



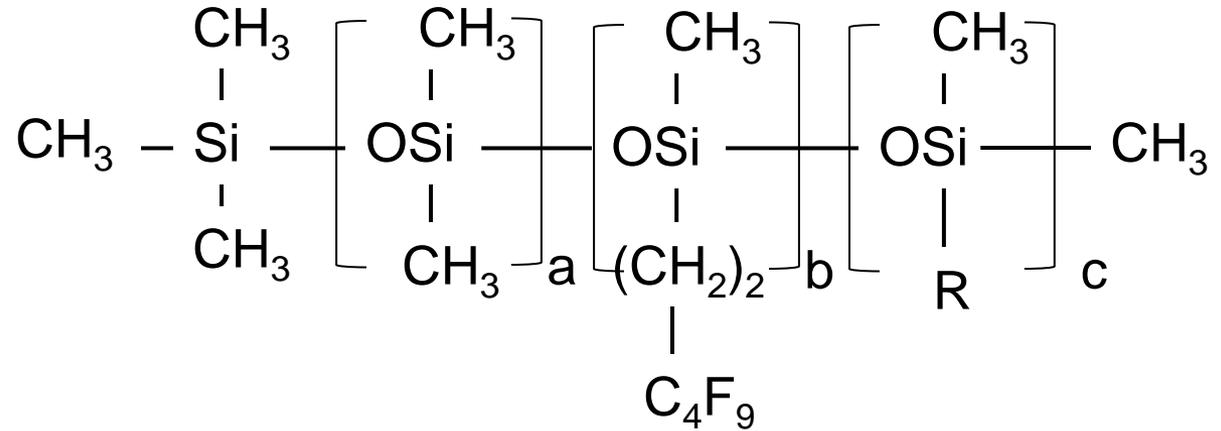
Fluoroalkyl Silicones in UV Cured Coatings Films

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Experimental and Methodology:

- ▶ The overall design is to use three UV cured coatings systems:
 - Urethane acrylate
 - Epoxy acrylate
 - Cationic UV cured epoxy silicone
- ▶ Various fluoroalkyl silicones are used.
- ▶ These are evaluated for slip, COF, mar resistance, stain resistance, finger print resistance and defects.

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%	7%	55%	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	

Testing

Coefficient of Friction (CoF /Slip): A ChemInstruments Coefficient of Friction-500 measures static and kinetic coefficients of friction directly. Test speed: 15 cm/min; travel length: 15 cm; Sled weight: 200 grams. The Sled surface is covered with ASTM-specified rubber.

Gloss: Measured with BYK-Gardner 60° micro-glossmeter.

Finger Print Resistance: Finger print resistance was determined by visual inspection of finger imprints remaining on the panel surface after gentle pressing and rubbing with fingers. A score of 10 is the best, which represents absence of finger prints, and 0 is the worst.

Testing (cont)

Mar Resistance: measured using a Sutherland 2000 Ink Rub Tester - Dry Rub method with the following settings: 500 rubs, 84 rpm stroke speed for all sample sets using a 4 lb test block and a 2"x 4" nylon scrubbing pad. Gloss is measured immediately after rubbing for each panel. Record the loss of gloss(%) before and after rubs and a subjective rating from 0 to 10 where 10 is the best and indicates no visible effect.

Testing (cont)

Stain Resistance: One drop of test fluid was applied and allowed to sit for one hour then wiped with a paper towel. Staining is observed and recorded from 1-10 (1 = worst, and 10 = completely clean.)

For System III, a Sutherland 2000 rub tester is used to wipe the stain with a Kimwipe saturated with water for 50 wipes at 84 rpm. The stain is evaluated again from 1-10.

Systems I and II differed in that only 42 rubs were used and a 64:1 diluted solution of commercial cleaner was used instead of water.

Test fluids: Blue pen ink, black marker ink, silicone pigments black sharpie ink, red sharpie ink, graphite pencil, printer ink, concentrated grape juice, crayon, and pencil crayon.

System I: Urethane acrylate

Component	Supplier	Wt%
CN910A70	Sartomer	74.26%
SR 355	Sartomer	4.95%
Irgacure 184	Ciba	4.95%
Fluoroalkyl silicone	Siltech	0.99%
Butyl Acetate		3.71%
Toluene		3.71%
Methyl Isobutyl Ketone		4.46%
Methyl Ethyl Ketone		2.97%

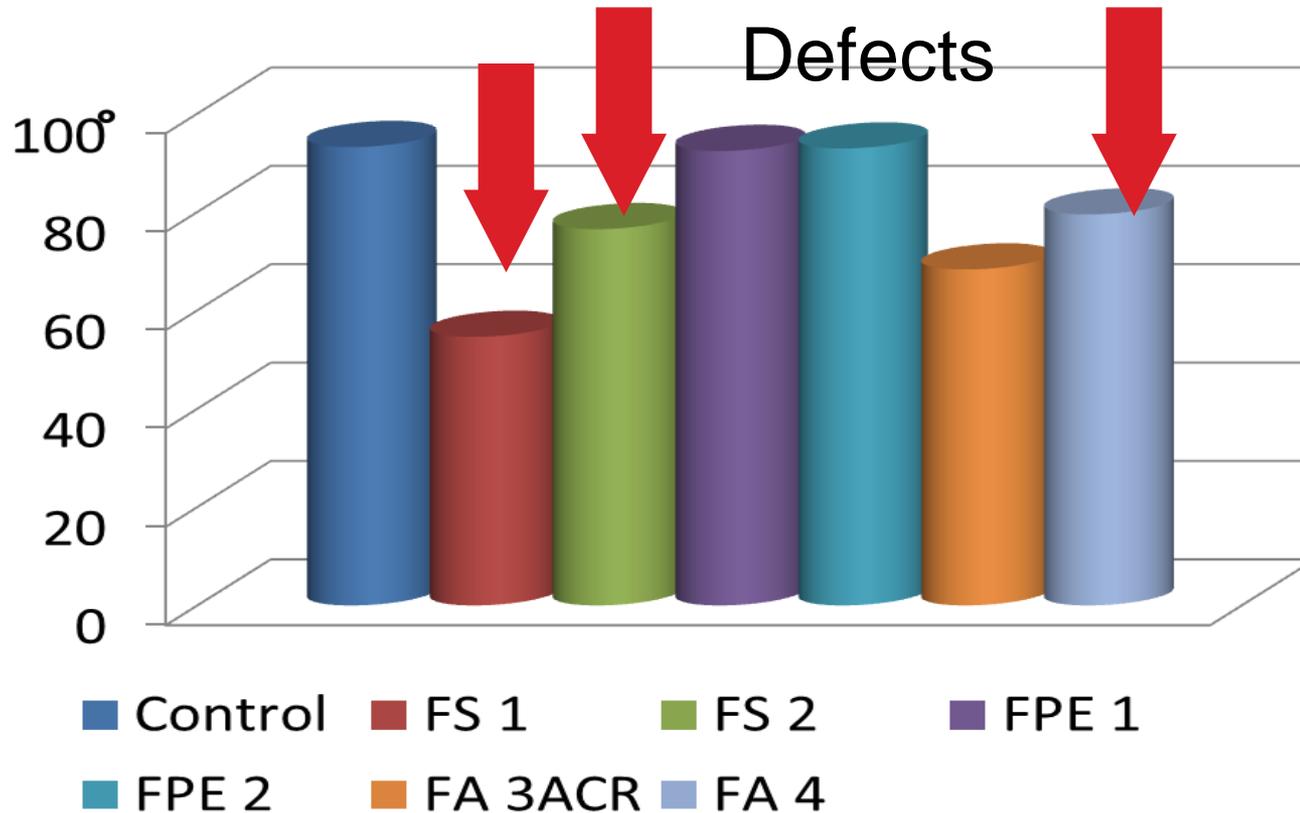
Preparation:

- 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"

Film Properties I: Urethane

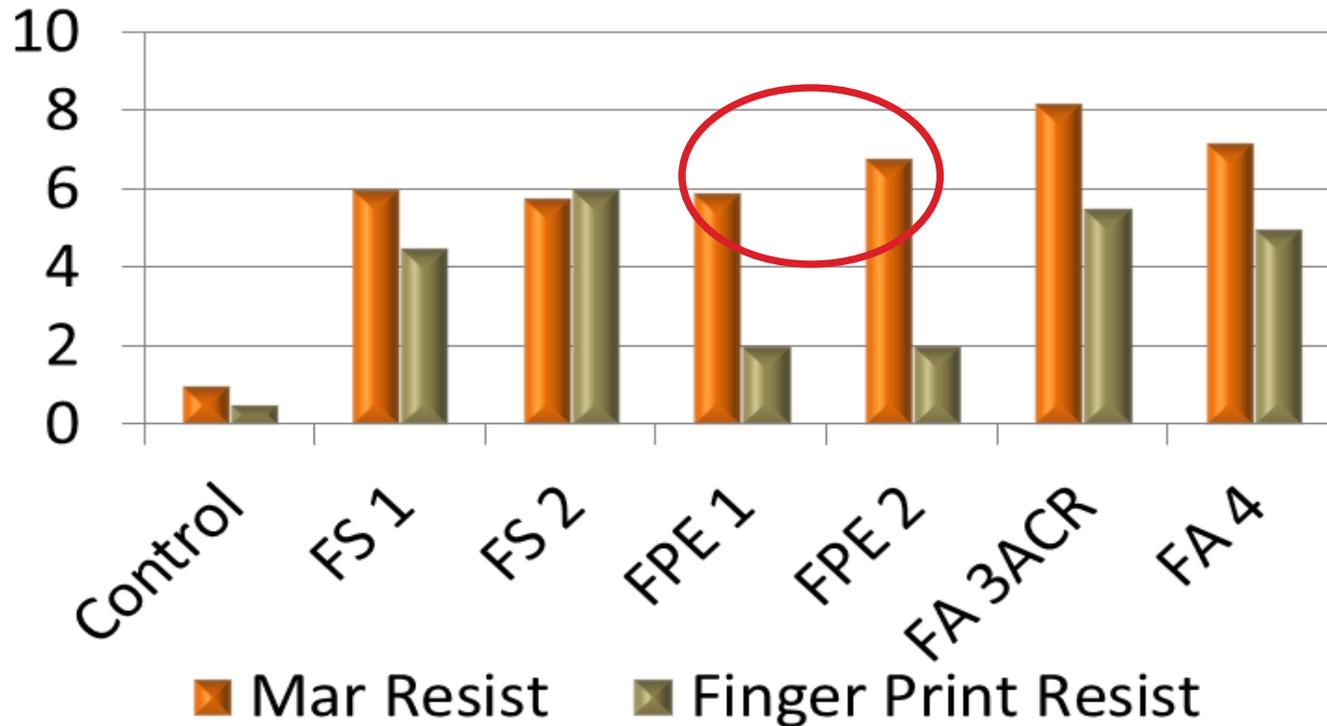
	60° Gloss	Stain Resist	Mar Resist	Static COF	Kinetic COF	Finger Print Resist	Surface Appearance
Control	93.2	1.7	1.0	1.99	2.18	0.5	Some craters
FS 1	54.6	4.0	6.0	0.93	0.93	4.5	Patches
FS 2	76.5	6.7	5.8	1.37	1.26	6.0	Patches
FPE 1	92.4	7.6	5.9	1.25	1.56	2.0	Smooth
FPE 2	92.9	7.6	6.8	1.31	1.34	2.0	Smooth
FA 3ACR	68.3	8.3	8.2	0.58	0.56	5.5	Smooth
FA 4	79.5	5.0	7.2	0.78	0.76	5.0	Wavy

Gloss I: Urethane Acrylate



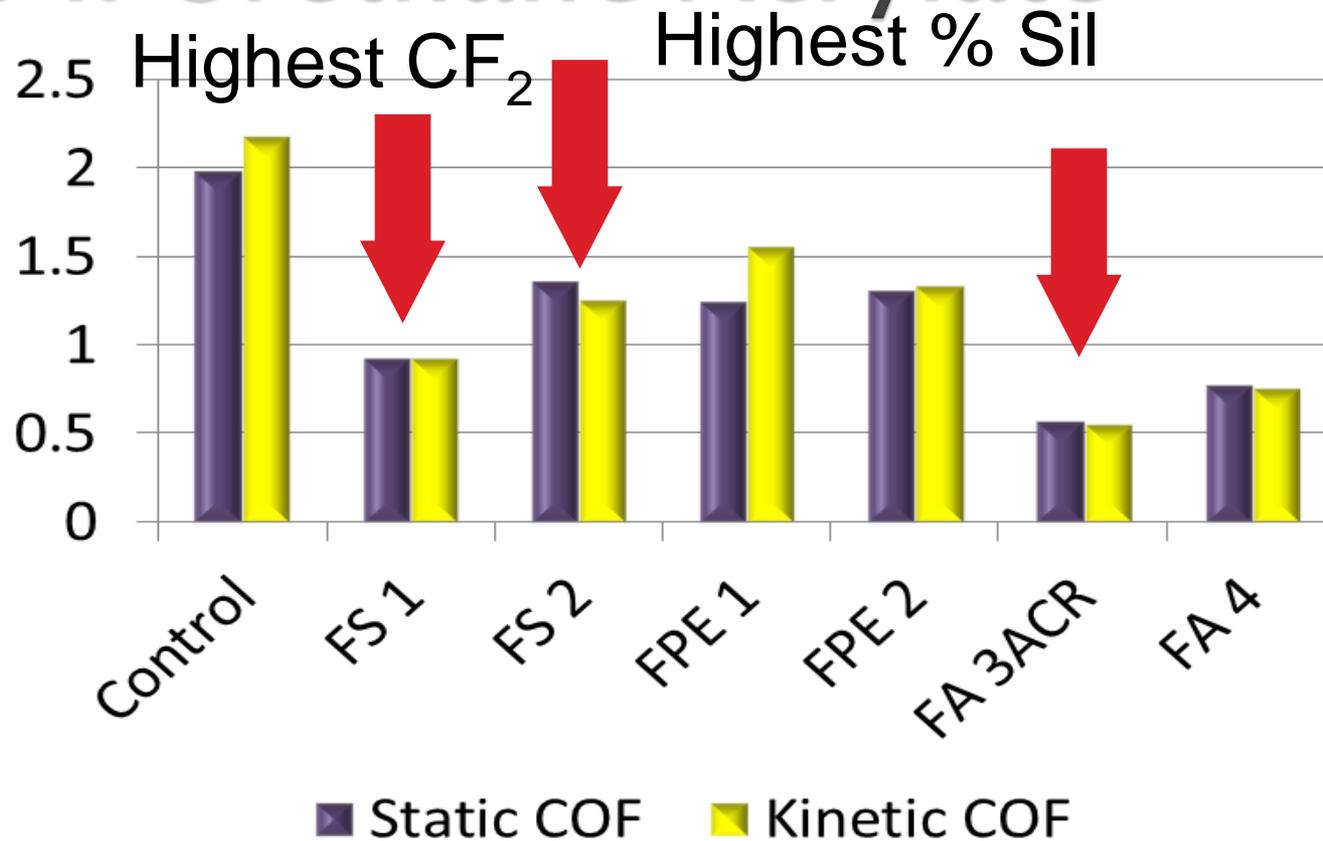
- FPE are most miscible, keep gloss
- FA and FS types decrease gloss

Mar/ Finger Print I: Urethane



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

Slip I: Urethane Acrylate

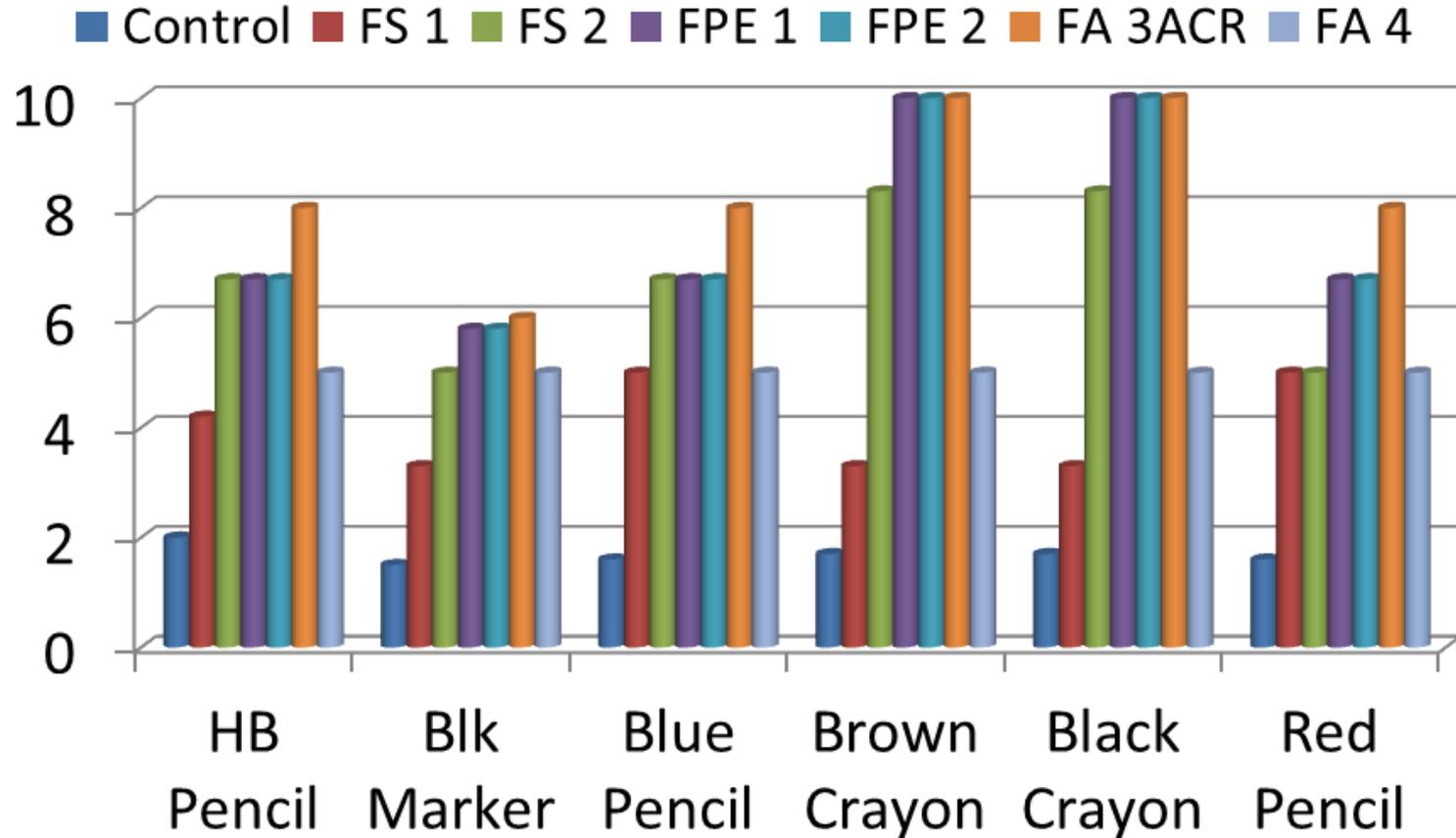


- All improve COF
- More with $>$ wt% CF_2

Stain Resist I: Urethane Acrylate

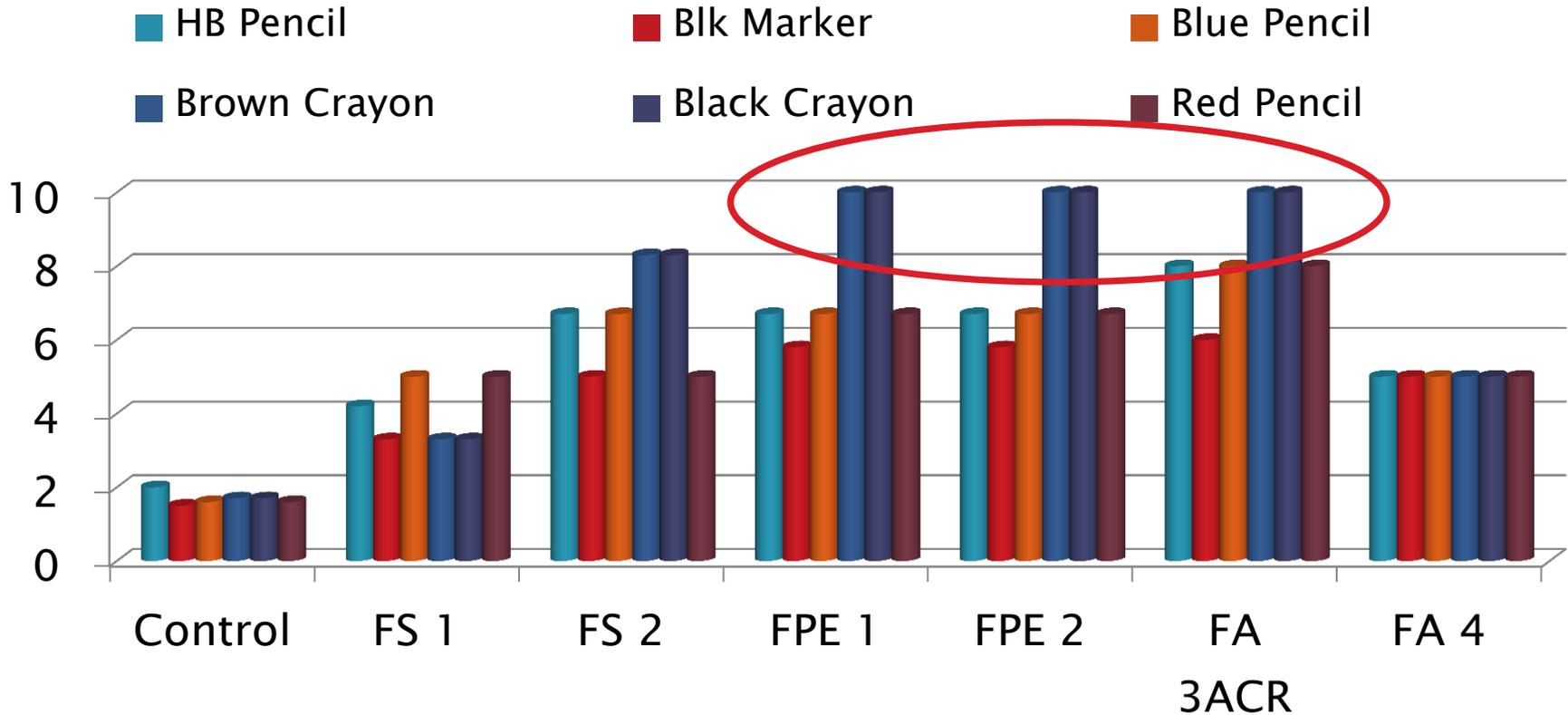
	HB Pencil	Black Crayons	Brown Crayon	Red pencil crayon	Blue pencil crayon	Black permanent marker	Average
Control	2.0	1.7	1.7	1.6	1.6	1.5	1.7
FS 1	4.2	3.3	3.3	5.0	5.0	3.3	4.0
FS 2	6.7	8.3	8.3	5.0	6.7	5.0	6.7
FPE 1	6.7	10.0	10.0	6.7	6.7	5.8	7.6
FPE 2	6.7	10.0	10.0	6.7	6.7	5.8	7.6
FA 3ACR	8.0	10.0	10.0	8.0	8.0	6.0	8.3
FA 4	5.0	5.0	5.0	5.0	5.0	5.0	5.0

Stain Resist I: Urethane Acrylate



- Crayons are effectively blocked by several

Stain Resist I: Urethane Acrylate



- FA 3 ACR and FPEs are effective

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

System II: Epoxy Acrylate

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

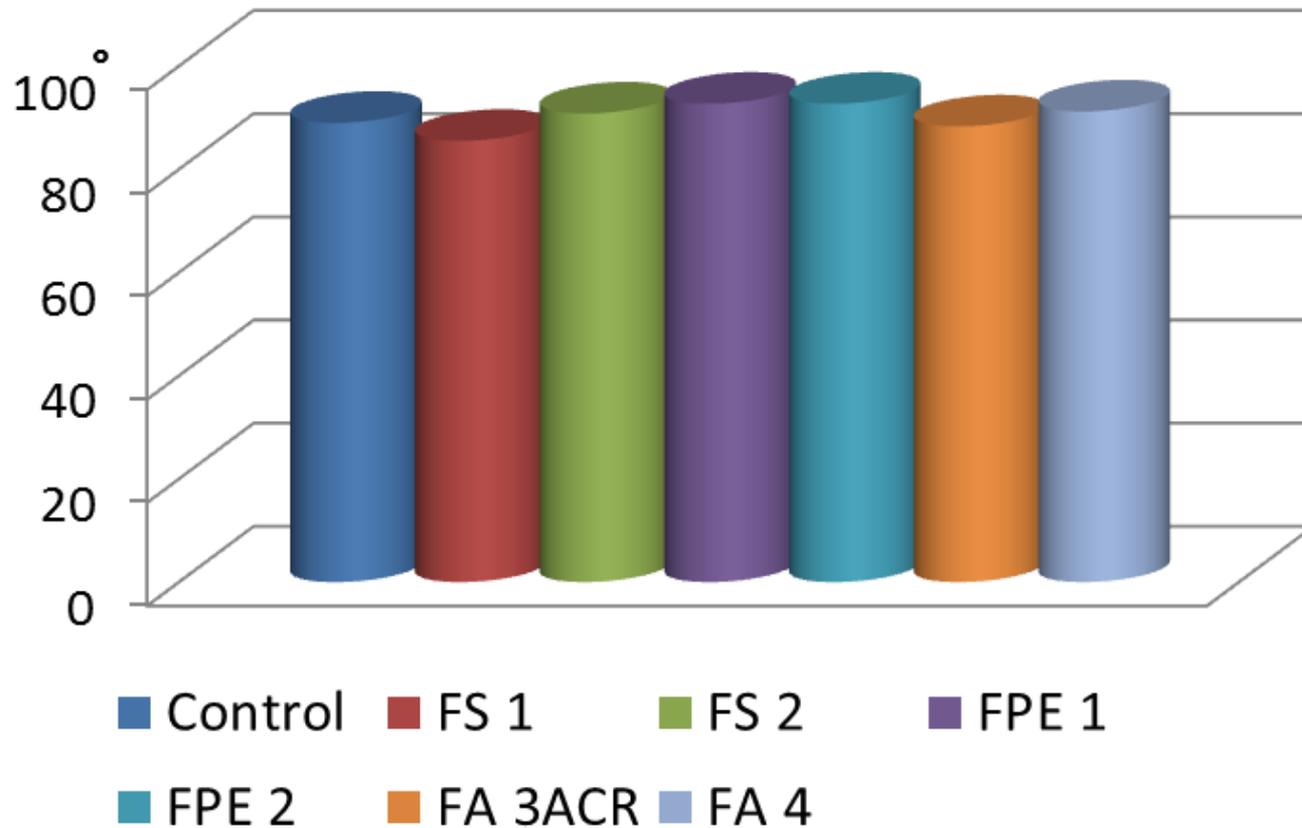
Preparation:

- Drawn down on a Leneta paper using a wire-wound rod #10.
- Cured for at least 1 hour in a 10 mW/cm² UV box.

Film Properties II: Epoxy Acrylate

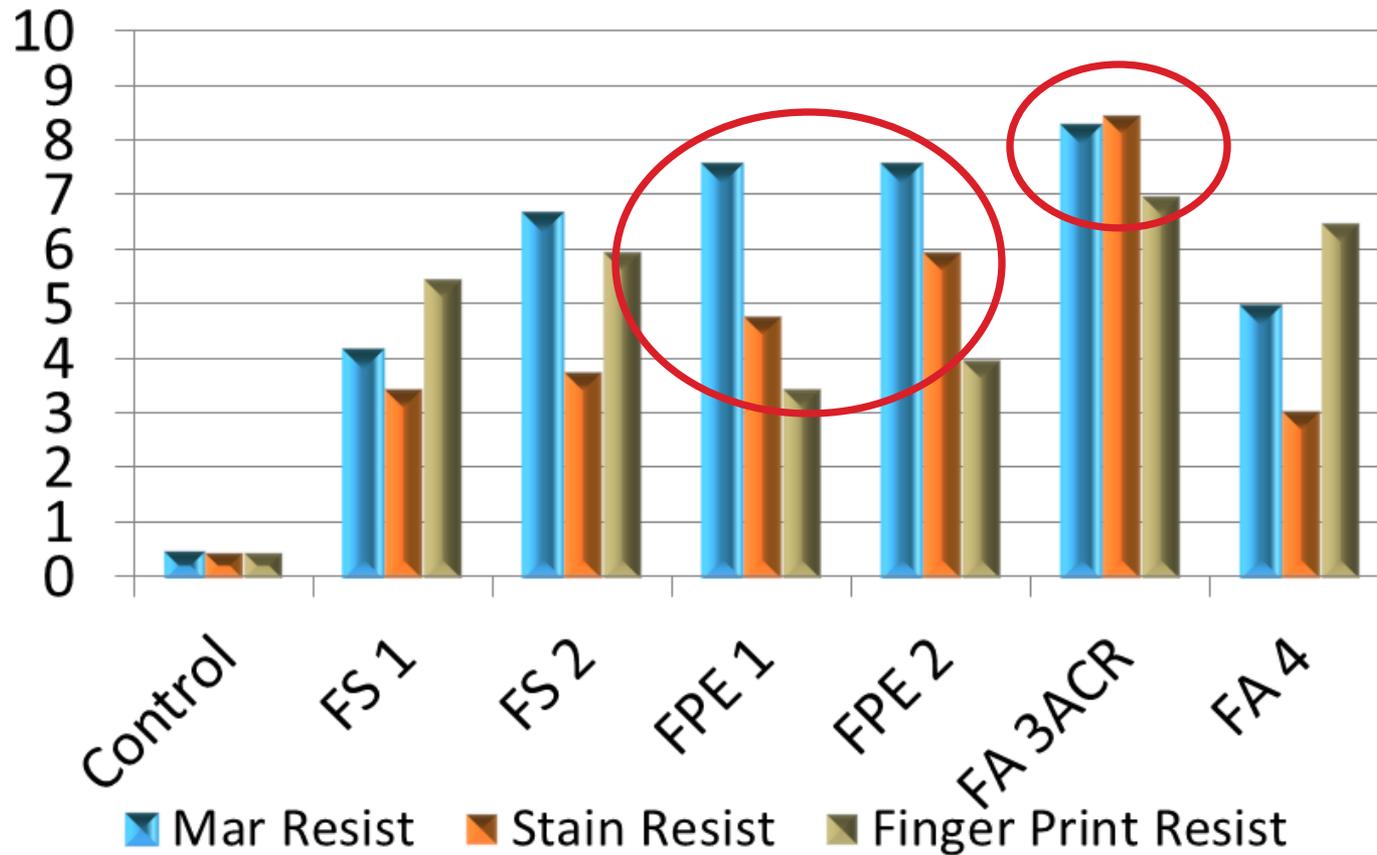
	60° Gloss	Stain Resistance	Mar Resistance	Static COF	Kinetic COF	Finger Print Resistance	Appearance
Control	89.0	0.5	0.5	2.78	2.80	0.5	Pinholes
FS 1	85.5	4.2	3.5	2.32	2.06	5.5	Patches
FA 4	91.2	5.0	3.1	1.88	1.80	6.5	Matte
FS 2	90.8	6.7	3.8	1.96	1.61	6.0	Patches
FPE 1	92.7	7.6	4.8	2.08	2.33	3.5	Smooth
FPE 2	92.7	7.6	6.0	2.26	2.76	4.0	Smooth
FA 3ACR	88.3	8.3	8.5	0.52	0.51	7.0	Smooth

Gloss II: Epoxy Acrylate



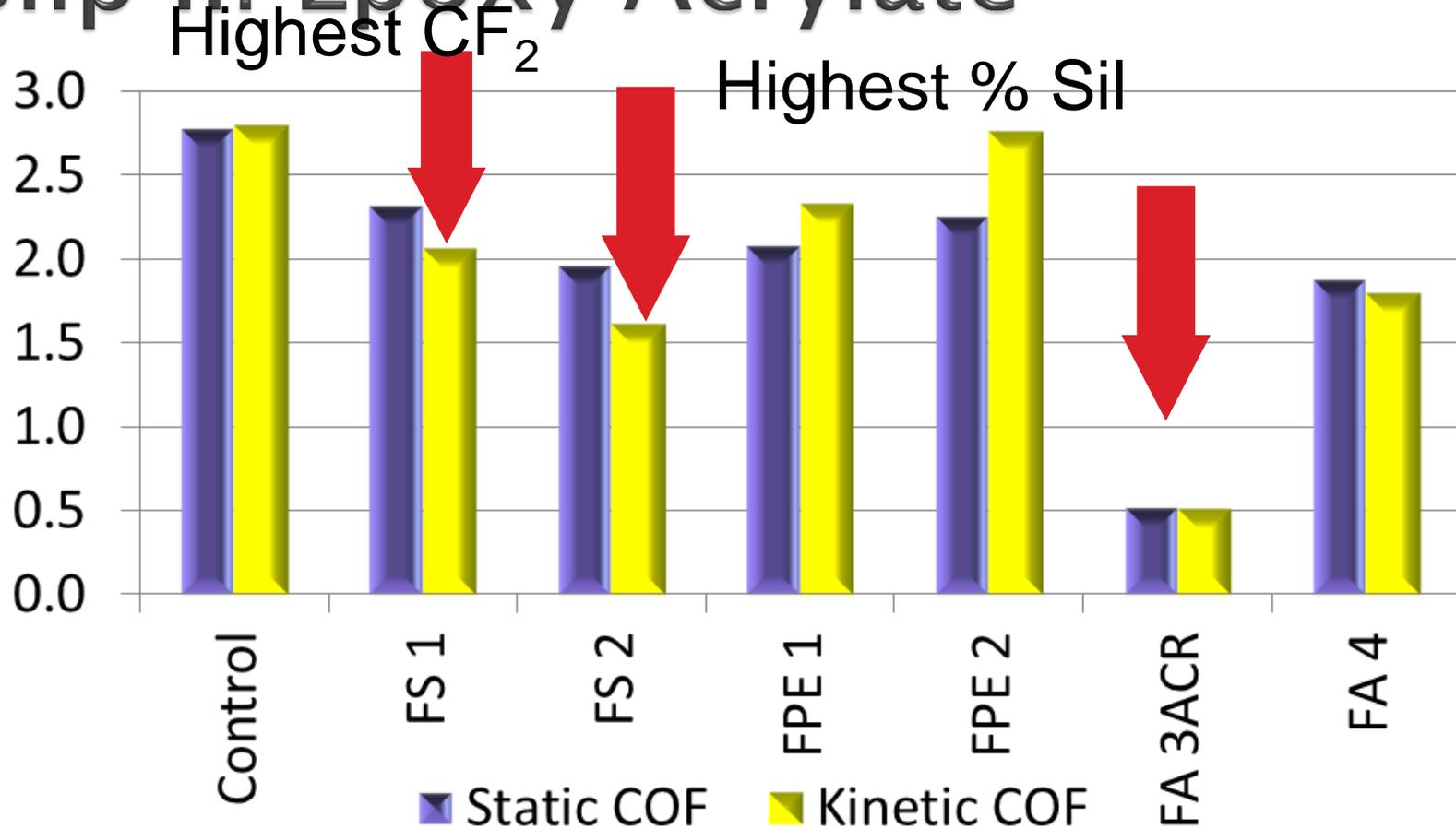
- Minor incompatibility

Mar, Stain, Print II: Epoxy Acrylate



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

Slip II: Epoxy Acrylate

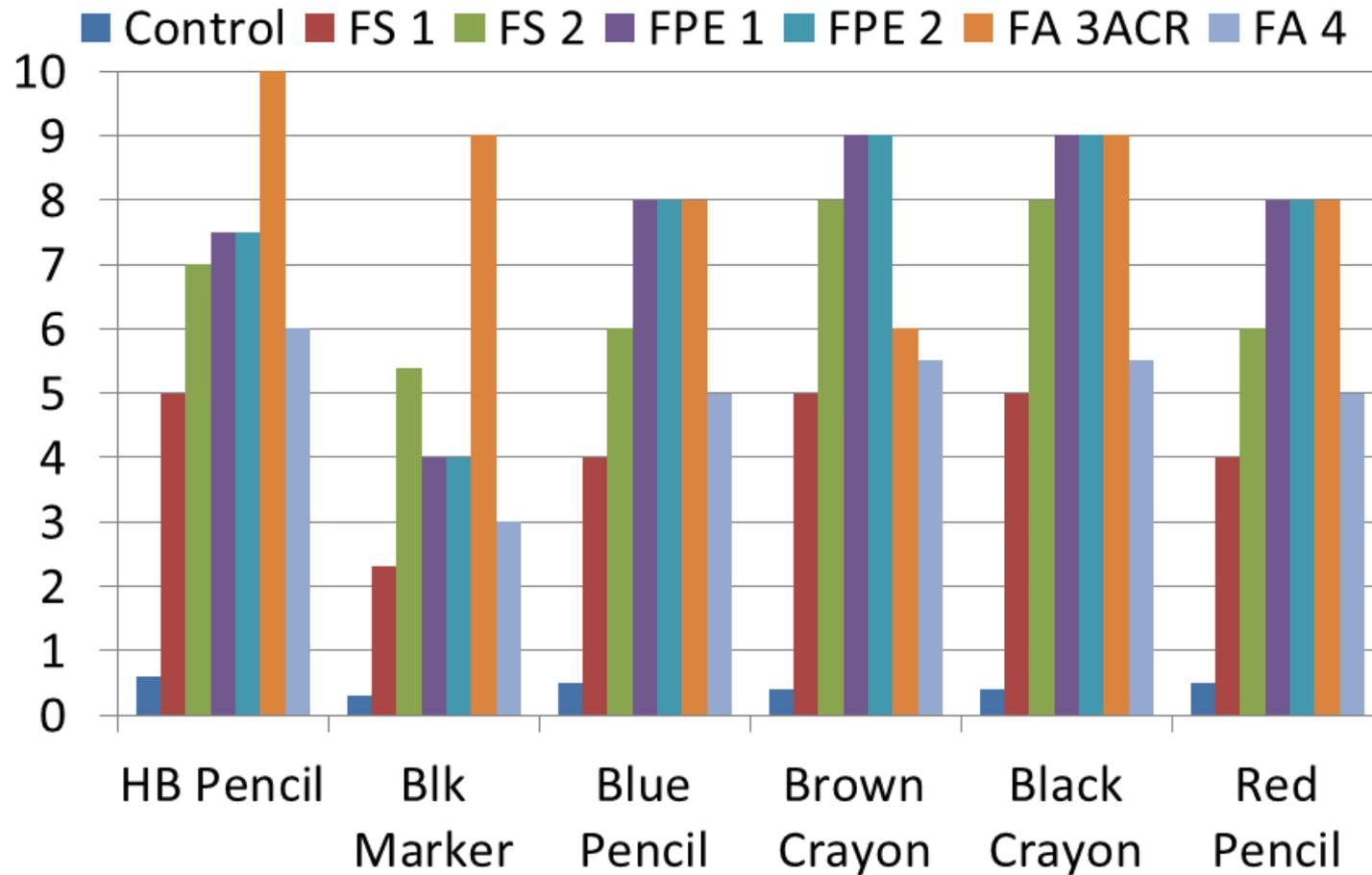


- All improve COF
- More with $>$ wt% silicone

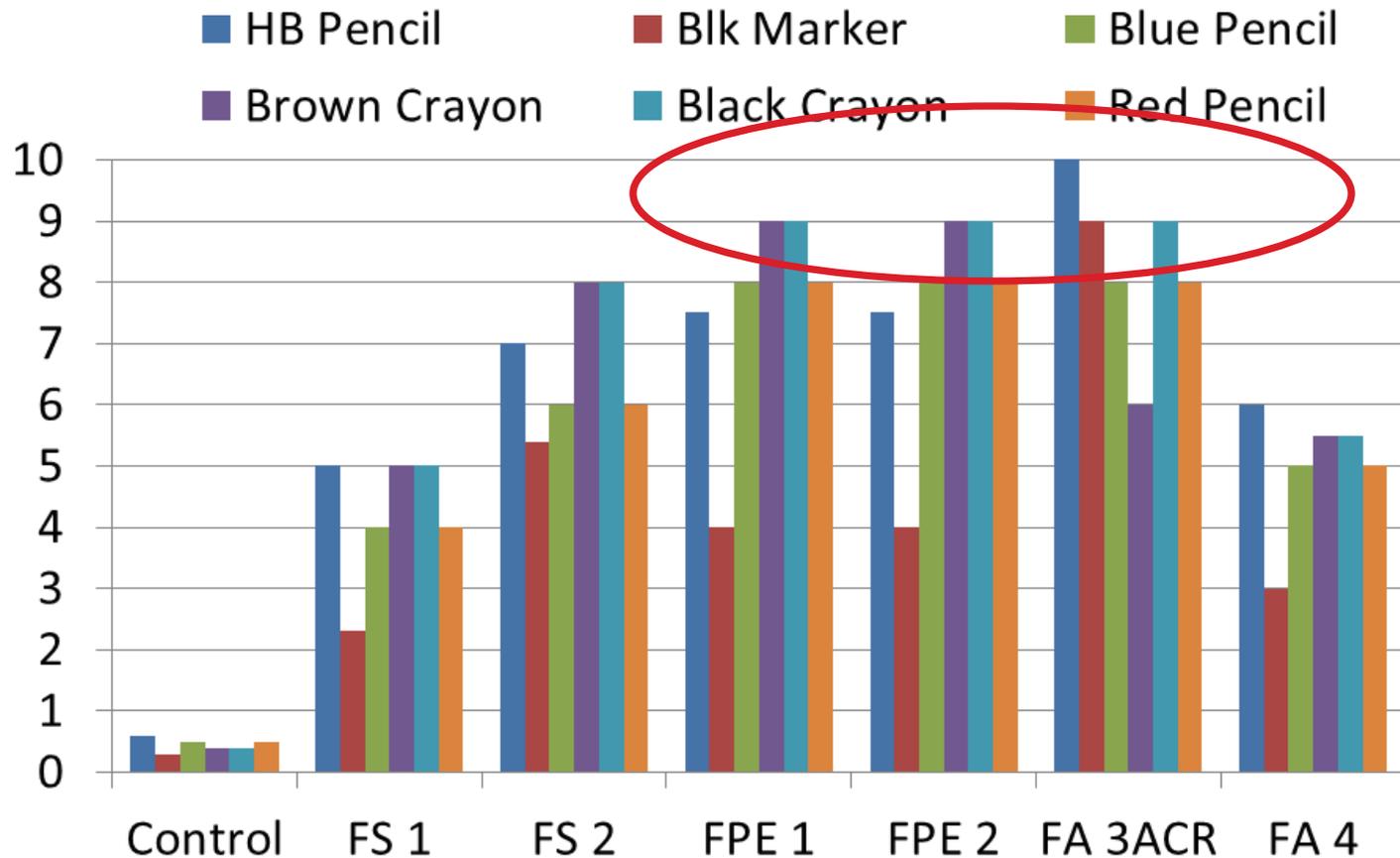
Stain II: Epoxy Acrylate

	HB Pencil	Black Crayon	Brown Crayon	Red pencil crayon	Blue pencil crayon	Black permanent marker	Average
Control	0.6	0.4	0.4	0.5	0.5	0.3	0.5
FS 1	5.0	5.0	5.0	4.0	4.0	2.3	4.2
FA 4	6.0	5.5	5.5	5.0	5.0	3.0	5.0
FS 2	7.0	8.0	8.0	6.0	6.0	5.4	6.7
FPE 2	7.5	9.0	9.0	8.0	8.0	4.0	7.6
FPE 1	7.5	9.0	9.0	8.0	8.0	4.0	7.6
FA 3ACR	10.0	9.0	6.0	8.0	8.0	9.0	8.3

Stain II: Epoxy Acrylate



Stain II: Epoxy Acrylate



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

Results System II: 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
- ▶ 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 % Sil, %CF₂, & %CH₂ – again gives a very good balance of properties.

System III: 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:

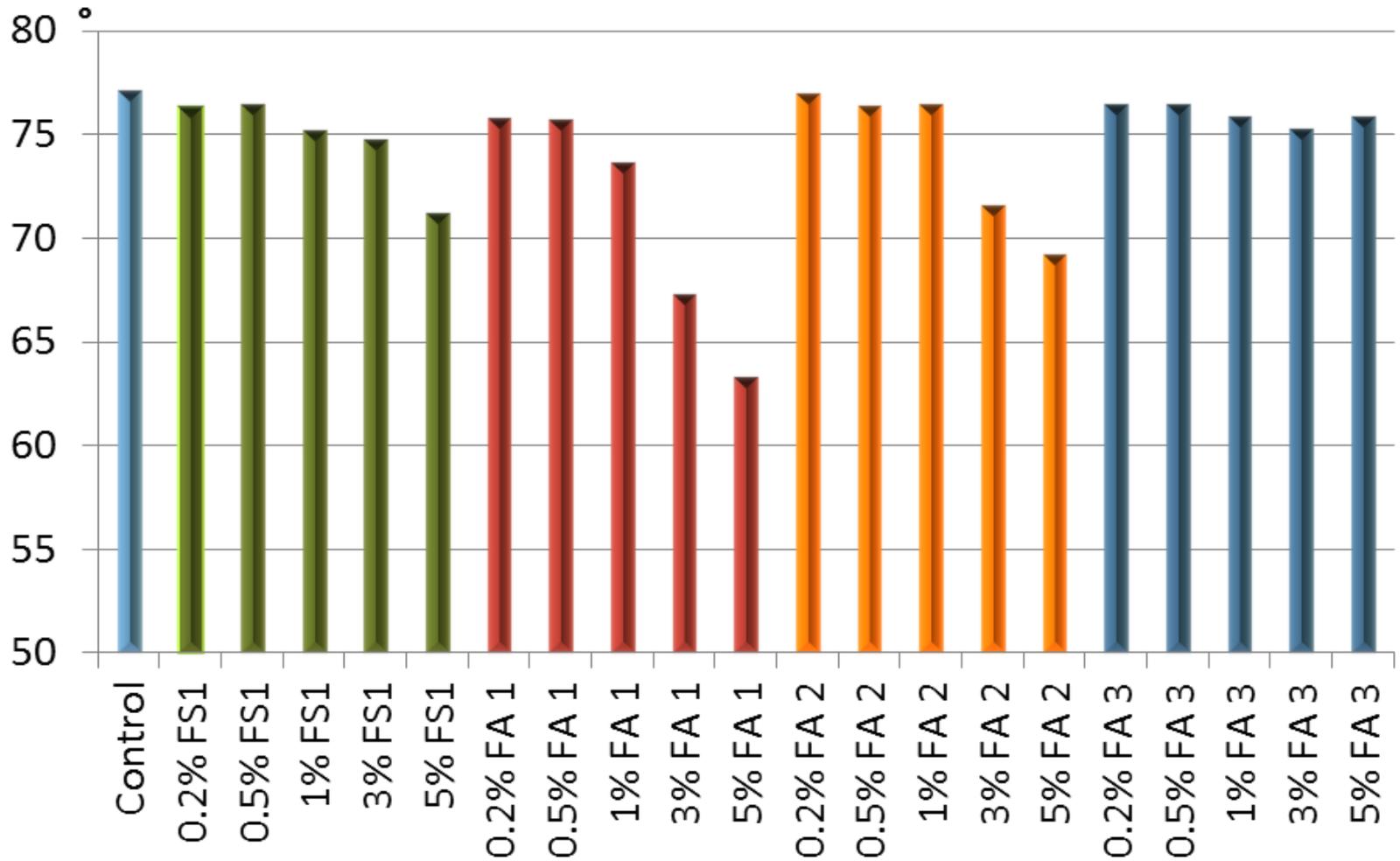
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	
FS 1	.2%	.5%	1%	3%	5%																
FA 3						.2%	.5%	1%	3%	5%											
FA 1											.2%	.5%	1%	3%	5%						
FA 2																	.2%	.5%	1%	3%	5%

- 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 III: Cationic

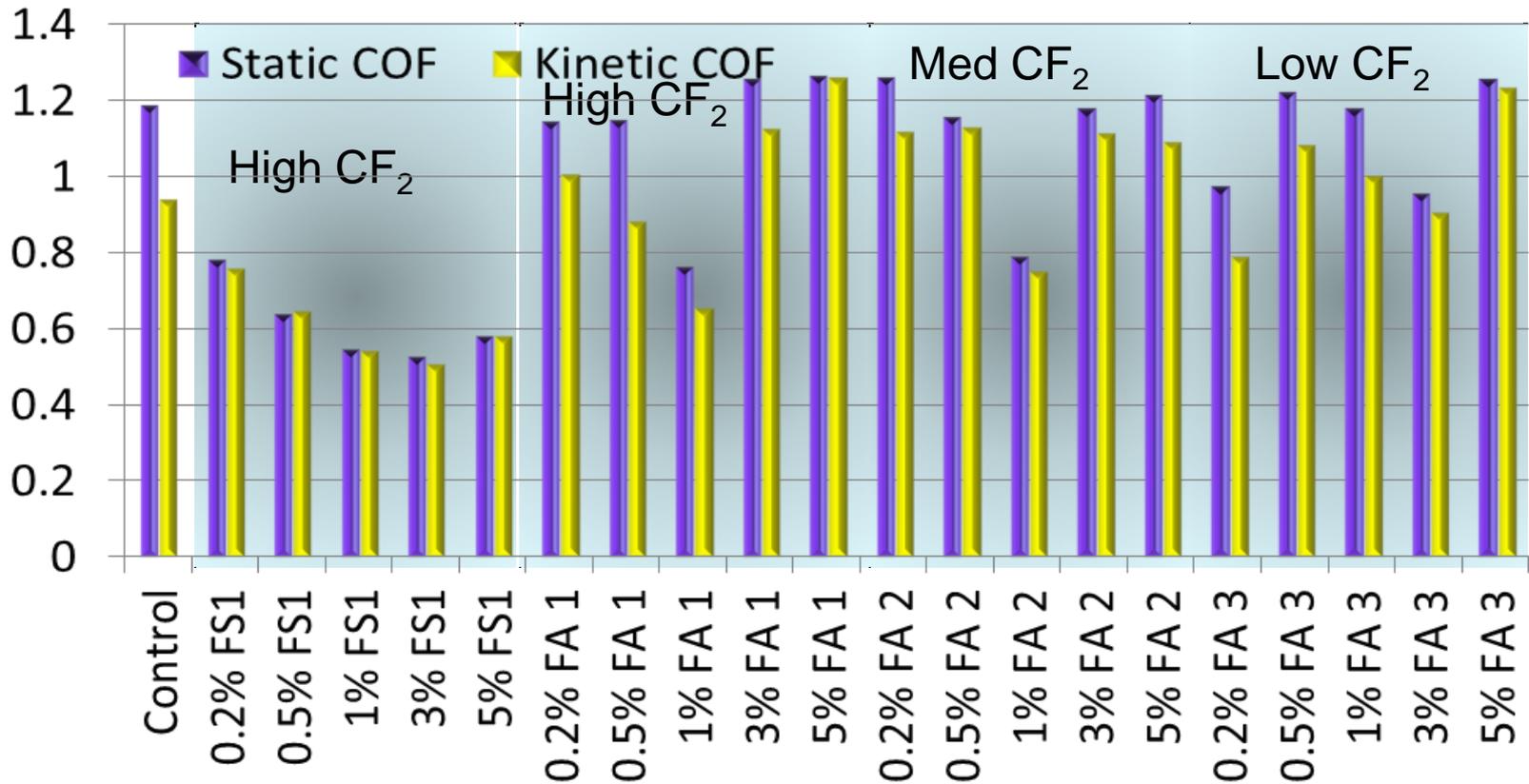
Additive	%FAS	Static COF	Kinetic COF	Gloss	%Gloss Retained	Mar Resistance	Stain Resistance	Appearance
Control	0%	1.188	0.94	77.1	17.8%	1.8	2.4	Smooth
FS1	0.2%	0.782	0.758	76.3	28.4%	2.8	2.4	Smooth
FS1	0.5%	0.639	0.648	76.5	26.2%	2.6	2.8	Smooth
FS1	1.0%	0.549	0.545	75.2	26.2%	2.6	3.6	Smooth
FS1	3.0%	0.528	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 III: Cationic UV Silicone



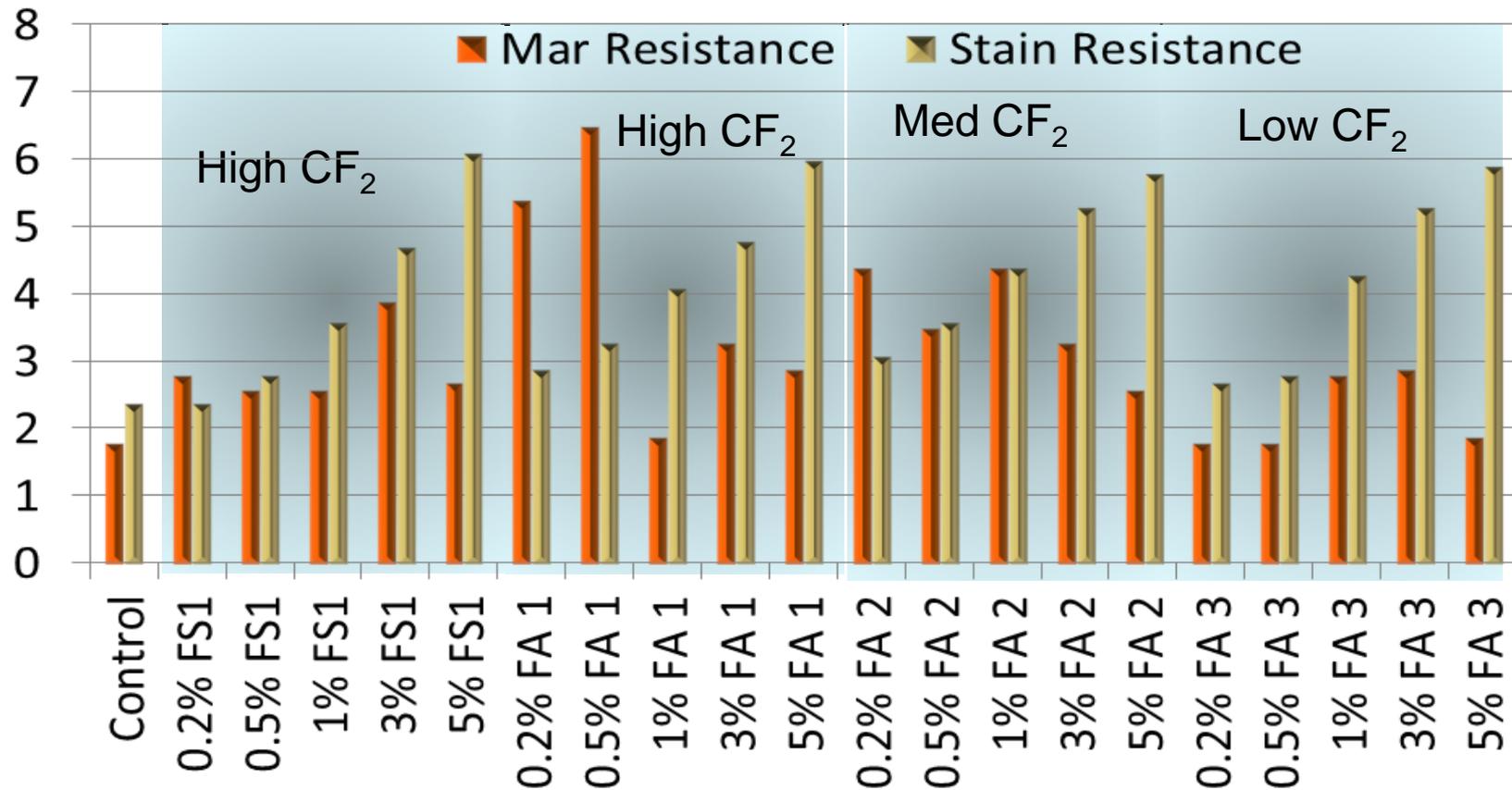
- Impact of use level

Slip III: Cationic Epoxy Silicone



- High CF₂ content lowers COF
- Higher use levels lower COF but can have too much

Stain and Mar III: Cationic

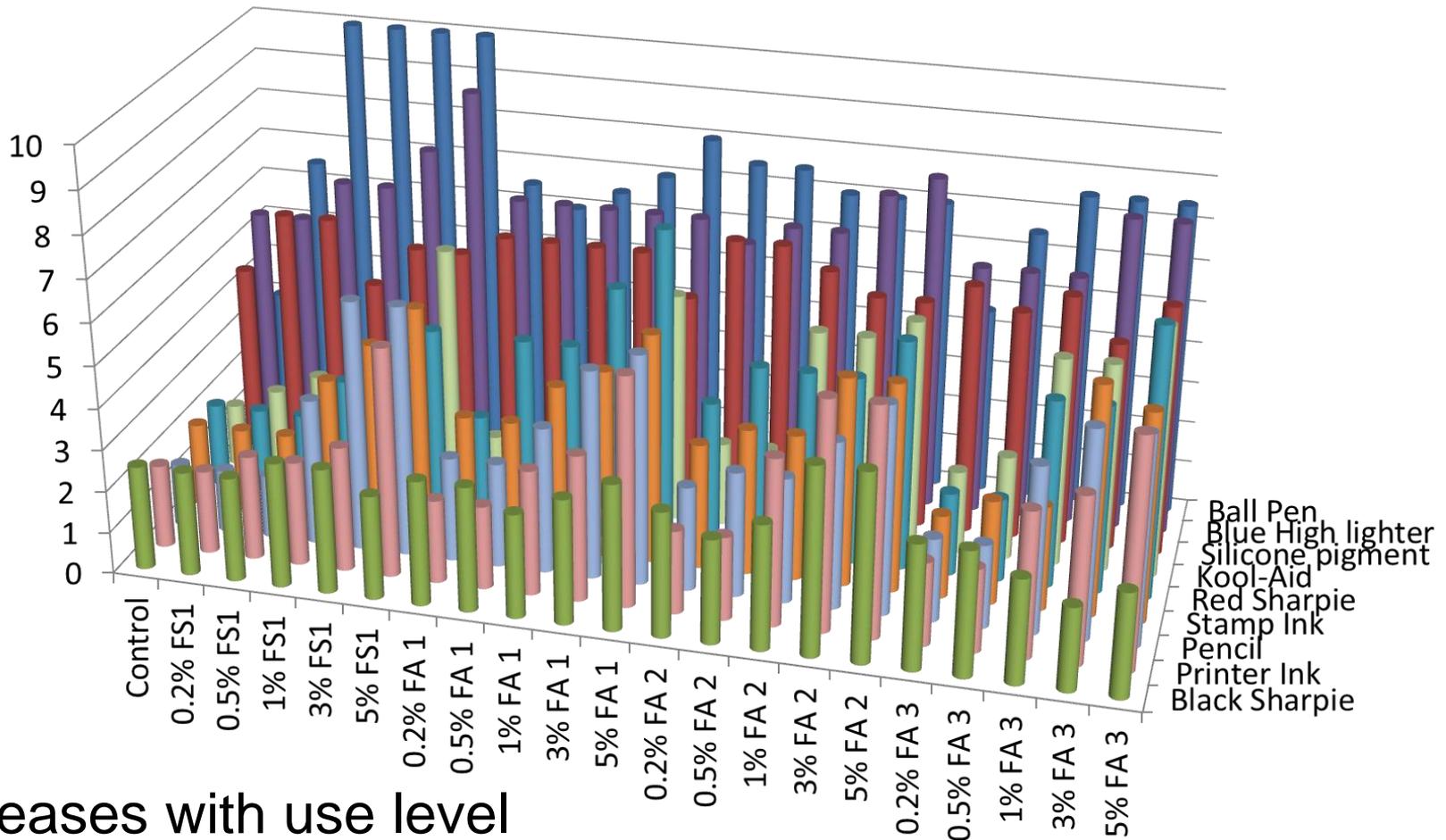


- Use level has most impact on stain
- Low CF₂ FAS just as good as high CF₂

Stain III: Cationic Epoxy

Additive	% FAS	Ball Pen	Silicone pigment	Black Sharpie	Blue Highlighter	Red Sharpie	Stamp Ink	Pencil	Printer Ink	Kool-Aid
Control	0.0%	3	4.5	2.5	5.5	2	2	1.5	2	1.5
FS 1	0.2%	6.5	6	2.5	5.5	2	2	1.5	2	2
FS 1	0.5%	10	6	2.5	6.5	2	2	1.5	2.5	2.5
FS 1	1.0%	10	4.5	3	6.5	3	3.5	3.5	2.5	2.5
FS 1	3.0%	10	5.5	3	7.5	3.5	4.5	6	3	3.5
FS 1	5.0%	10	5.5	2.5	9	4.5	5.5	6	5.5	6
FA 3	0.2%	4.5	6	3	6	2	2	2	2	2
FA 3	0.5%	6.5	5.5	3	6	2	2.5	2	2	2.5
FA 3	1.0%	7.5	6	2.5	6	4.5	2.5	4	3.5	5
FA 3	3.0%	7.5	5	2	7.5	4.5	5.5	5	4	5
FA 3	5.0%	7.5	6	2.5	7.5	6.5	5	5	5.5	6
FA 1	0.2%	6.5	6	3	6.5	2.5	3	2.5	2	1.5
FA 1	0.5%	6	6	3	6.5	4.5	3	2.5	2	1.5
FA 1	1.0%	6.5	6	2.5	6.5	4.5	4	3.5	3	3
FA 1	3.0%	7	6	3	6.5	6	4.5	5	3.5	3
FA 1	5.0%	8	5	3.5	6.5	7.5	5.5	5.5	5.5	5.5
FA 2	0.2%	7.5	6.5	3	6	3.5	3	2.5	2	2
FA 2	0.5%	7.5	6.5	2.5	6.5	4.5	3.5	3	2	2
FA 2	1.0%	7	6	3	6.5	4.5	3.5	3	4	5
FA 2	3.0%	7	5.5	4.5	7.5	4.5	5	4	5.5	5
FA 2	5.0%	7	5.5	4.5	8	5.5	5	5	5.5	5.5

Stain III: Cationic Epoxy Silicone

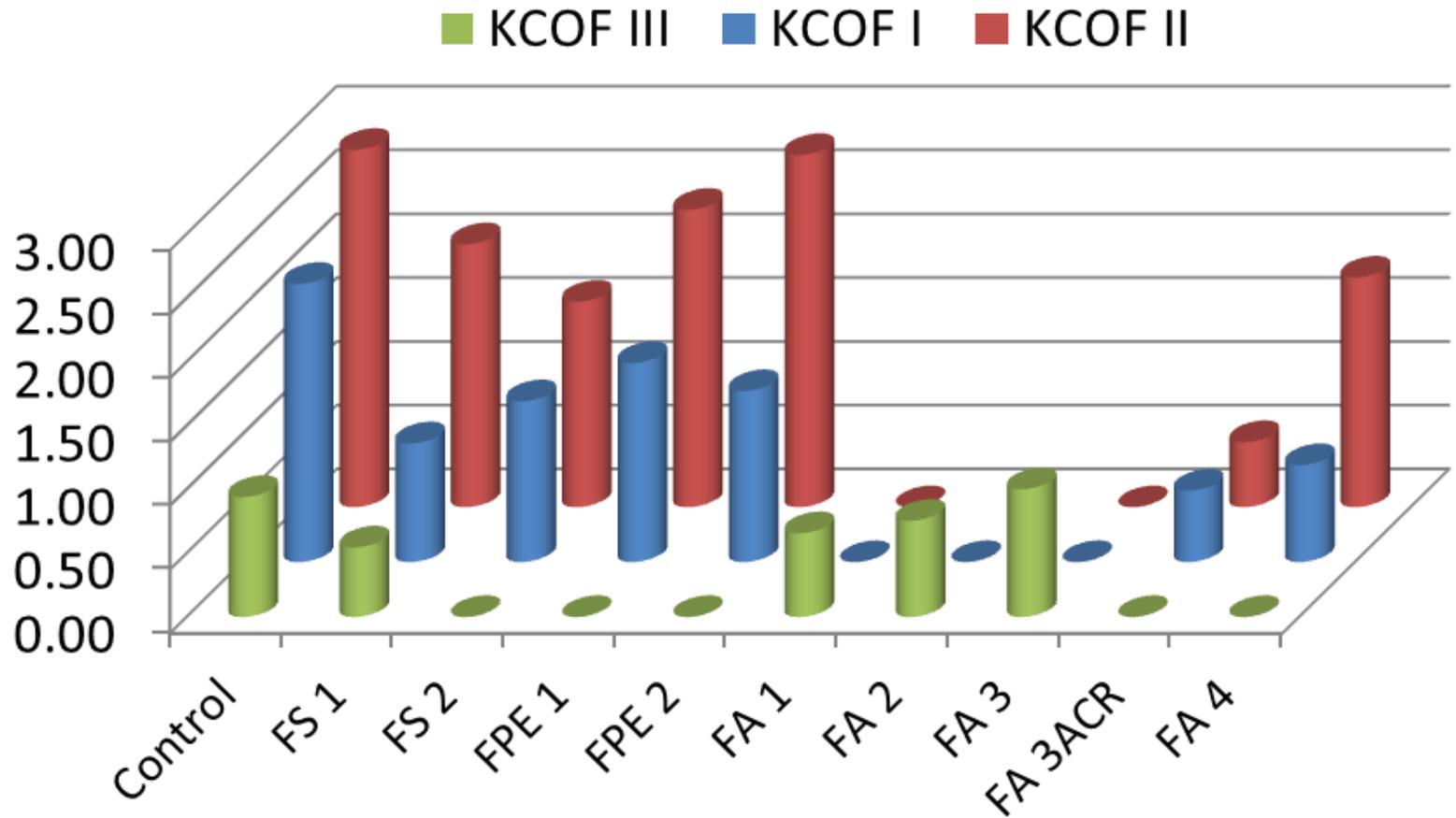


- Increases with use level
- Stain dependent
- Similar across FAS but high CF_2 good for two

Summary III: Cationic Epoxy Silicone

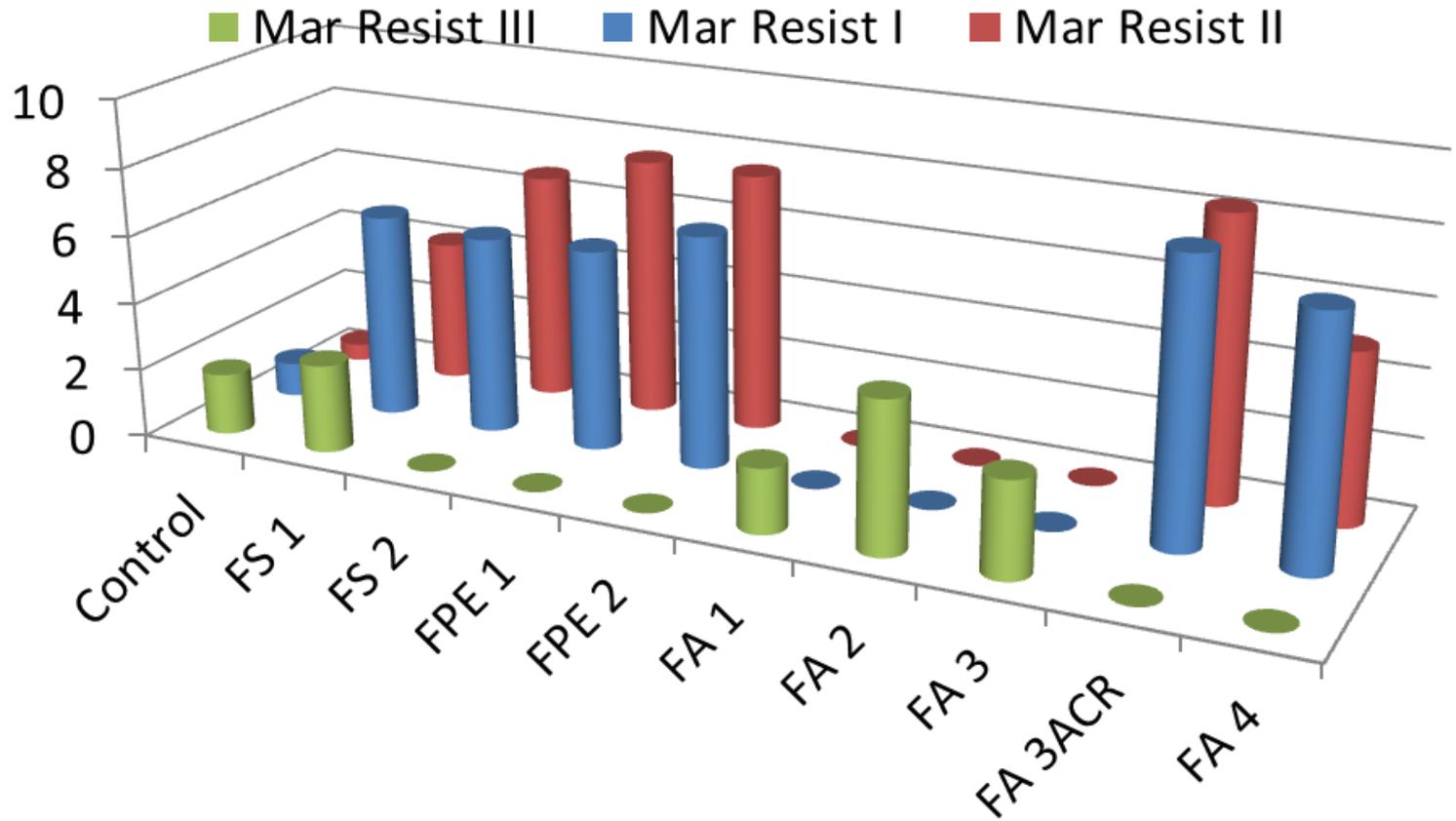
- All FAS are compatible with silicone epoxy resin.
- 60° Gloss is slightly reduced and no surface defects are seen. More FAS does lower gloss more.
- Most FAS show improvements to mar resistance. This is seen at low use levels and barely improved or somewhat lost at higher use levels.
- Only FS 1 – with the highest CF_2 content – shows the dramatic lowering of COF that one usually sees with silicone or fluoroalkyl additives. Performance lost at highest use levels.
- Stain resistance was similar for each additive, stain dependent, and increased with use level of FAS.

Summary Slip



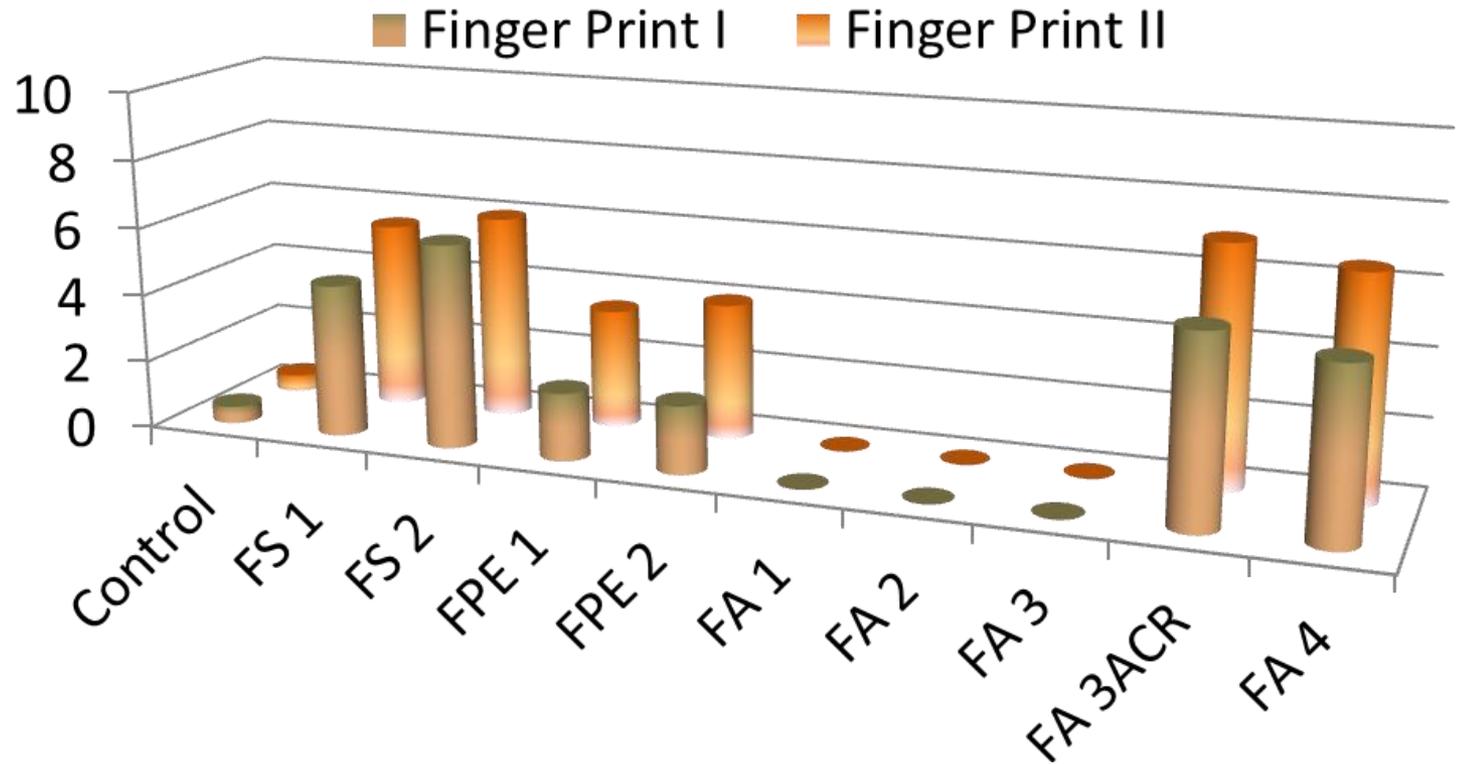
- FA 3ACR with moderate %CF₂ is best
- FPEs are good for low %Sil and CF₂

Summary Mar



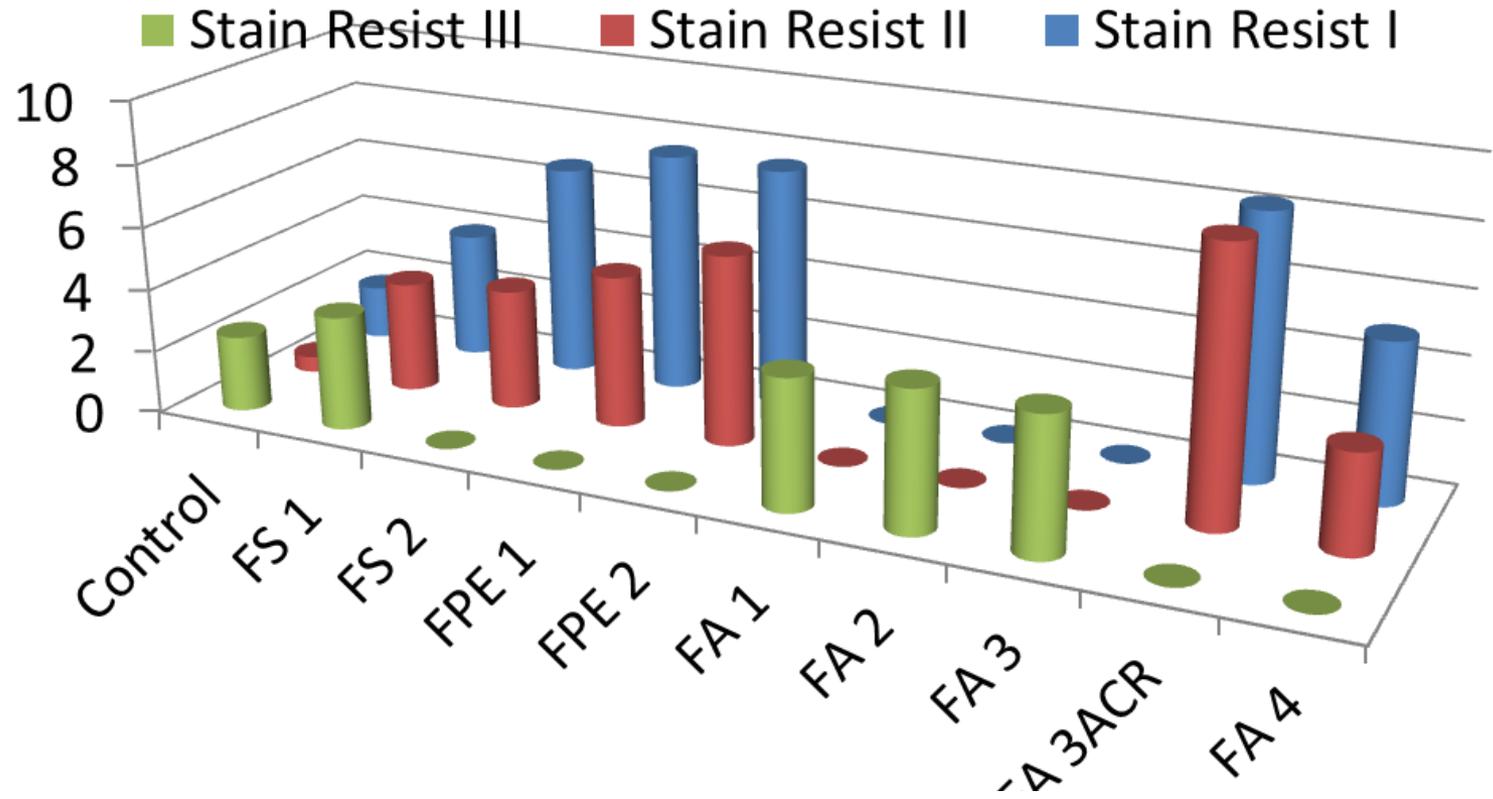
- FAS with both high %Sil and %CF₂ work
- FA 3 ACR (reactive) is very good
- FPEs are surprisingly good

Summary Fingerprint



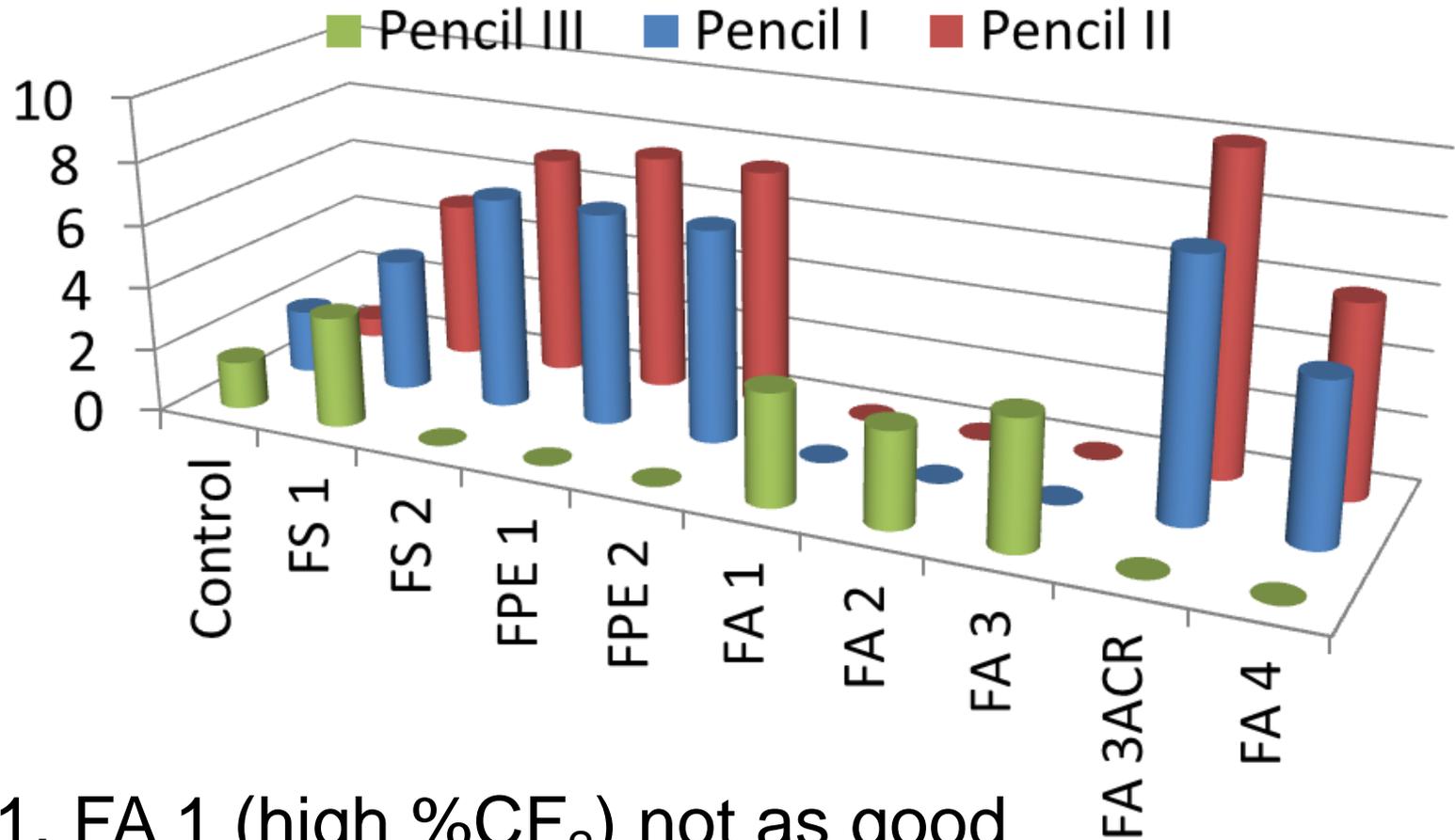
- Similar in both systems
- High %CF₂ content works better
- But high %Sil best

Summary Average Stain



- High %Sil works best
- FA 3 ACR (reactive) is very good
- FPEs are very good for low %Sil and CF_2

HB Pencil: graphite



- FS 1, FA 1 (high %CF₂) not as good
- FA 3, FS 2 (high % Sil) & FPE (high % CH₂) work the best

Summary WB Stains

Stamp Ink

Printer Ink

Red Sharpie

Kool-Aid

Blk Marker III

Blue High lighter

Blk Marker II

Blk Marker I

Ball Pen

10

8

6

4

2

0

Control

FS 1

FS 2

FPE 1

FPE 2

FA 1

FA 2

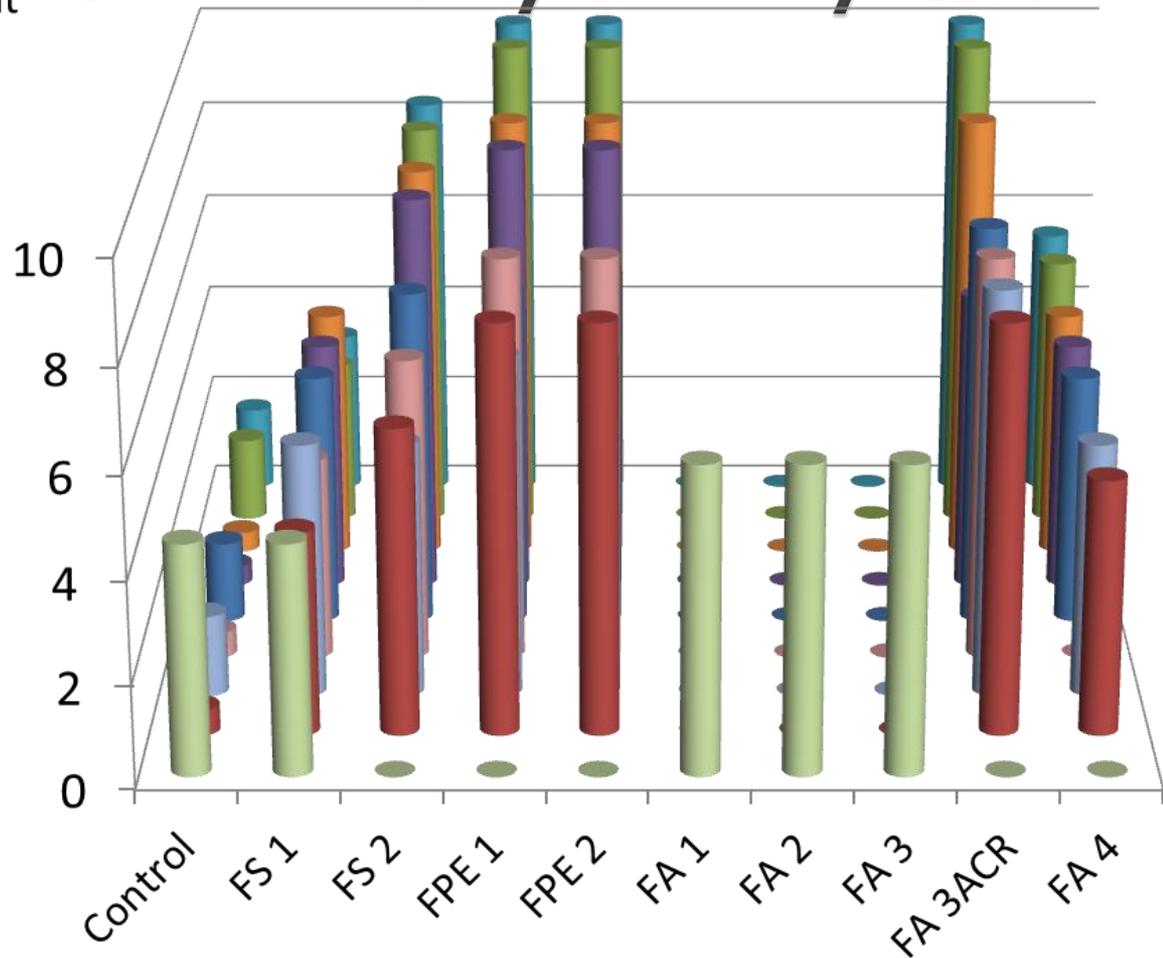
FA 3

FA 3ACR

FA 4

- FA 1 (high %CF₂) better here
- FS 1 (high %CF₂) not effective
- FA 3, FS 2 (high % Sil) are good

Summary Waxy Stains



- FS 2 (high %CF₂) does well but...
- FA 3 ACR, FS 2 (high % Si) & FPE (high %CH₂) are best

Stain summary

- ▶ High % Silicone FAS materials are best on Graphite, WB and Waxy stains
- ▶ High % CF_2 helps for waxes but still not as good as above
- ▶ High MW makes little difference
- ▶ More is better

Summary of Film Properties

	Compatible			Slip			Mar			Stain			Finger print	
	Urethane	Epoxy	Cat. Silicone	Urethane	Epoxy	Cat. Silicone	Urethane	Epoxy	Cat. Silicone	Urethane	Epoxy	Cat. Silicone	Urethane	Epoxy
FPE 1	++	++		+	+		++	++		+	++		+	+
FPE 2	++	++		+	+		++	++		+	++		+	+
FS 1	-	-	+	++	+	++	++	+	+	+	+	+	+	++
FS 2	-	+		+	+		++	+		++	+		++	++
FA 1			-			-			-			++		
FA 2			-			-			-			++		
FA 3			+			-			-			++		
FA 3ACR	-	+		++	++		++	++		++	++		++	++
FA 4	-	+		++	+		++	+		++	+		++	++

Stain Resistance Summary

	Ink			Black marker		Crayon		Pencil Crayon		
	Cat. Silicone	Urethane	Epoxy	Cat. Silicone	Urethane	Epoxy	Urethane	Epoxy	Cat. Silicone	
FPE 1		++	+		++	++	++	++		
FPE 2		++	+		++	++	++	++		
FS 1	++	-	-	-	-	++	+	+	++	
FS 2		+	+		++	++	+	+		
FA 1	+			-					++	
FA 2	+			-					++	
FA 3	+			+					++	
FA 3ACR		++	++		++	++	+	++		
FA 4		+	+		+	+	+	+		

THANK YOU

