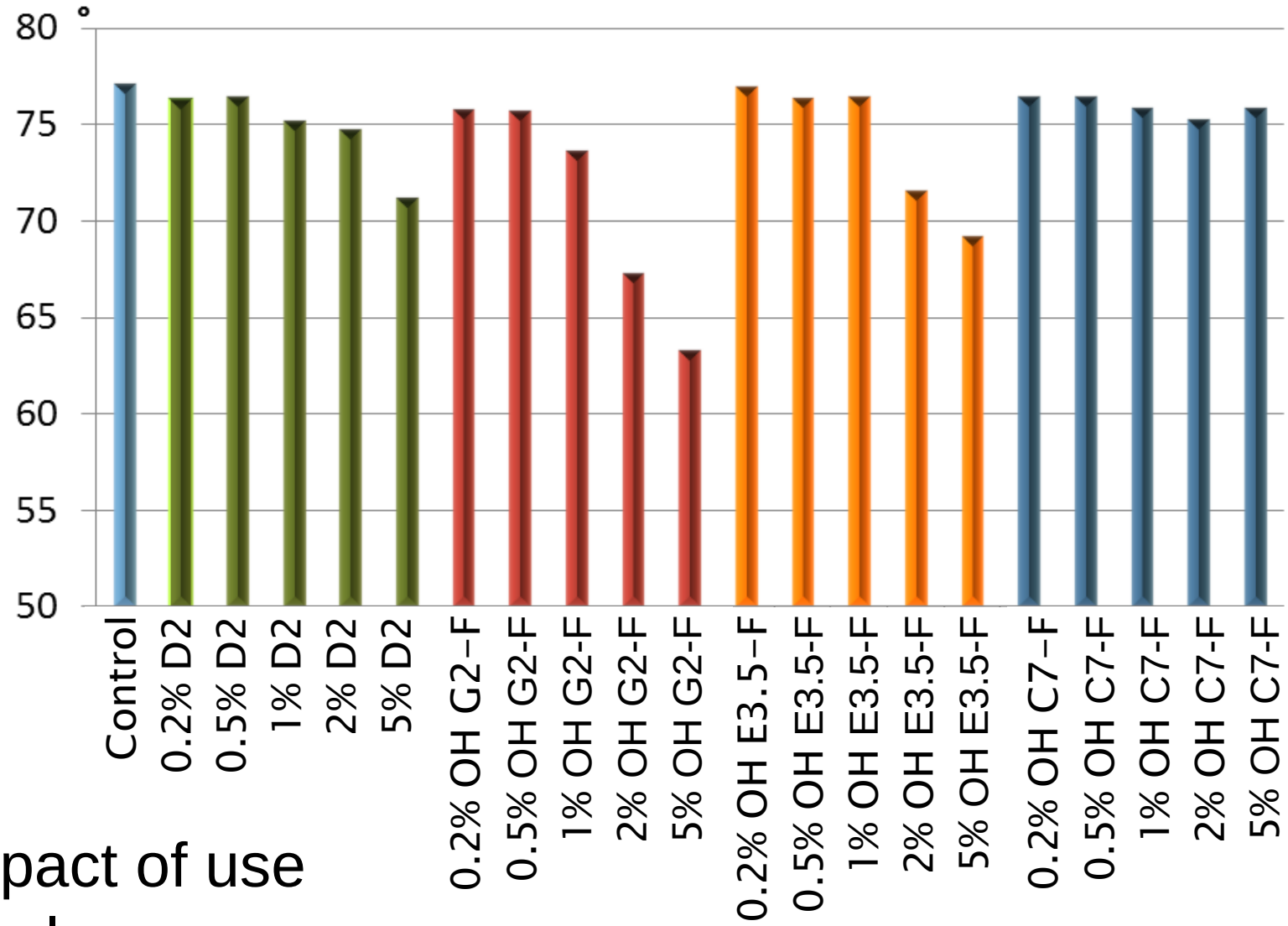
Gloss IV: Cationic UV Silicone



- Impact of use level

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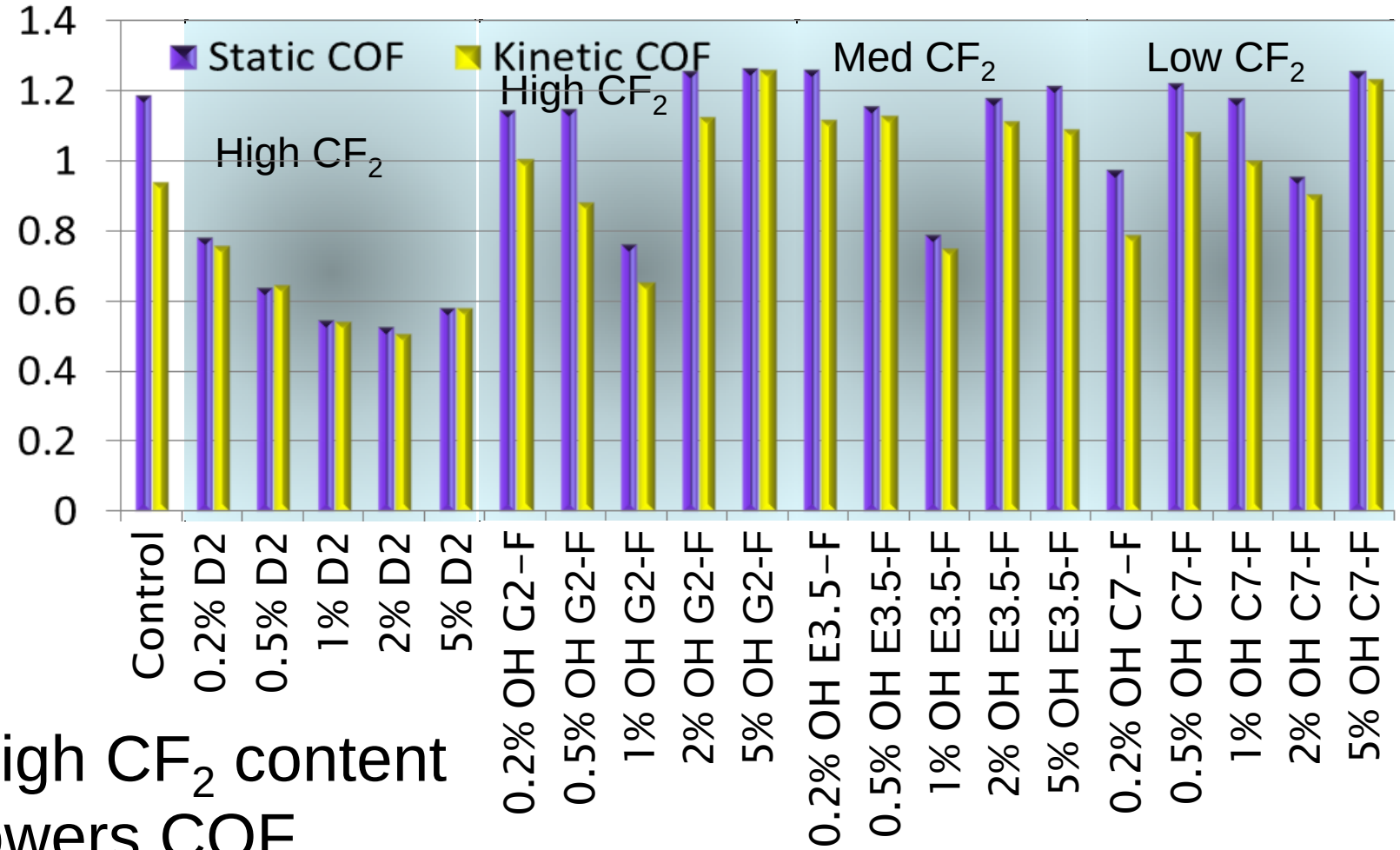
Slip IV: Cationic Epoxy Silicone



- High CF_2 content lowers COF
- High use levels lowers COF

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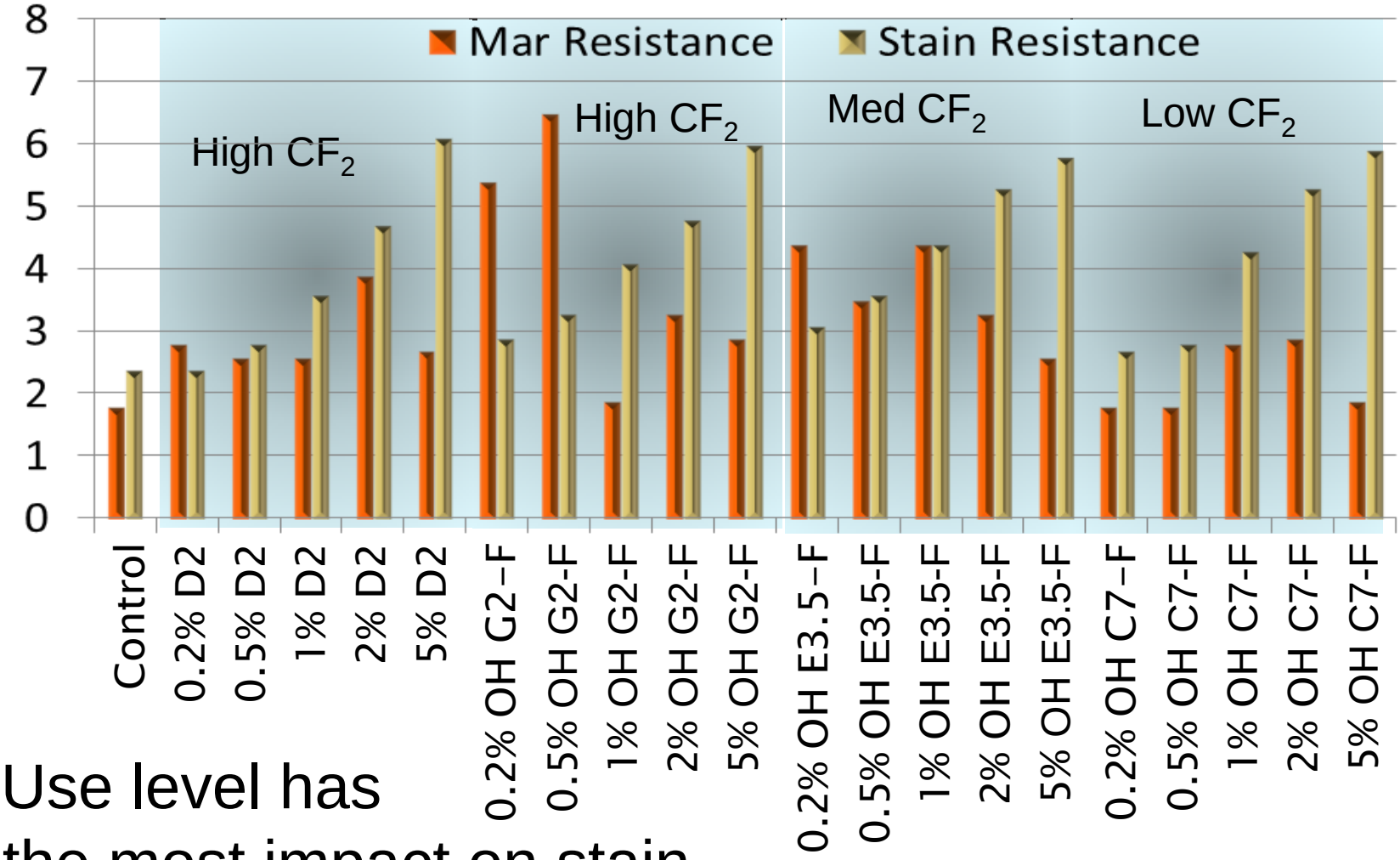
Stain and Mar IV: Cationic



- Use level has the most impact on stain
- Low CF_2 FAS just as good as high CF_2

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Cationic Epoxy Silicone Chemical Resistance – additive level and chemistry impact performance.

Additive	% Additive	IPA	Vinegar	Soap	NH_4OH	HCl	Mineral Oil	Rank
OH C7-2F	0.20%	6	2	5	4	5	7	8.18
	5.00%	3	1	3	5	4	4	1.00
OH C50	0.20%	5	3	5	3	4	5	4.55
	5.00%	7	4	5	4	5	6	8.00
OH D2	0.20%	7	2	5	5	4	7	4.00
	5.00%	6	2	5	6	5	6	9.09
Control	0%	6	4	6	5	4	6	4.00
D2	0.20%	5	3	5	6	6	7	6.32
	5.00%	6	2	4	4	5	6	3.68
OH C7-1F	0.20%	7	5	6	7	7	7	10.00
	5.00%	5	4	3	4	4	4	2.11
OH G2-1F	0.20%	5	2	3	3	4	6	6.00
	5.00%	7	3	6	3	4	6	4.74
OH E3.5-1F	0.20%	5	2	3	4	6	6	8.00
	5.00%	5	3	4	6	6	6	5.26

Non-flouro performs, but only at high levels.

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Summary IV: Cationic Epoxy Silicone

- All FAS are compatible with silicone epoxy resin.
- Most FAS show improvements to mar resistance. This is seen at low use levels and barely improved or somewhat lost at higher use levels.
- Only D2 – with the highest CF_2 content – shows the dramatic lowering of COF that one usually sees with silicone or fluoroalkyl additives.
- Stain resistance was similar for each additive, stain dependent, and increased with use level of FAS.
- Chemical resistance is poor with high fluoro, but good with high non-fluoro addtives.

System V: commercial paint

- Retail flat white paint.
- Post-added 1% and 5% samples.
- Drawn down on Leneta paper in a 1 mil thickness using a # 10 rod .
- Dried/ conditioned at ambient for seven days.

Film Properties V: post add

	%	Static CoF	Kinetic CoF	60° Gloss	Mar Resist	Stain Resist	Film Appearance
Control	0%	0.896	0.847	2.7	1.1	1.9	Smooth
OH G2-F	1%	0.887	0.803	2.9	5.5	2.5	Fisheyes
	5%	0.826	0.719	3.5	7.8	3.5	Fisheyes
OH E3.5-F	1%	0.908	0.826	2.8	5.6	3.0	Fisheyes
	5%	0.860	0.748	3.4	5.6	4.5	Fisheyes
OH C7-F	1%	0.886	0.801	2.9	6.7	3.0	Fisheyes
	5%	0.851	0.778	3.2	7.8	4.6	Fisheyes
H418	1%	0.878	0.810	2.9	7.8	2.0	Fisheyes
	5%	0.877	0.808	3.3	8.9	3.6	Fisheyes
D2	1%	0.872	0.814	2.9	6.7	2.5	Fisheyes
	5%	0.871	0.800	3.3	7.8	3.0	Fisheyes
2010	1%	0.774	0.688	5.3	3.3	1.8	Smooth
	5%	0.815	0.698	8.9	5.6	2.7	Smooth
2110	1%	0.821	0.730	7.5	3.3	1.7	Smooth
	5%	0.851	0.717	8.5	6.7	3.0	Smooth

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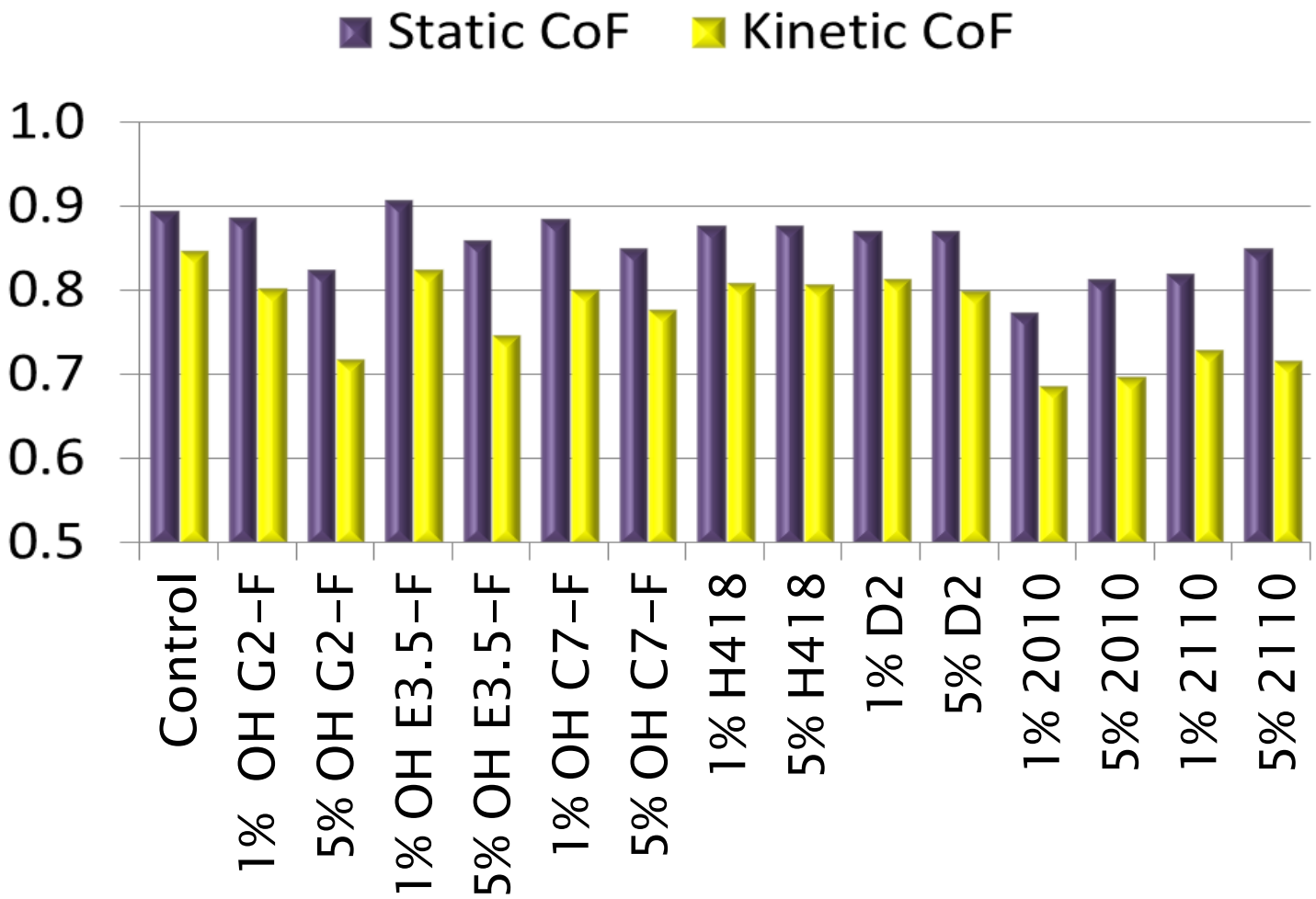
Slip V: Post add



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

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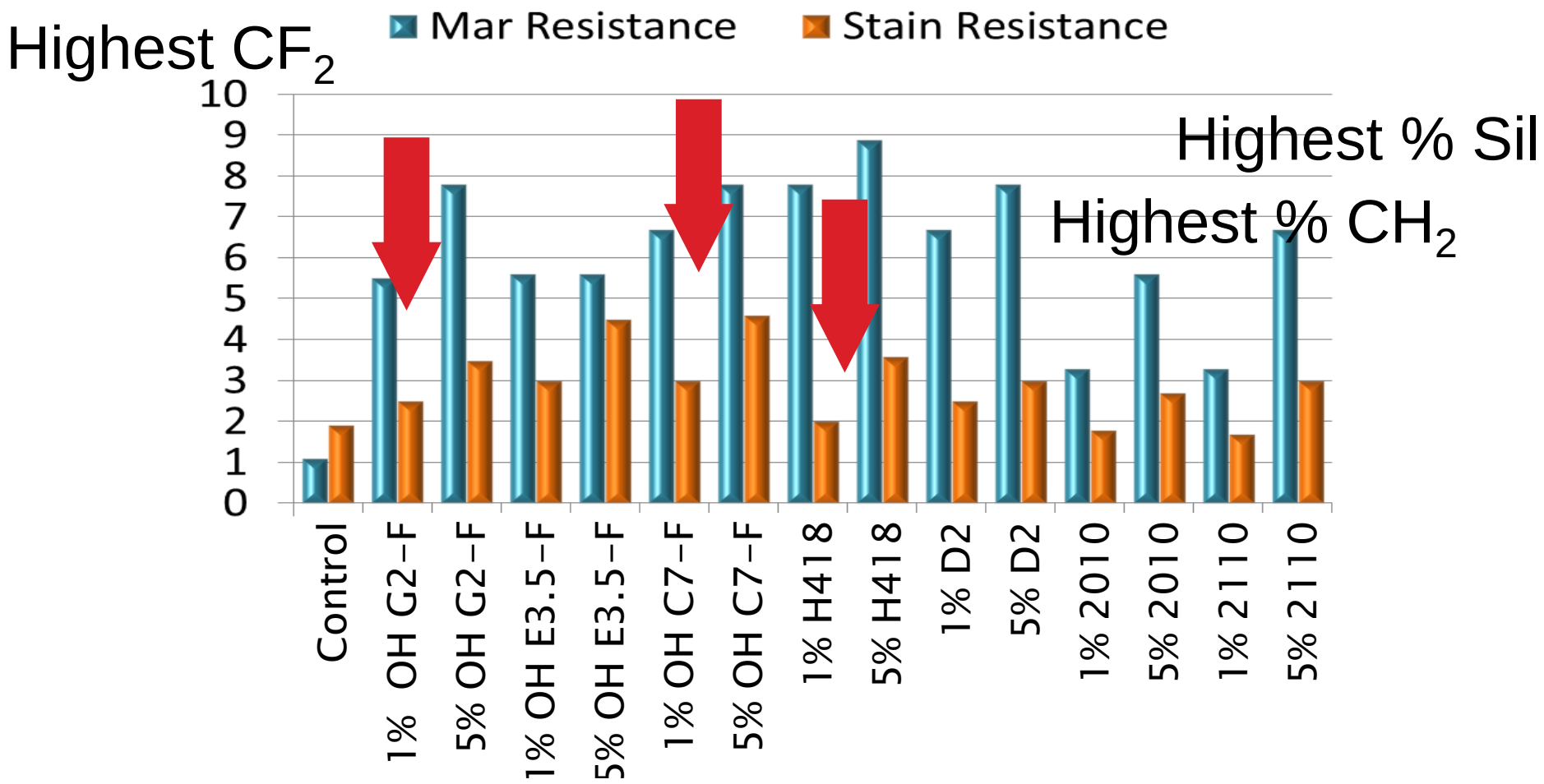
Mar and Stain V: post add



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

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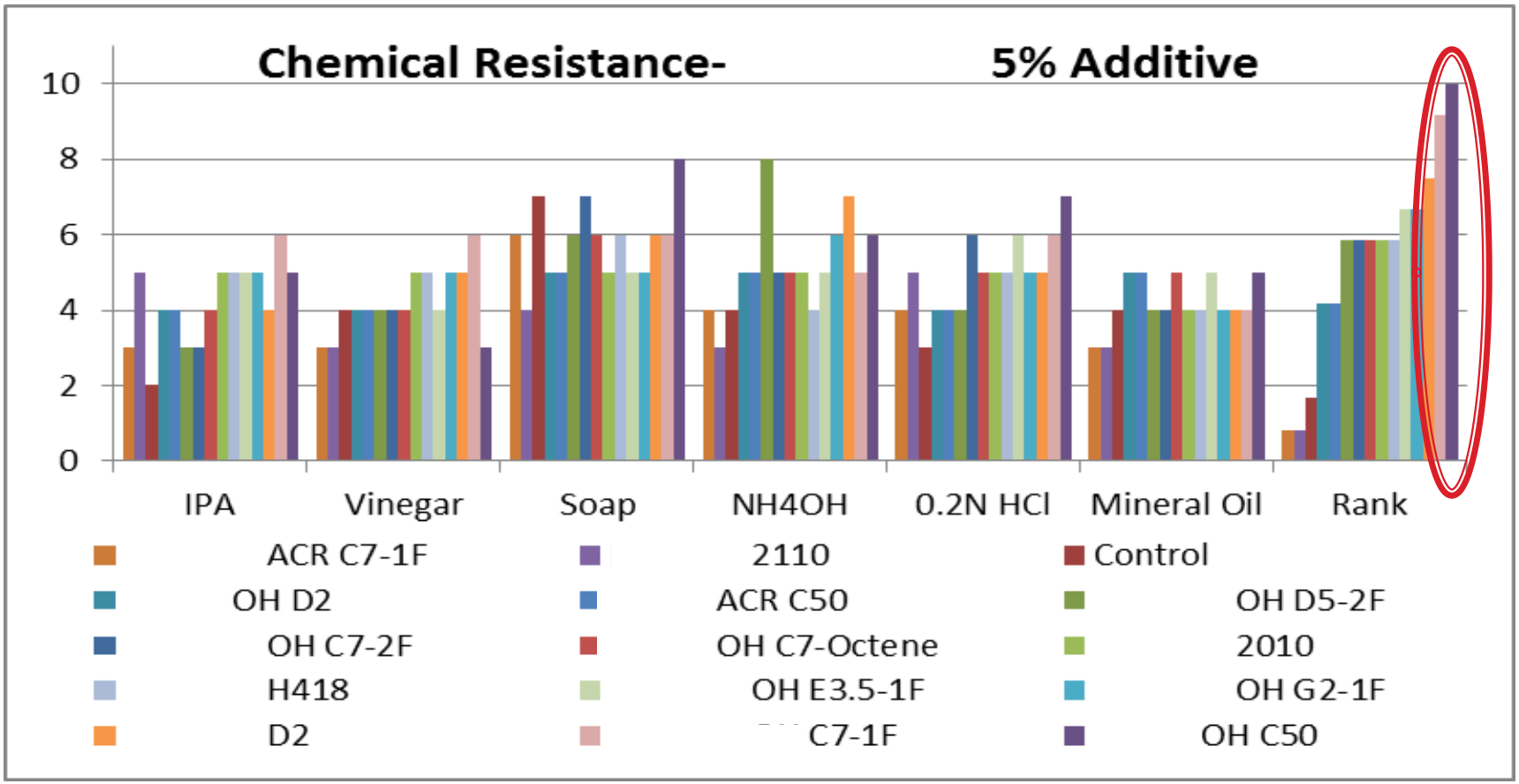
Summary Chemical V: Post add

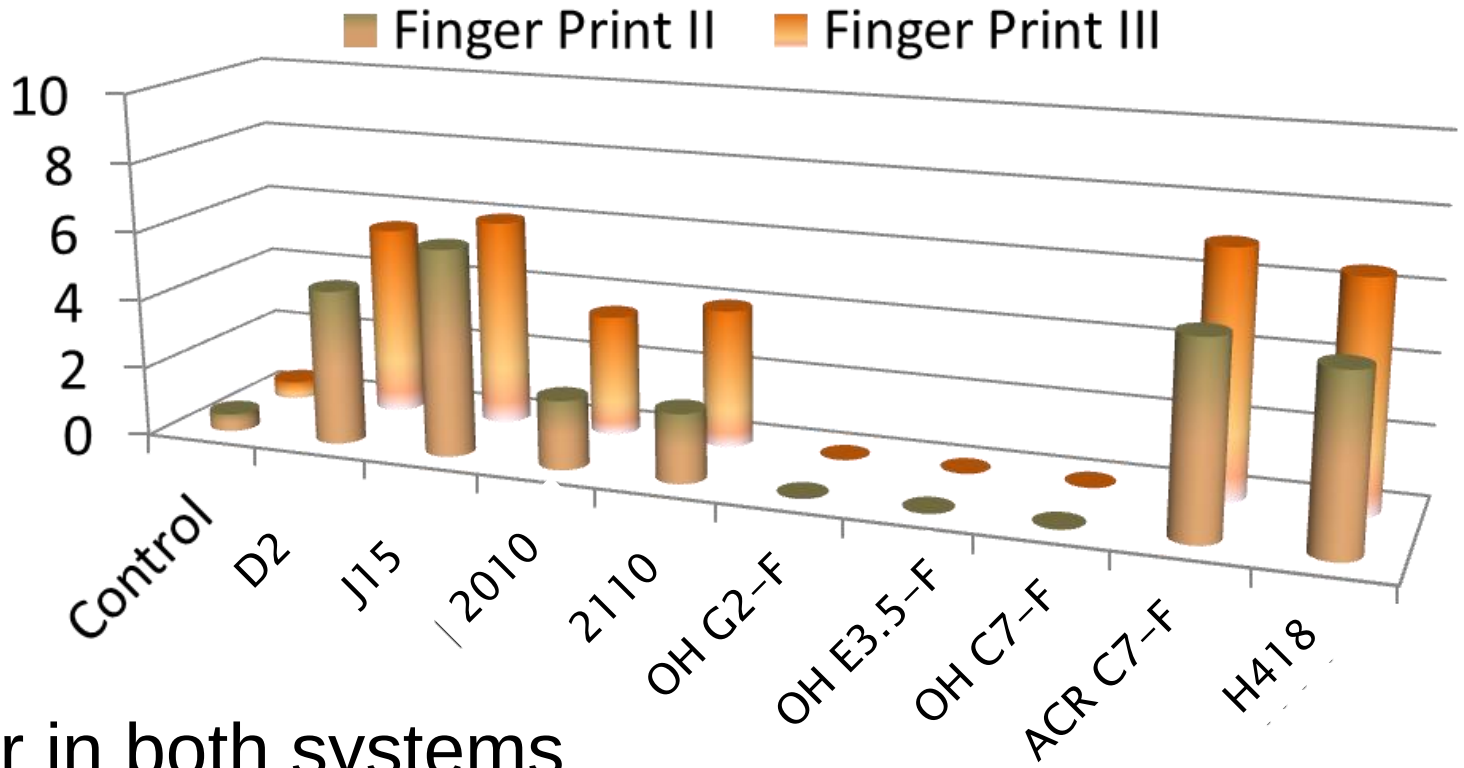


- Non- fluorinated performed best at this level

Summary post add paints

- Post-added FAS have little effect on slip and gloss but do affect mar and stain resistance.
- FPEs are compatible.
- Mar resist is easy.
- Chemical resistance is good with low or non-fluoro
- Stain resist is a mix of different factors but FAS seem better that Silicone alone.
- More is better for mar and stain.

Summary Fingerprint



- Similar in both systems
- High CF_2 content works
- But high %Sil best

Stain summary

- While non-flouro improve stain resistance, flouro provides best performance
- High % Silicone FAS materials are best on Graphite, WB and Waxy stains
- High % CF_2 better for waxy stains but still not as good as above
- High MW makes little difference
- More is better

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Final Recommendations/Observations

- Fluorinated silicone polyethers are very good for all but fingerprint resistance.
- Alkyl-flouroalkyl silicones are best overall including fingerprint resistance.
  - *They are not always compatible.*
- 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, in others poor.*
- Use levels needed were up to 5% and more is better in most cases.
- Increasing % fluoro very often is not the best in performance.

THANK YOU!

QUESTIONS?

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