



Fluoroalkyl Silicones in Coatings Films

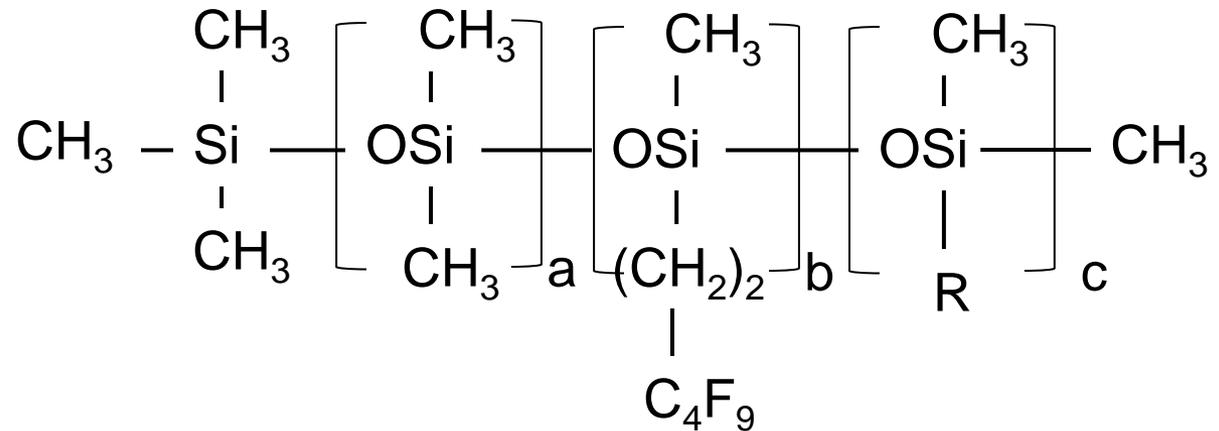
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Experimental and Methodology:

- ▶ The overall design is to use five systems:
 - SB Urethane
 - Urethane acrylate
 - Epoxy acrylate
 - Cationic UV cured epoxy silicone
 - Commercial Paint
- ▶ Various fluoroalkyl silicones are evaluated for slip, COF, defects and mar, stain, and fingerprint resistance.



Silicone Variations



	C	R
FPE	>0	$(\text{CH}_2)_3(\text{OC}_2\text{H}_4)_d(\text{OC}_3\text{H}_6)_e \text{OH}$
FS	0	
FA	>0	$\text{C}_n\text{H}_{(2n)} \text{R}'$



Structural Details

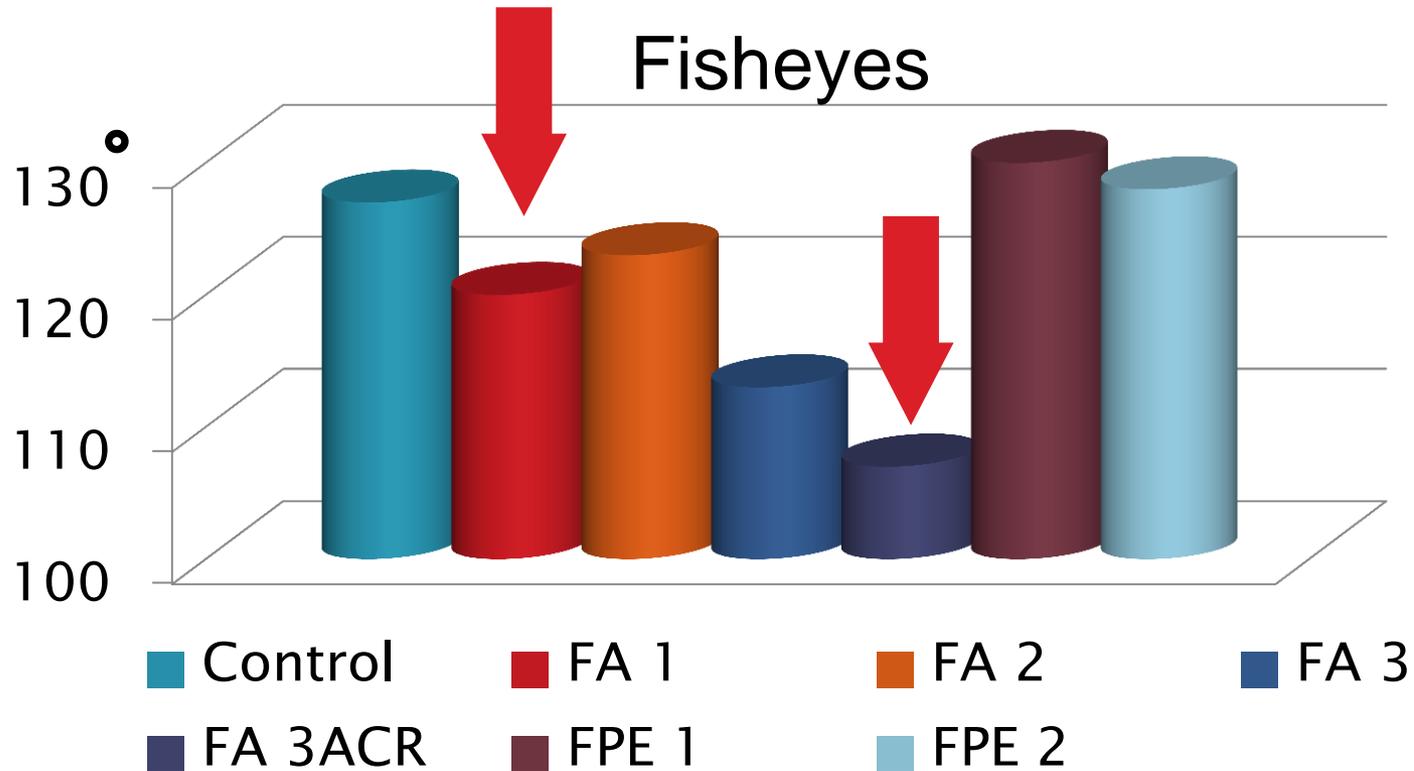
	Wt % Silicone	Wt % CF ₂	Wt % organic	Reactive Site	Water Miscible	MW	Type
FPE 1	38%	8%	54%	OH	1%	3000	fluoroalkyl polyether silicone
FPE 2	33%	3%	64%	OH	10%	7000	
FS 1	56%	44%	0%	no	no	2000	fluoroalkyl silicone
FS 2	86%	14%	0%	no	no	14000	
FA 1	57%	41%	2%	OH	no	3000	alkyl, fluoroalkyl silicone
FA 2	68%	30%	2%	OH	no	3000	
FA 3	81%	17%	2%	OH	no	2000	
FA 3ACR	81%	17%	2%	ACR	no	2000	
FA 4	63%	16%	21%	no	no	5000	

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
FA 1	1.274	1.204	120	95.0%	6.4	Fisheyes
FA 2	0.940	1.115	123	86.2%	4.3	Smooth
FA 3	0.794	0.756	113	87.1%	4.3	Smooth
FA 3ACR	0.405	0.422	107	93.1%	6.4	Fisheyes
FPE 1	0.577	0.631	130	96.7%	6.4	Smooth
FPE 2	0.681	0.711	128	96.4%	6.4	Smooth

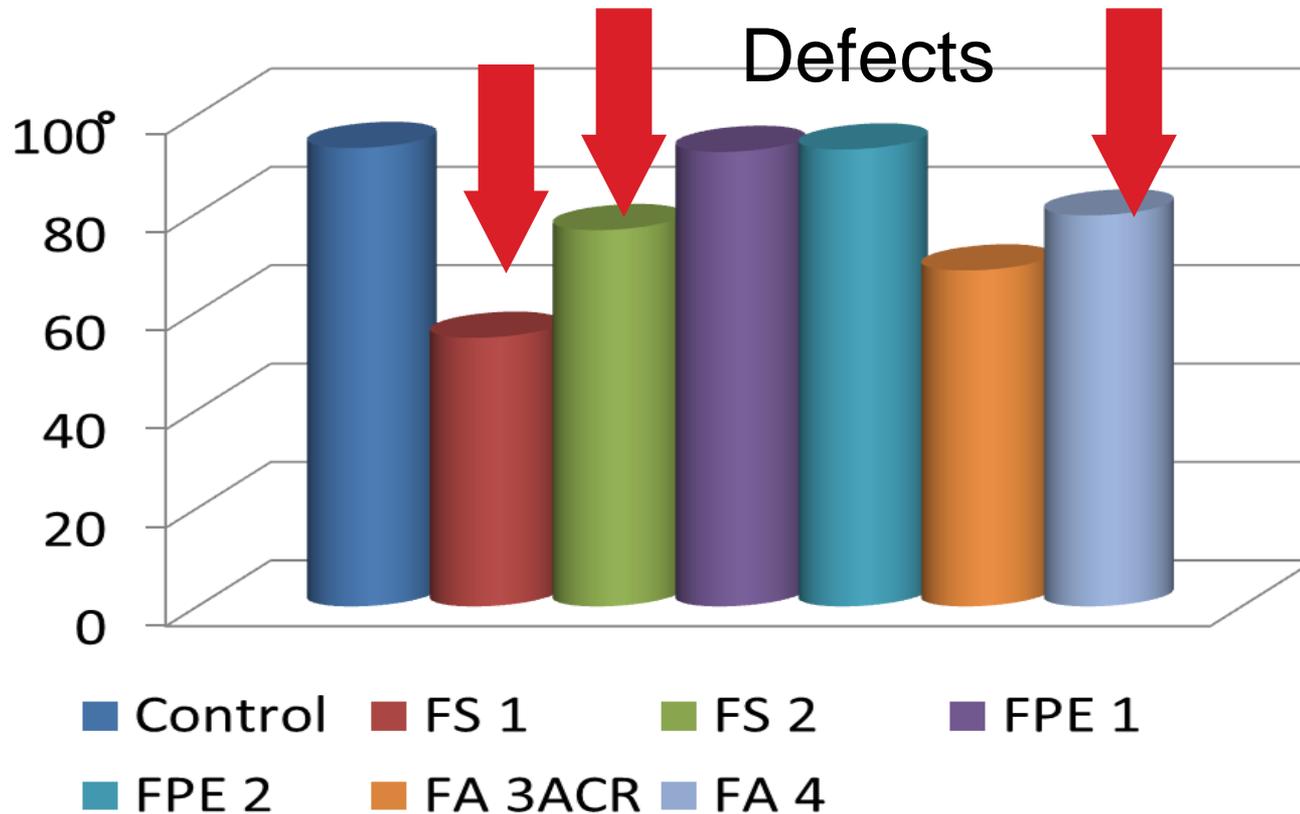


Gloss: SB Urethane



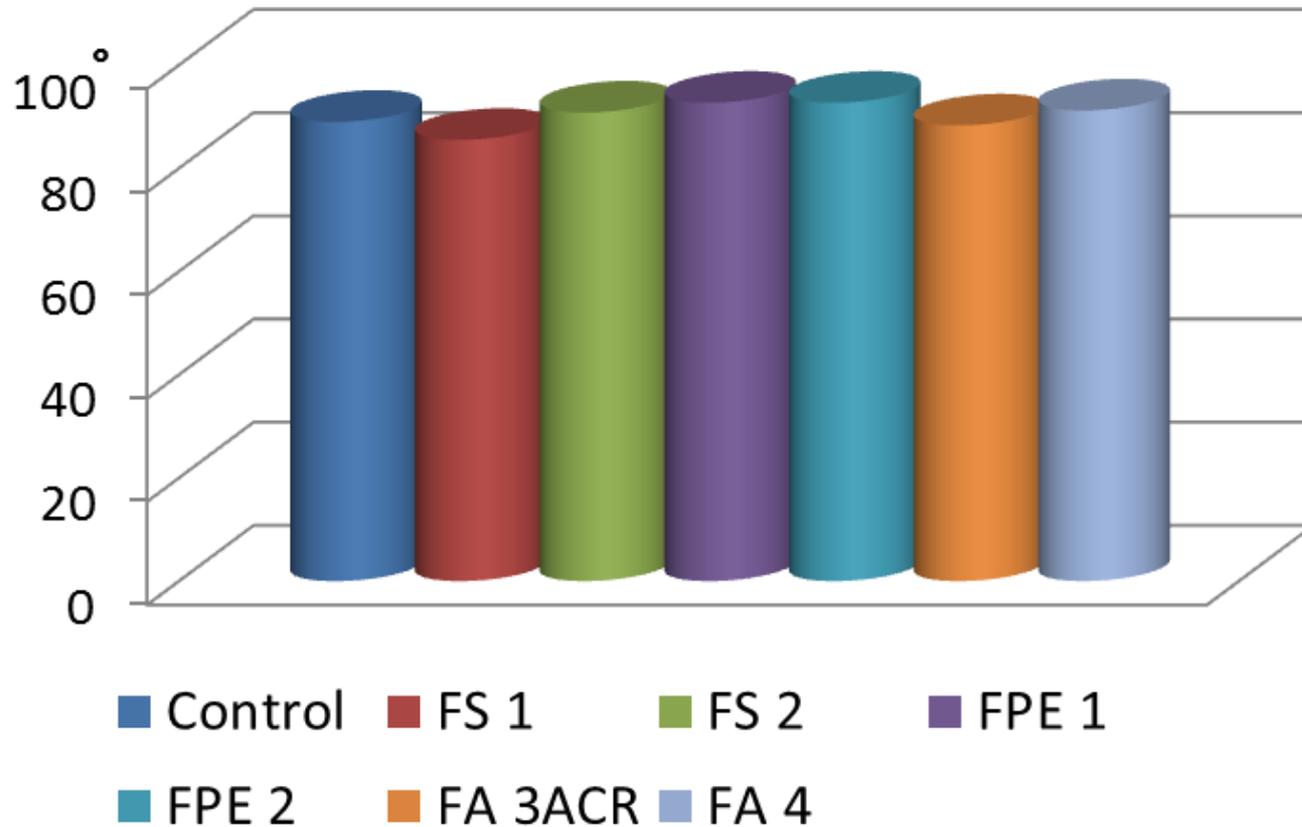
- FPE are most miscible, improve gloss
- FA type decrease gloss cause defects

Gloss: UV Urethane Acrylate



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

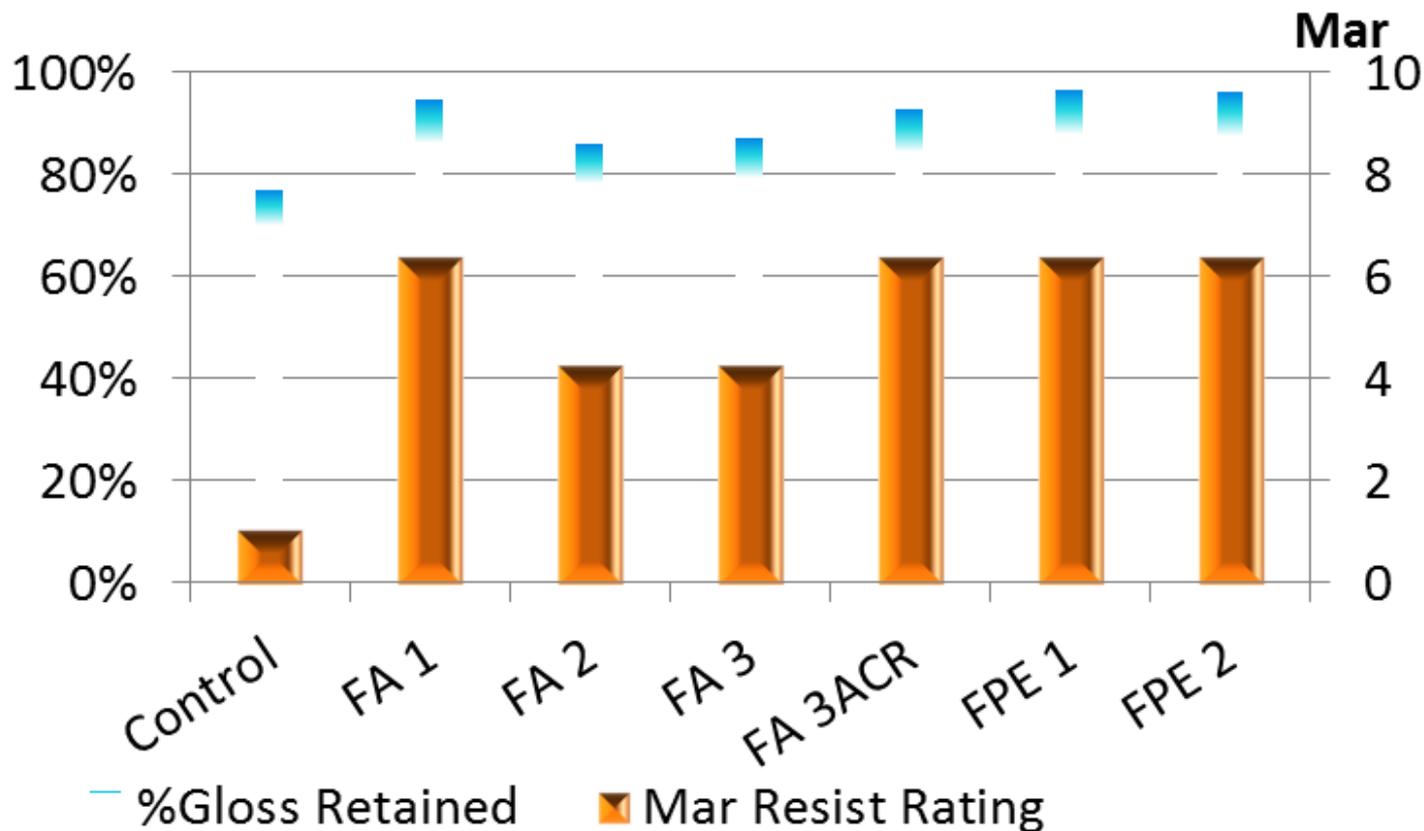
Gloss: UV Epoxy Acrylate



- Minor incompatibility

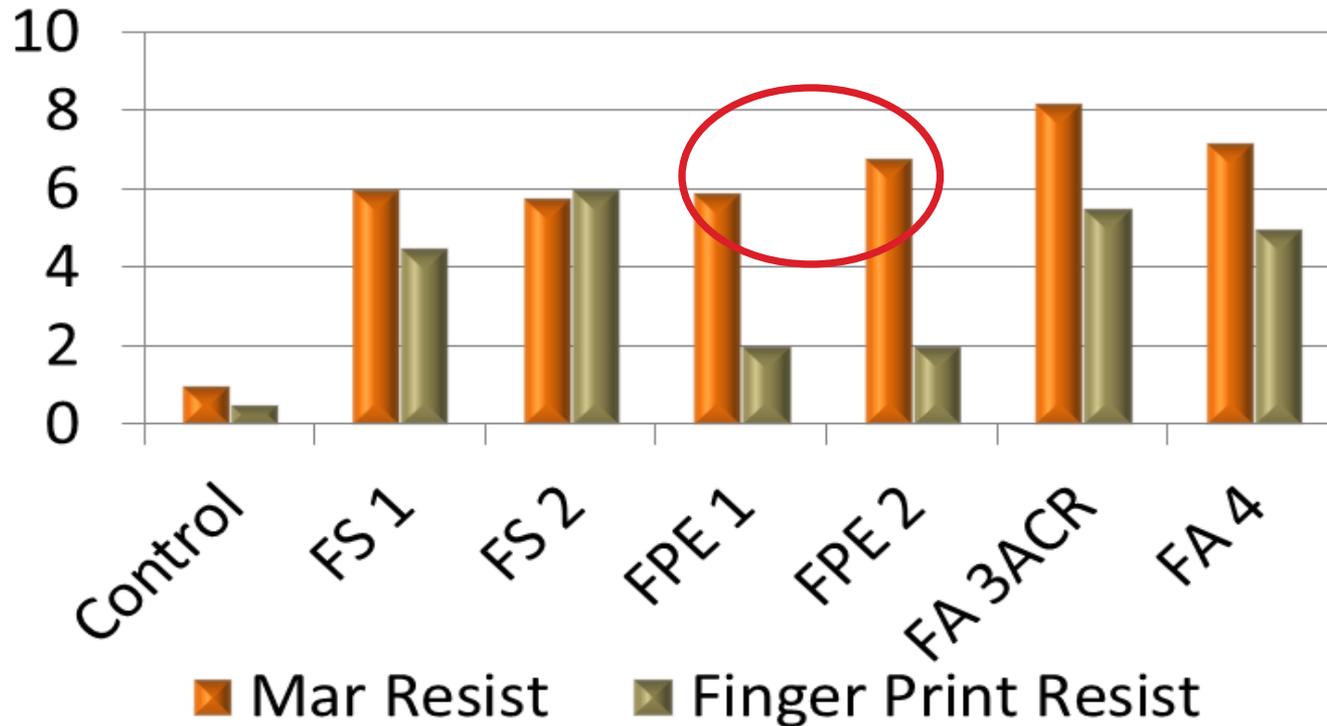


Mar Resist: SB Urethane



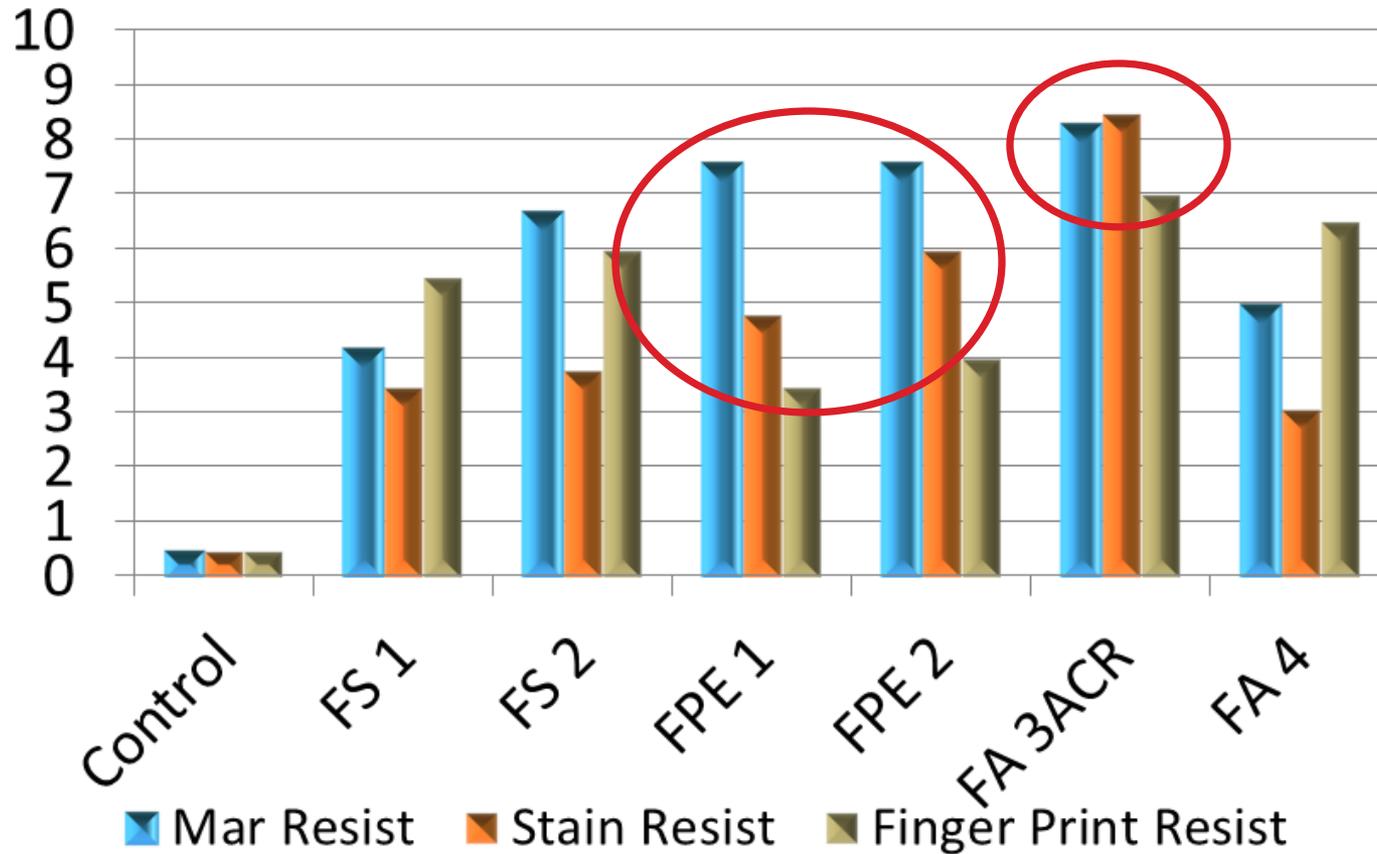
- All improve mar resistance

Mar/ Finger Print: UV Ureth. Acry.



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

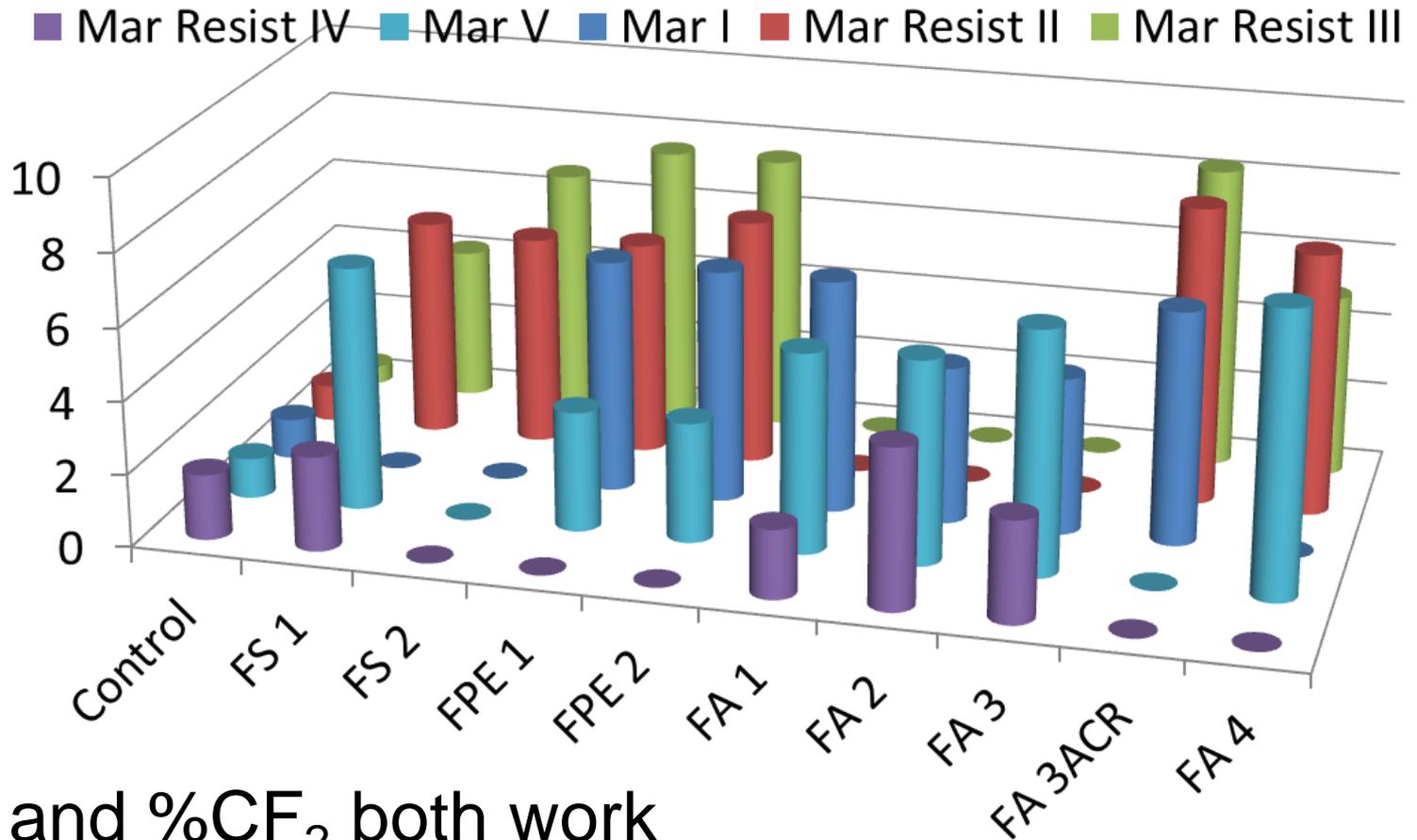
Mar, Stain, Print: UV Epoxy Acrylate



- All improved, more with %sil
- FPEs weak on fingerprint
- FA3 ACR strong on all

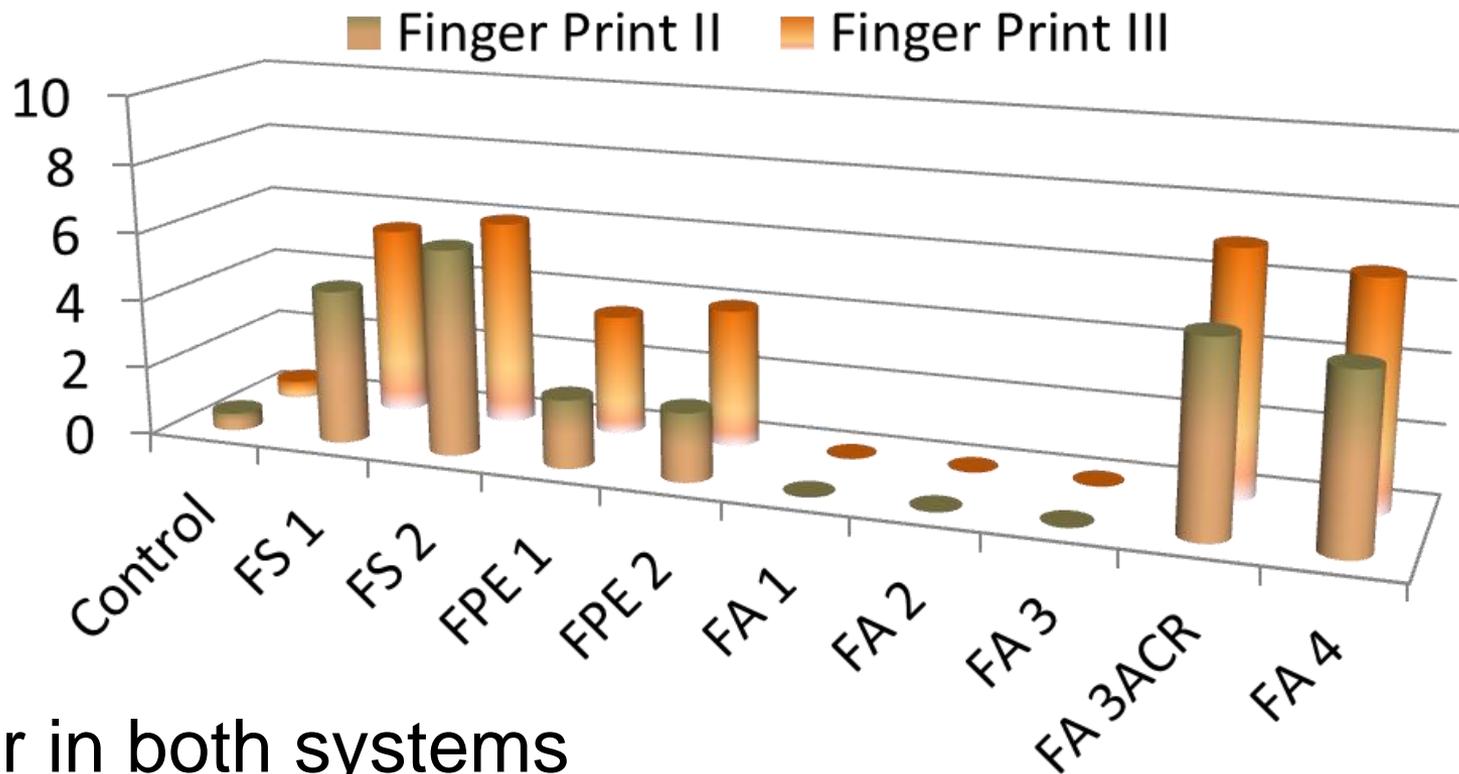
Summary

Mar



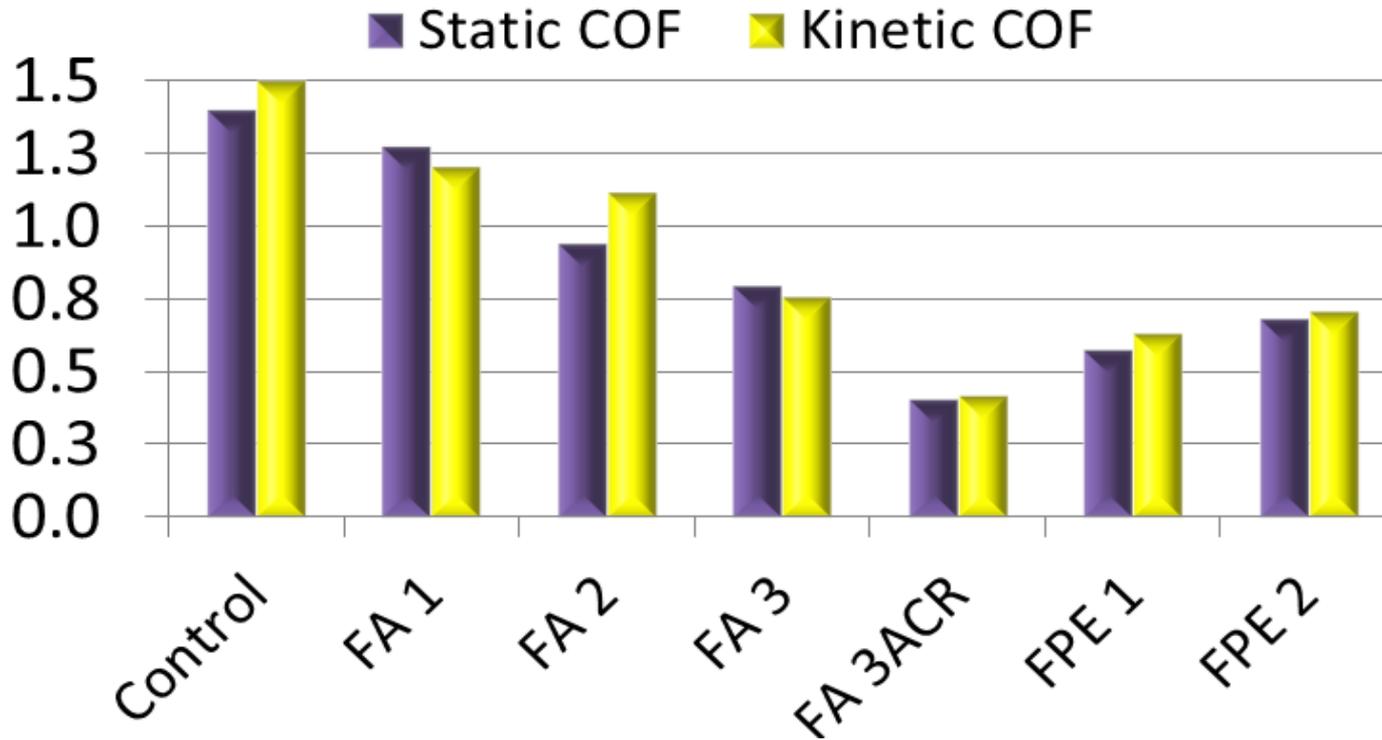
- %SiI and %CF₂ both work
- FA 3 ACR is very good
- FPEs are very good

Summary Fingerprint



- Similar in both systems
- High CF_2 content works
- But best has both

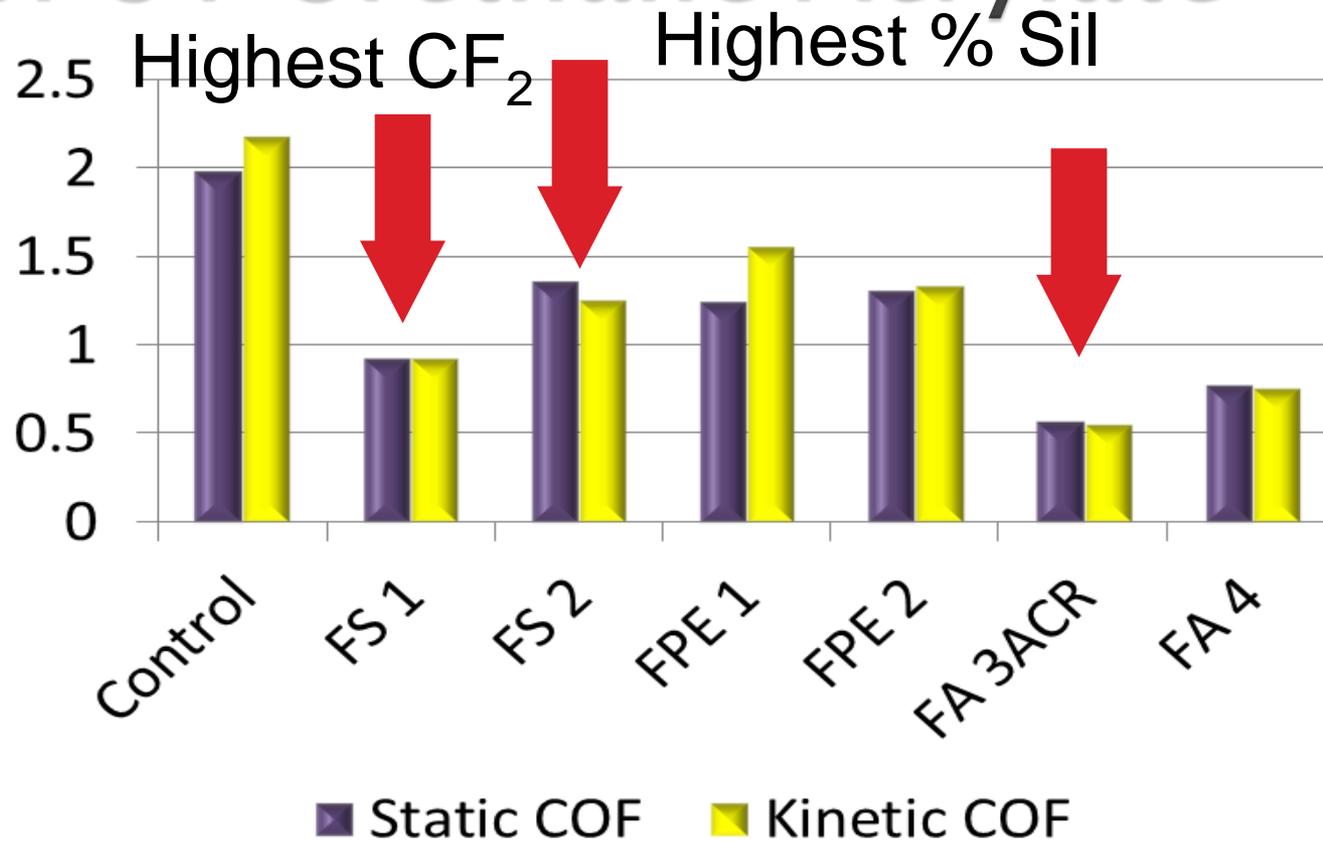
COF Reduction: SB Urethane



- All improve COF
- More with $>$ wt% silicone



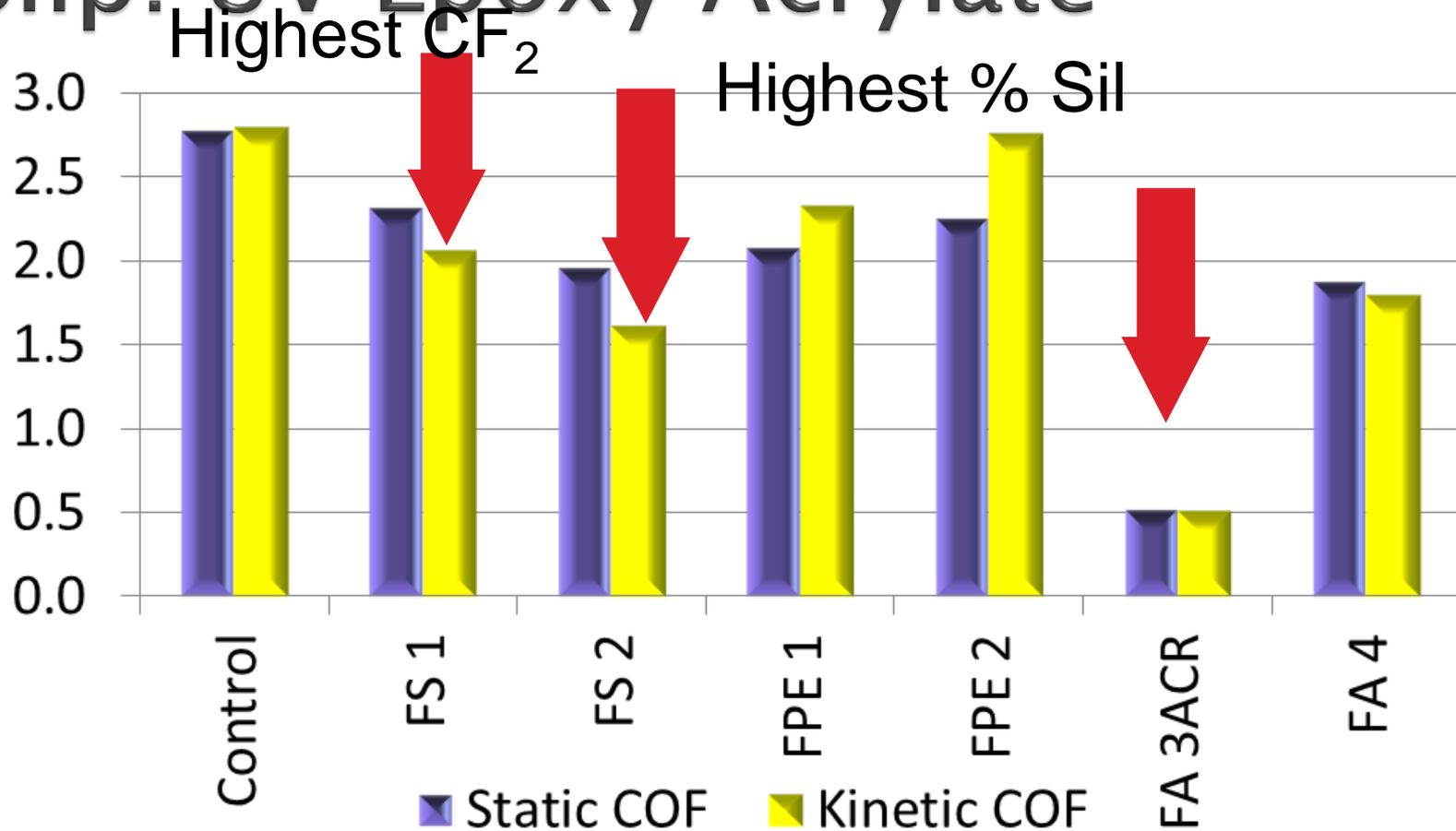
Slip: UV Urethane Acrylate



- All improve COF
- More with $>$ wt% CF_2

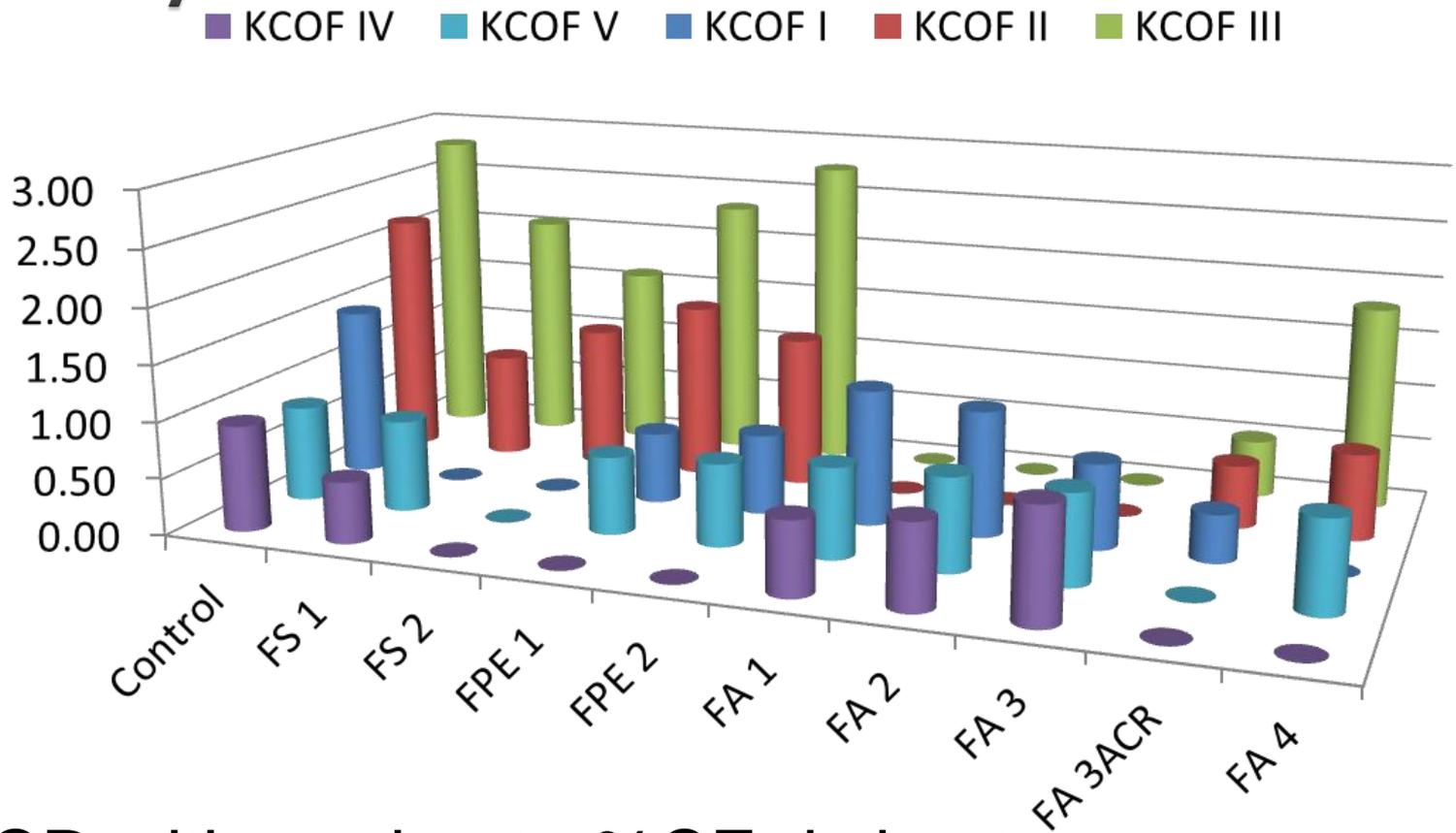


Slip: UV Epoxy Acrylate



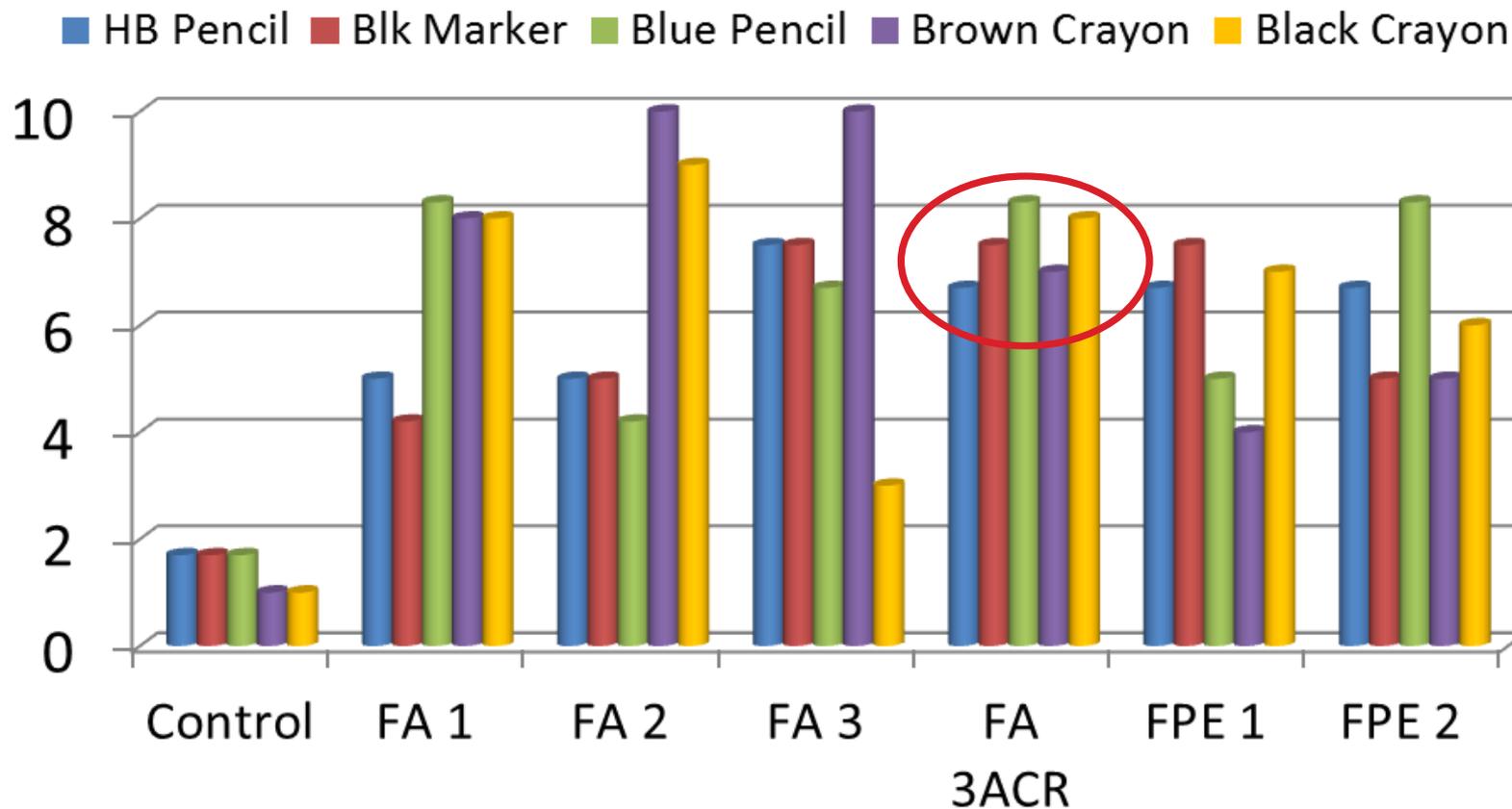
- All improve COF
- More with > wt% silicone

Summary Slip



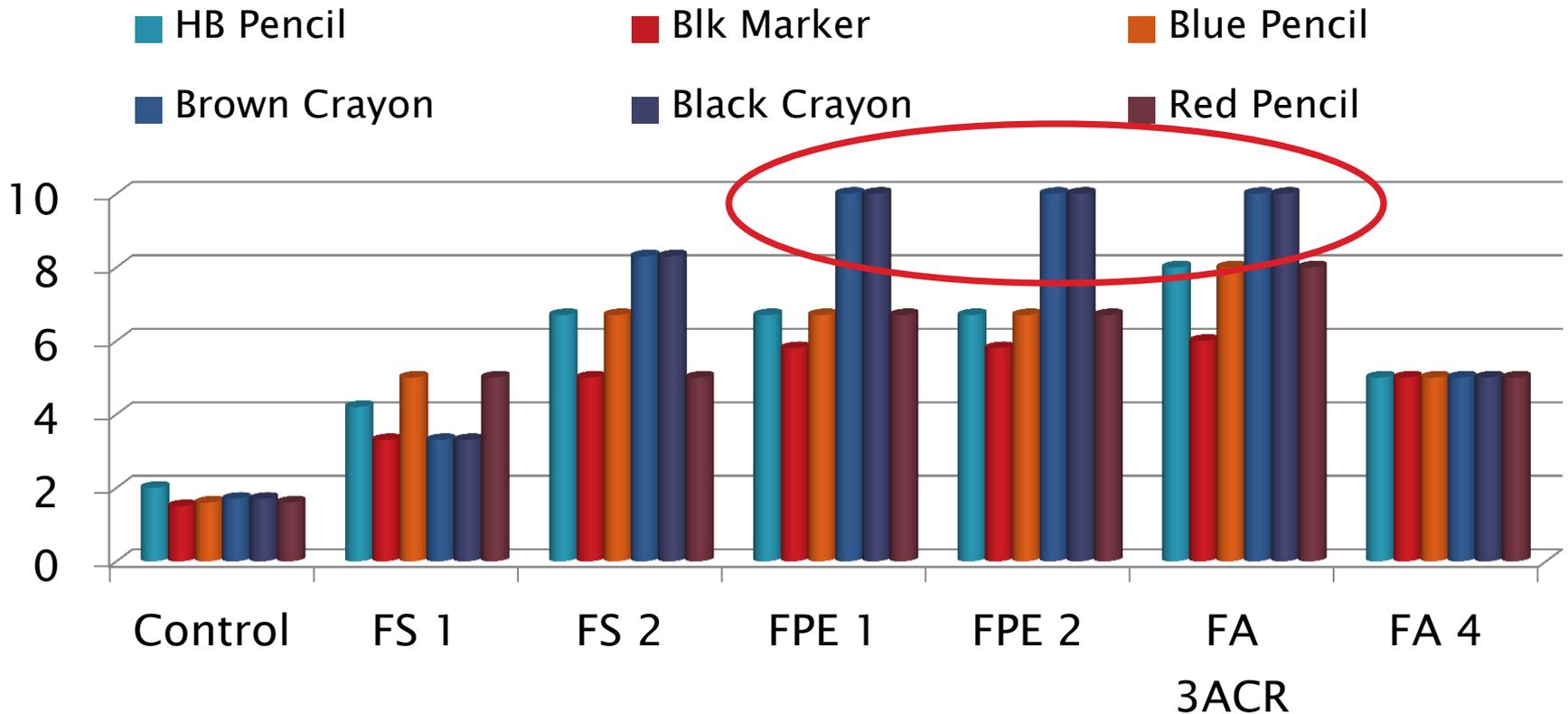
- FA 3ACR with moderate %CF₂ is best
- FPEs, FS1 are good

Stain Resist: SB Urethane



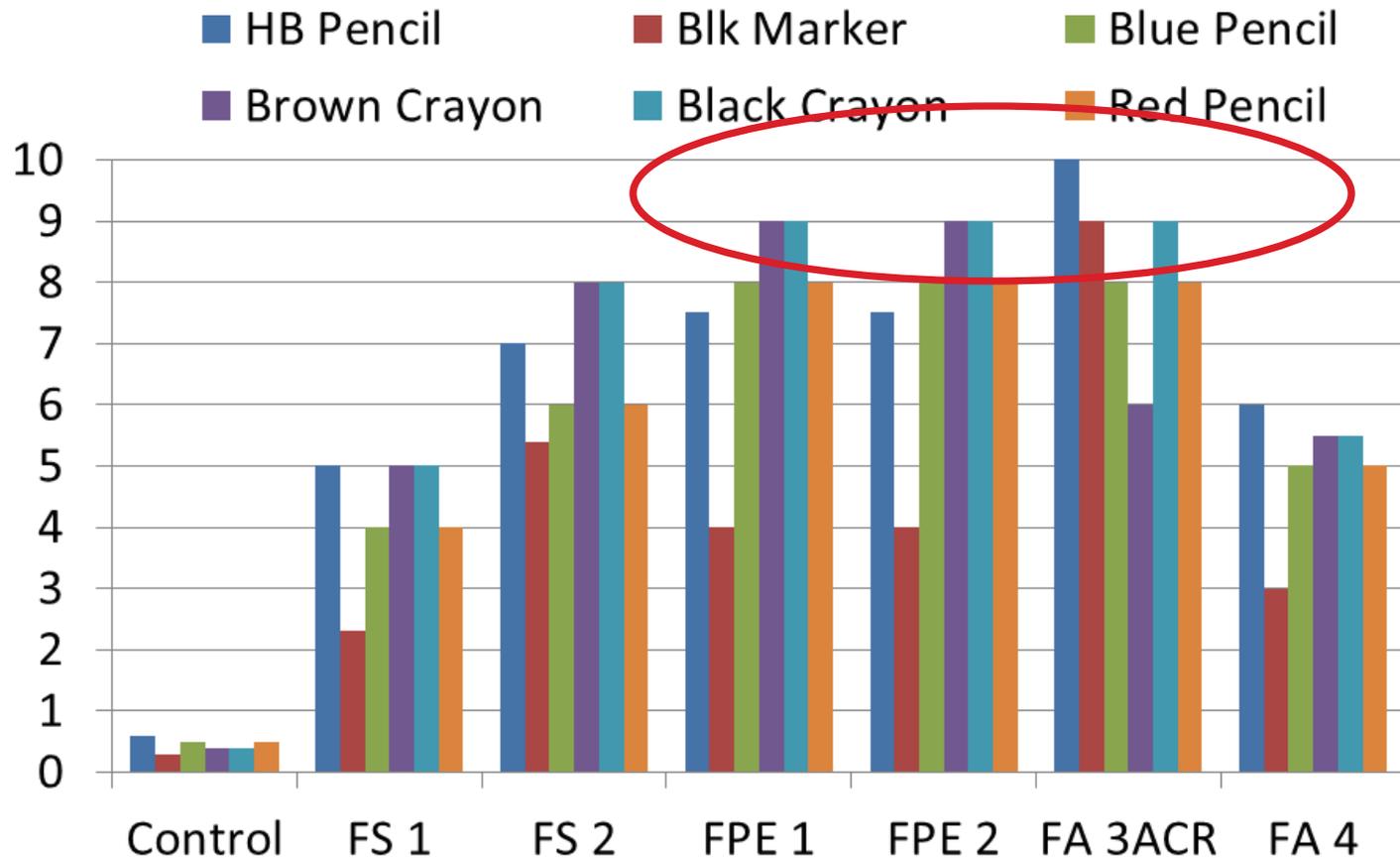
- In this view, FA 3 and FA 3 ACR are strong

Stain Resist: UV Urethane Acrylate



- FA 3 ACR and FPEs are effective

Stain: UV Epoxy Acrylate



- Highest %CF₂ is least effective
- FA 3 ACR and FPEs are effective



Summary:

- ▶ 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
- ▶ FA 3ACR, FPE 1 & FPE 2 again give relatively high ratings for gloss, mar and stain resistance.
- ▶ Best results for crayons
- ▶ FS 2, FA 4 & FA 3ACR give the best fingerprint resist.
- ▶ FA 4 – which has a balance of % SiI, %CF₂, & %CH₂ – again gives a very good balance of properties.



System: Cationic Silicone Resin

An in house, all silicone epoxy resin based cationic UV epoxy cured system uses a cycloaliphatic epoxy silicone (Silmer EPC E9 from Siltech) with the relevant percentage of FAS (0.2%, 0.5%, 1%, 3%, 5%) added, along with 0.5% UV9380C by Momentive (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	
FS 1	.2%	.5%	1%	3%	5%																
FA 3						.2%	.5%	1%	3%	5%											
FA 1											.2%	.5%	1%	3%	5%						
FA 2																	.2%	.5%	1%	3%	5%

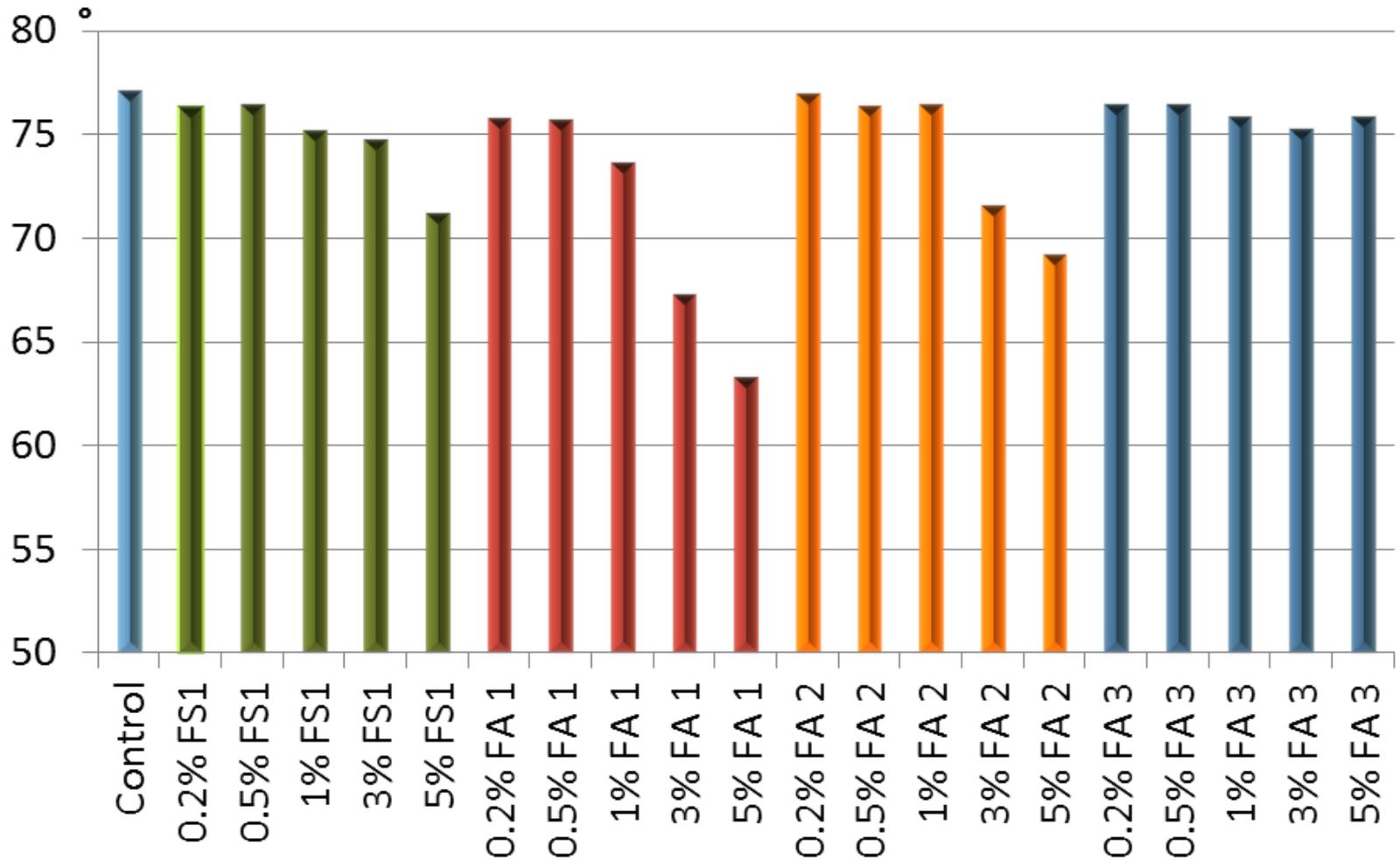
- Drawn down on Leneta paper with a wire-wound rod #10.
- Cured with a 10 mW/cm² UV box for 1 hour
- Kept at room temperature for one day



Film Properties: Cationic

Additive	%FAS	Static COF	Kinetic COF	Gloss	%Gloss Retained	Mar Resistance	Stain Resistance	Appearance
Control	0%	1.188	0.94	77.1	17.8%	1.8	2.4	Smooth
FS1	0.2%	0.782	0.758	76.3	28.4%	2.8	2.4	Smooth
FS1	0.5%	0.639	0.648	76.5	26.2%	2.6	2.8	Smooth
FS1	1.0%	0.549	0.545	75.2	26.2%	2.6	3.6	Smooth
FS1	3.0%	0.528	0.508	74.8	39.0%	3.9	4.7	Smooth
FS1	5.0%	0.582	0.583	71.2	27.1%	2.7	6.1	Smooth
FA 3	0.2%	0.977	0.789	76.5	18.0%	1.8	2.7	Smooth
FA 3	0.5%	1.221	1.084	76.5	18.0%	1.8	2.8	Smooth
FA 3	1.0%	1.182	1.001	75.9	28.3%	2.8	4.3	Smooth
FA 3	3.0%	0.955	0.905	75.3	28.7%	2.9	5.3	Smooth
FA 3	5.0%	1.256	1.236	75.9	18.9%	1.9	5.9	Smooth
FA 1	0.2%	1.147	1.005	75.8	54.5%	5.4	2.9	Smooth
FA 1	0.5%	1.149	0.883	75.7	64.8%	6.5	3.3	Smooth
FA 1	1.0%	0.764	0.656	73.7	18.9%	1.9	4.1	Smooth
FA 1	3.0%	1.257	1.128	67.3	32.9%	3.3	4.8	Smooth
FA 1	5.0%	1.265	1.262	63.3	28.9%	2.9	6.0	Smooth
FA 2	0.2%	1.262	1.12	77.0	43.5%	4.4	3.1	Smooth
FA 2	0.5%	1.158	1.129	76.4	35.1%	3.5	3.6	Smooth
FA 2	1.0%	0.791	0.754	76.5	43.9%	4.4	4.4	Smooth
FA 2	3.0%	1.179	1.114	71.6	33.3%	3.3	5.3	Smooth
FA 2	5.0%	1.215	1.093	69.2	25.7%	2.6	5.8	Smooth

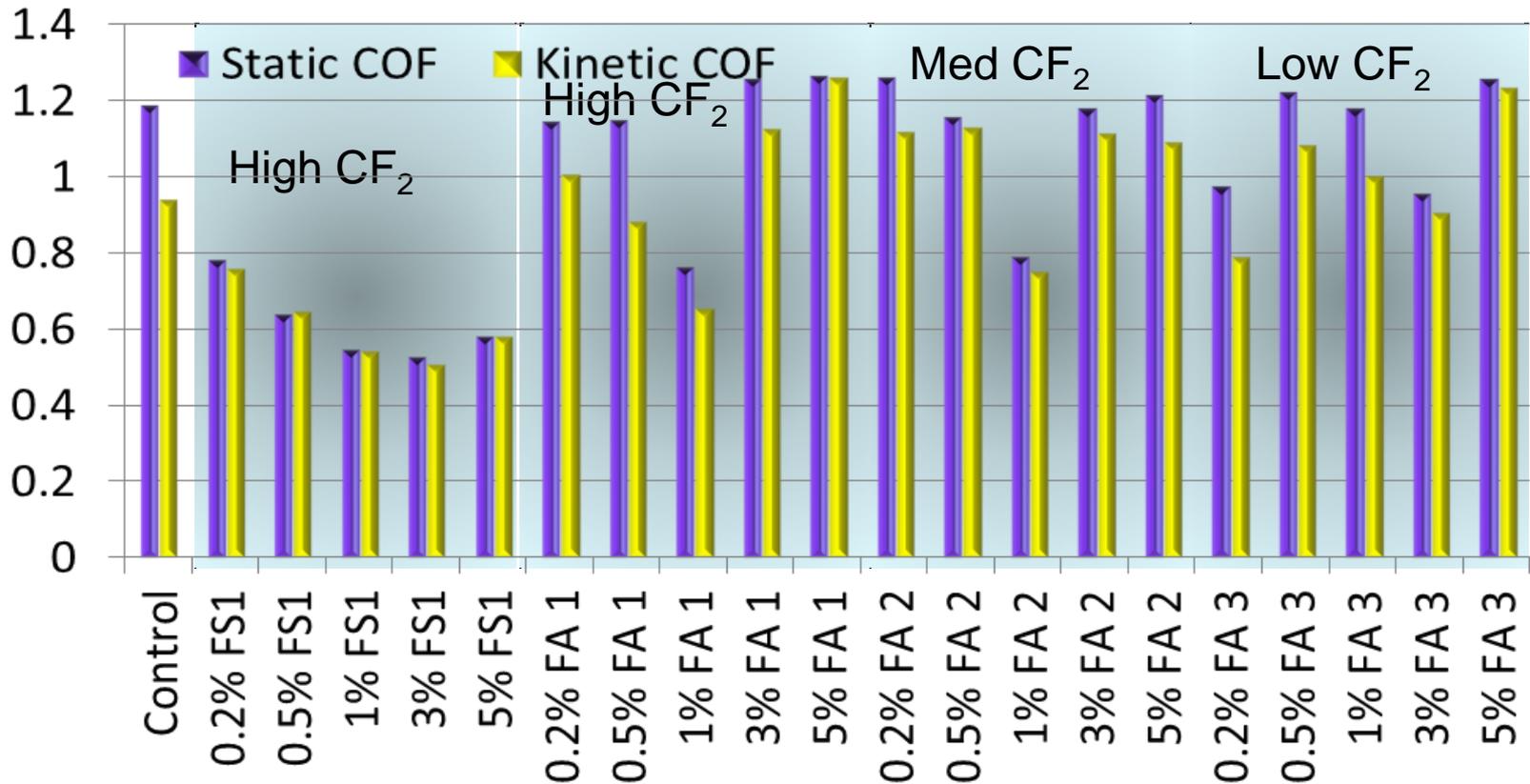
Gloss: Cationic UV Silicone



- Impact of use level



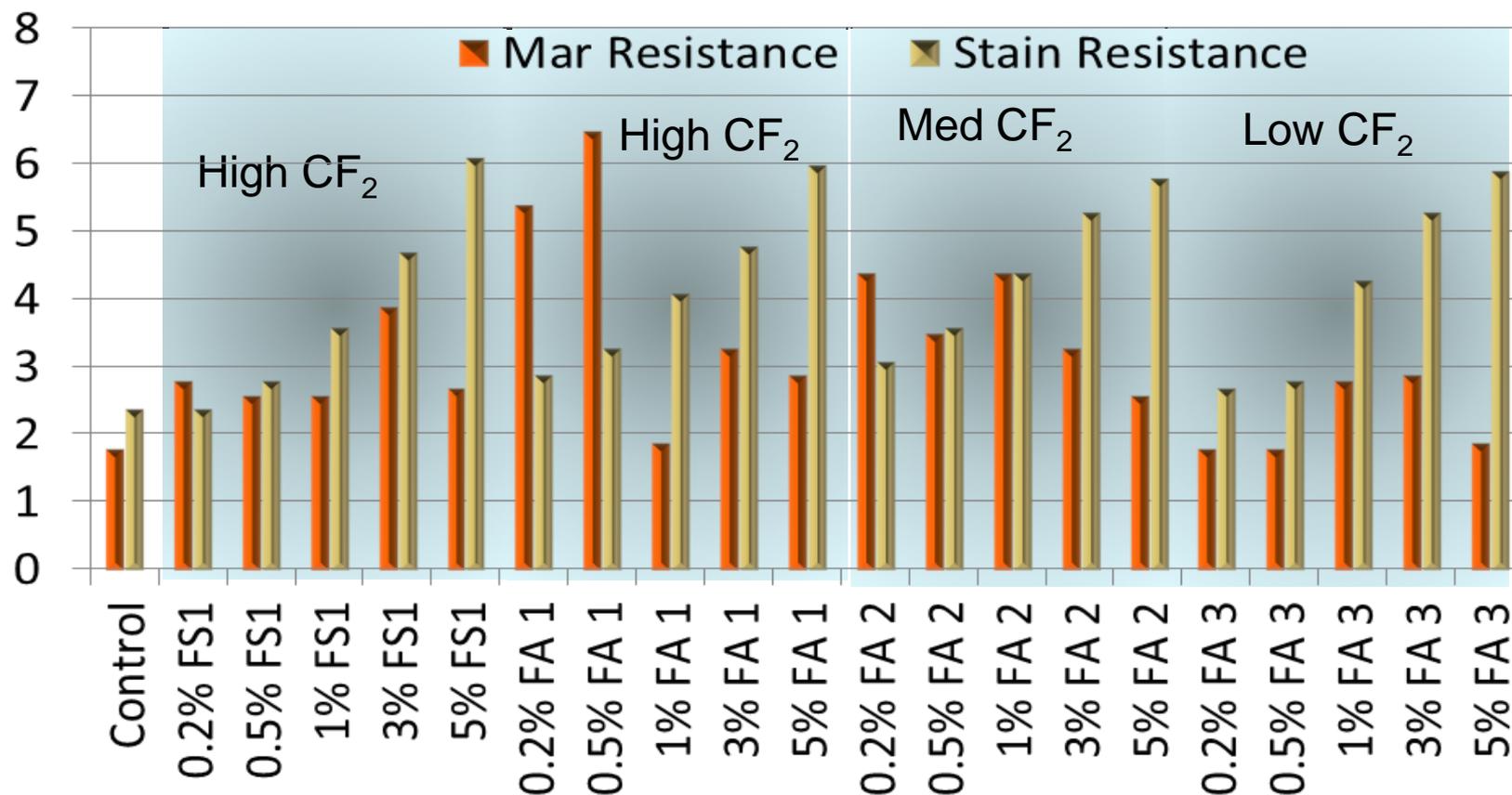
Slip: Cationic Epoxy Silicone



- High CF₂ content lowers COF
- High use levels lowers COF



Stain and Mar: Cationic



- Use level has most impact on stain
- Low CF₂ FAS just as good as high CF₂

Summary: Cationic Epoxy Silicone

- All FAS are compatible with silicone epoxy resin.
- 60° Gloss is slightly reduced and no surface defects are seen. More FAS does lower gloss more.
- 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 FS 1 – 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.



Stain summary

- ▶ High % Silicone FAS materials are best on Graphite, WB and Waxy stains
- ▶ High % CF₂ better for waxes but still not as good as above
- ▶ High MW makes little difference
- ▶ More is better



Summary of film properties

	Compatible					Slip					Mar				
	SB Urethane	UV Urethane	UV Epoxy	Cat. Silicone	Paint	SB Urethane	UV Urethane	UV Epoxy	Cat. Silicone	Paint	SB Urethane	UV Urethane	UV Epoxy	Cat. Silicone	Paint
FPE 1	++	++	++		++	++	+	+		-	++	++	++		+
FPE 2	++	++	++		++	++	+	+		-	++	++	++		+
FS 1		-	-	+	-		++	+	++	-		++	+	+	+
FS 2		-	+				+	+				++	+		
FA 1	-			-	-	-			-	-	++			-	++
FA 2	+			-	-	+			-	-	+			-	++
FA 3	+			+	-	+			-	-	+			-	++
FA 3ACR	-	-	+			++	++	++			++	++	++		
FA 4		-	+		-		++	+		-		++	+		++



Summary of film properties

	Average Stain					Finger print	
	SB Urethane	UV Urethane	UV Epoxy	Cat. Silicone	Paint	UV Urethane	UV Epoxy
FPE 1	+	+	++		-	+	+
FPE 2	+	+	++		-	+	+
FS 1		+	+	+	-	+	++
FS 2		++	+			++	++
FA 1	++			++	-		
FA 2	++			++	-		
FA 3	++			++	-		
FA 3ACR	++	++	++			++	++
FA 4		++	+		-	++	++

WB Stain Resistance Summary

	Ink	Black marker				Juices		
	Cat. Silicone	SB Urethane	UV Urethane	UV Epoxy	Cat. Silicone	Paint	Paint	Cat. Silicone
FPE 1		++	++	+		-	-	
FPE 2		+	++	+		-	++	
FS 1	++		-	-	++	+	-	+
FS 2			+	+				
FA 1	+	+			+	+	+	+
FA 2	+	+			+	++	++	++
FA 3	+	++			+	++	++	++
FA 3ACR		++	++	++				
FA 4			+	+		+	++	



Waxy Stain Resistance Summary

	Crayon			Pencil Crayon			Silicone Pigment	
	SB Urethane	UV Urethane	UV Epoxy	Urethane	UV Epoxy	Cat. Silicone	Cat. Silicone	Paint
FPE 1	+	++	++	++	++			++
FPE 2	+	++	++	++	++			++
FS 1		-	++	+	+	++	-	-
FS 2		++	++	+	+			
FA 1	++					++	+	-
FA 2	++					++	+	+
FA 3	+					++		+
FA 3ACR	++	++	++	+	++			
FA 4		+	+	+	+			-



Recommendations

- ▶ FSE 1, FSE 2 are available as Fluorosil® 2010, Fluorosil 2110. These are very good for all but fingerprint resistance
- ▶ R&D product FA3 and FA3 ACR is best overall including for fingerprint resistance. It is not always compatible.
- ▶ Use levels are up to 5% and more is better in most cases.



THANK YOU



chemaxia srl

