



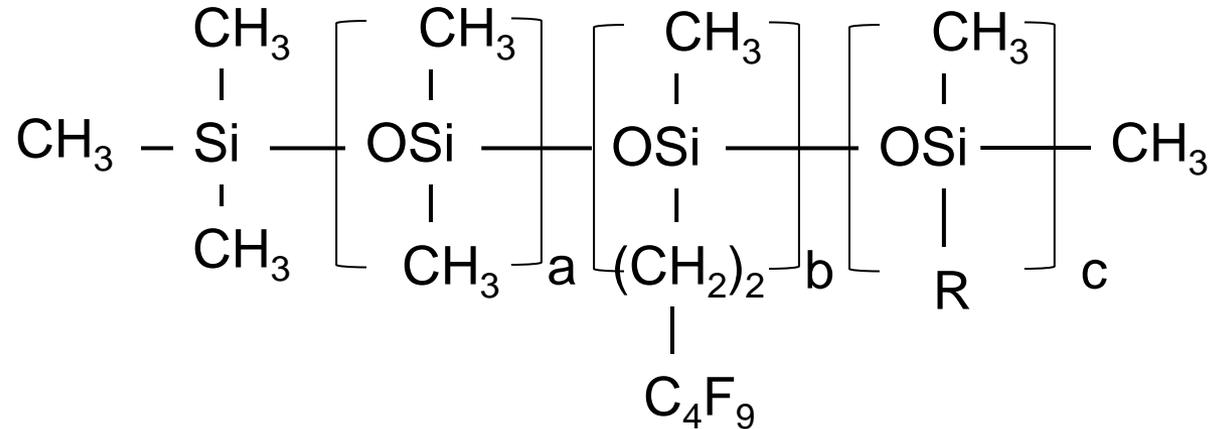
Fluoroalkyl Silicones in Coatings Films

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Experimental and Methodology:

- ▶ The overall design is to use three coatings systems: SB, UV and Paint
- ▶ 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 Systems I and 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.

System 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: SB Urethane

Part A:	Supplier	Wt%
Desmophen A870 BA	Bayer	46.5%
Desmophen 670A-80		31.0%
Additive	Siltech	1.0%
Dabco T-12	Air Products	0.1%
n-BA		5.5%
PMA		7.2%
EEP		8.7%

Part B:

Desmodur N-3390 BA/SN	Bayer	A/B = 73.3/26.7
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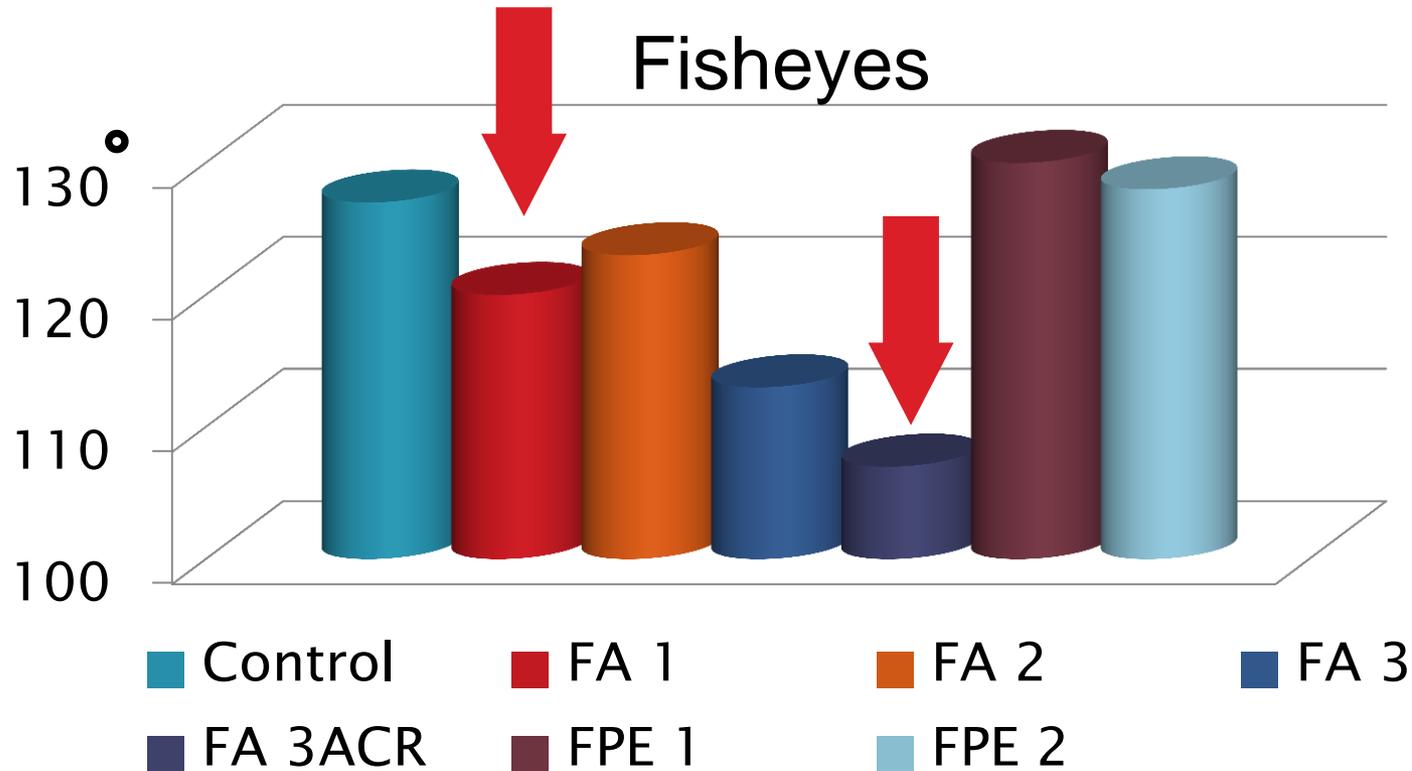
Preparation:

- 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

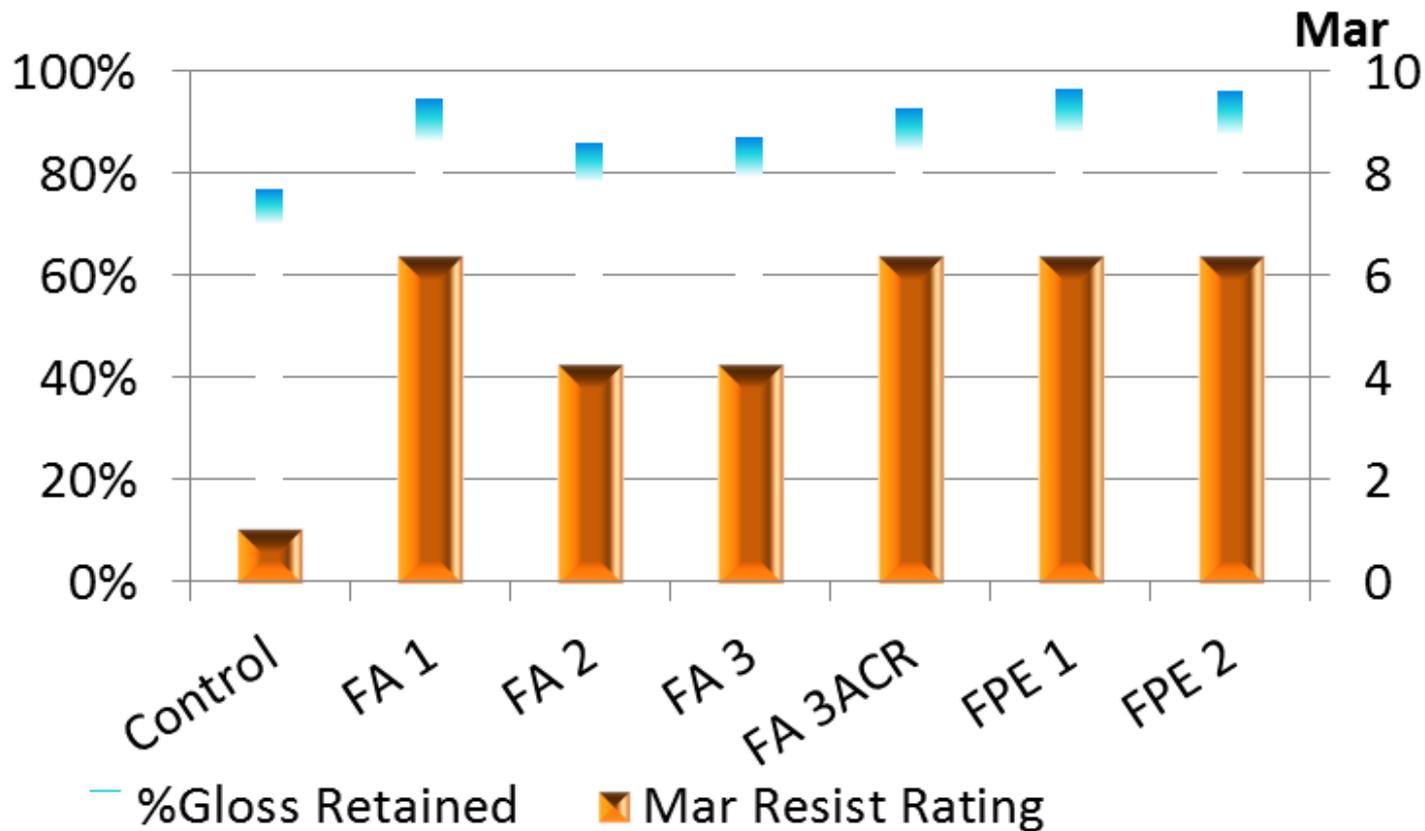
	Static COF	Kinetic COF	Gloss	%Gloss Retained	Mar Resist	Surface appearance
Control	1.397	1.500	127	77.2%	1.1	Smooth
FA 1	1.274	1.204	120	95.0%	6.4	Fisheyes
FA 2	0.940	1.115	123	86.2%	4.3	Smooth
FA 3	0.794	0.756	113	87.1%	4.3	Smooth
FA 3ACR	0.405	0.422	107	93.1%	6.4	Fisheyes
FPE 1	0.577	0.631	130	96.7%	6.4	Smooth
FPE 2	0.681	0.711	128	96.4%	6.4	Smooth

Gloss I: SB Urethane



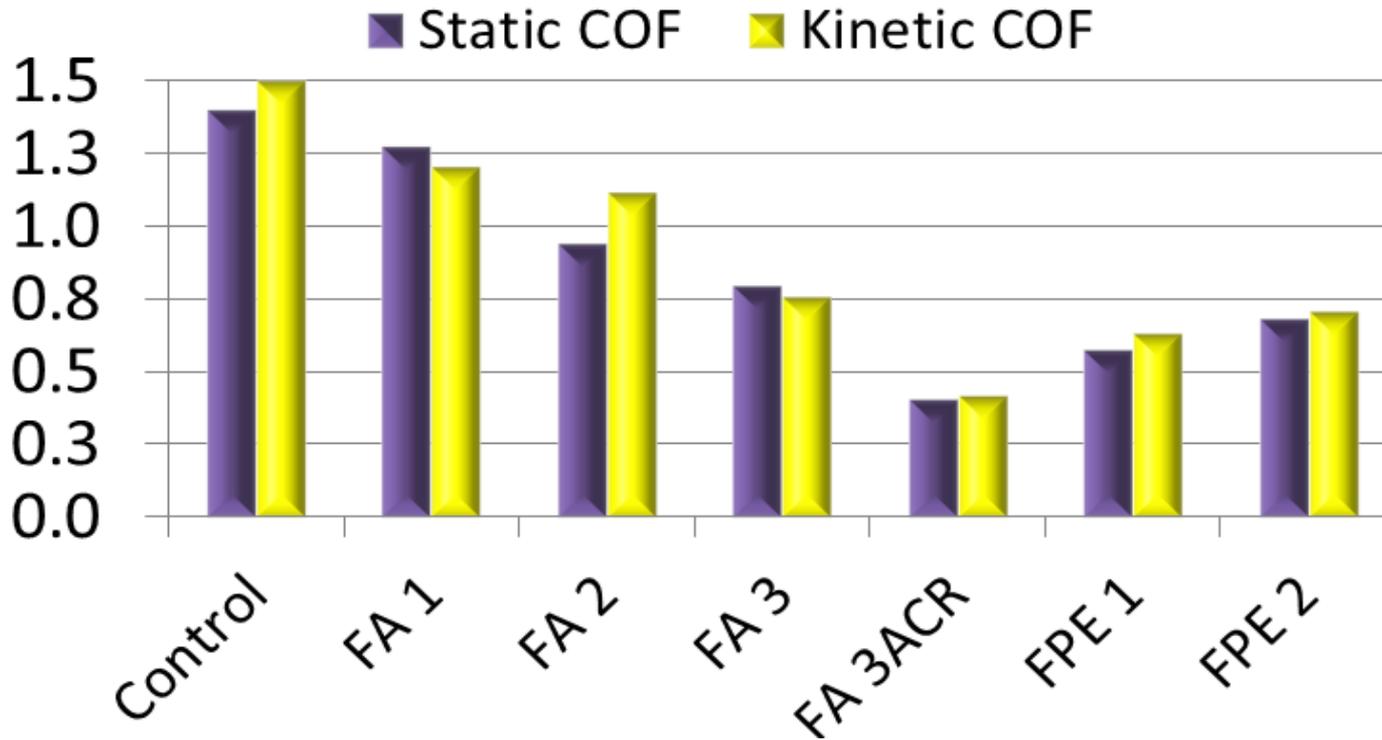
- FPE are most miscible, improve gloss
- FA type decrease gloss cause defects

Mar Resist I: SB Urethane



- All improve mar resistance

COF Reduction I: SB Urethane

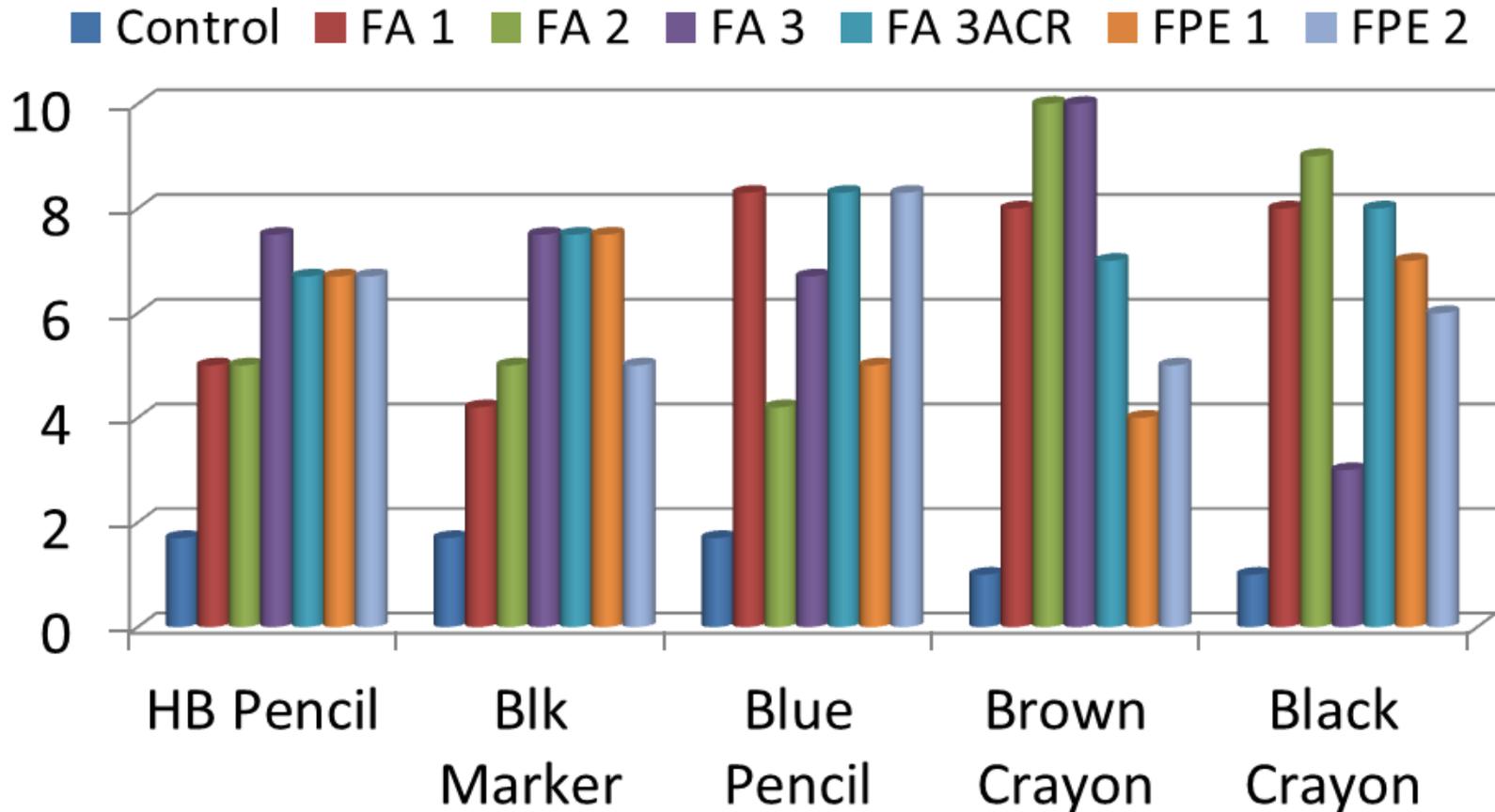


- All improve COF
- More with $>$ wt% silicone

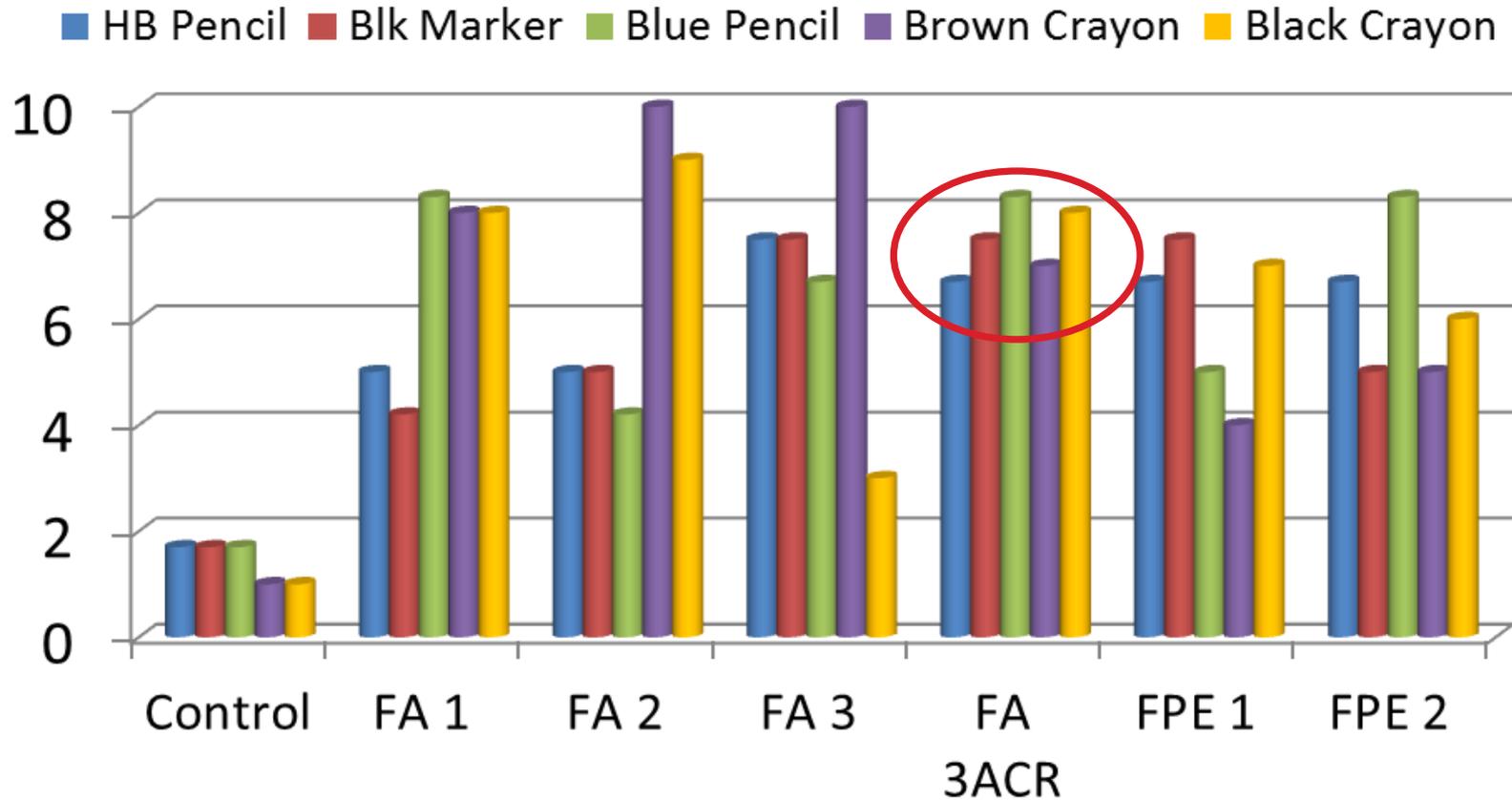
Stain Resistant I: SB Urethane

	HB Pencil	Black permanent marker	Blue pencil Crayon	Brown Crayon	Black Crayon	Average Stain
Control	1.7	1.7	1.7	1.0	1.0	1.4
FA 1	5.0	4.2	8.3	8.0	8.0	6.7
FA 2	5.0	5.0	4.2	10.0	9.0	6.6
FA 3	7.5	7.5	6.7	10.0	3.0	6.9
FA 3ACR	6.7	7.5	8.3	7.0	8.0	7.5
FPE 1	6.7	7.5	5.0	4.0	7.0	6.0
FPE 2	6.7	5.0	8.3	5.0	6.0	6.2

Stain Resist I: SB Urethane



Stain Resist I: SB Urethane



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

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.
- ▶ FA 3 ACR is very good for stain, COF, and Mar, even over FA 3

System II: UV cured

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%

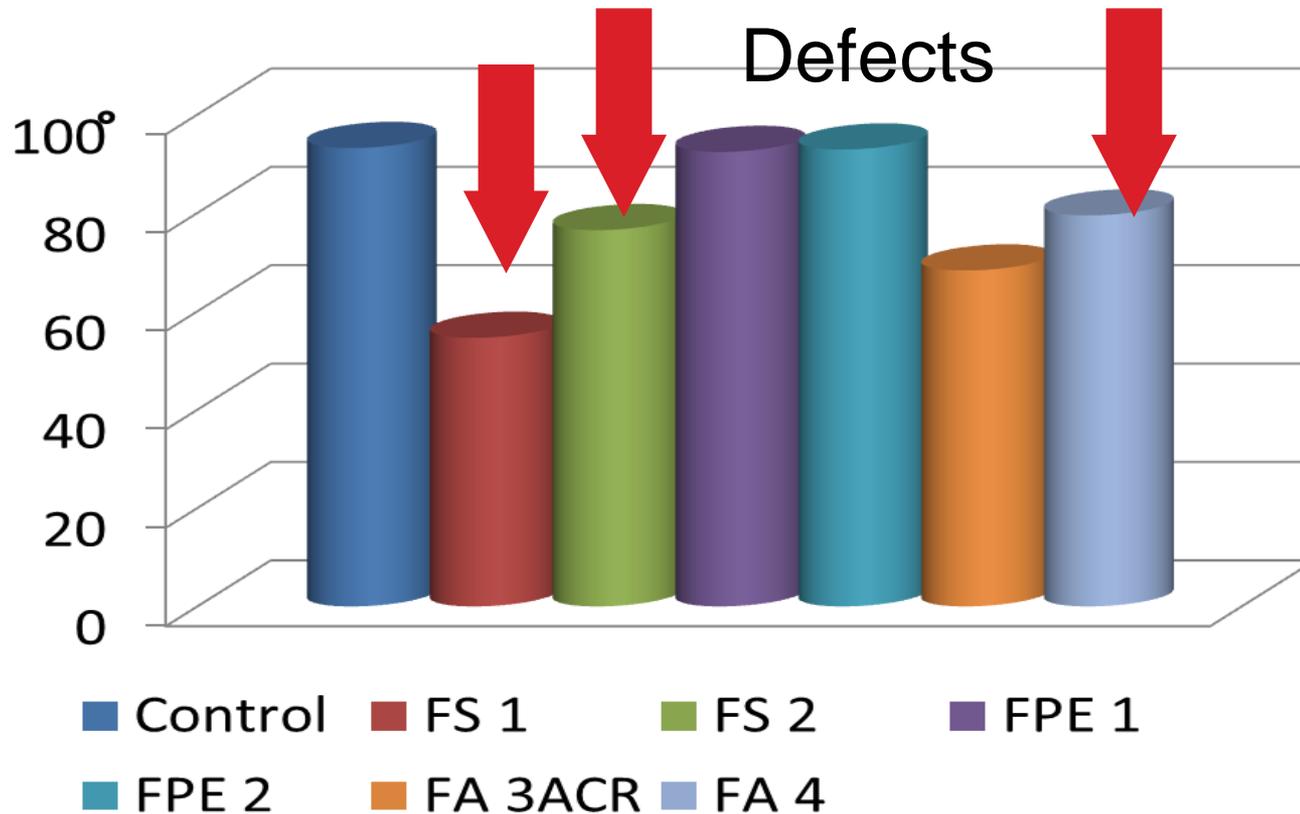
Preparation:

- 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 II: UV cured

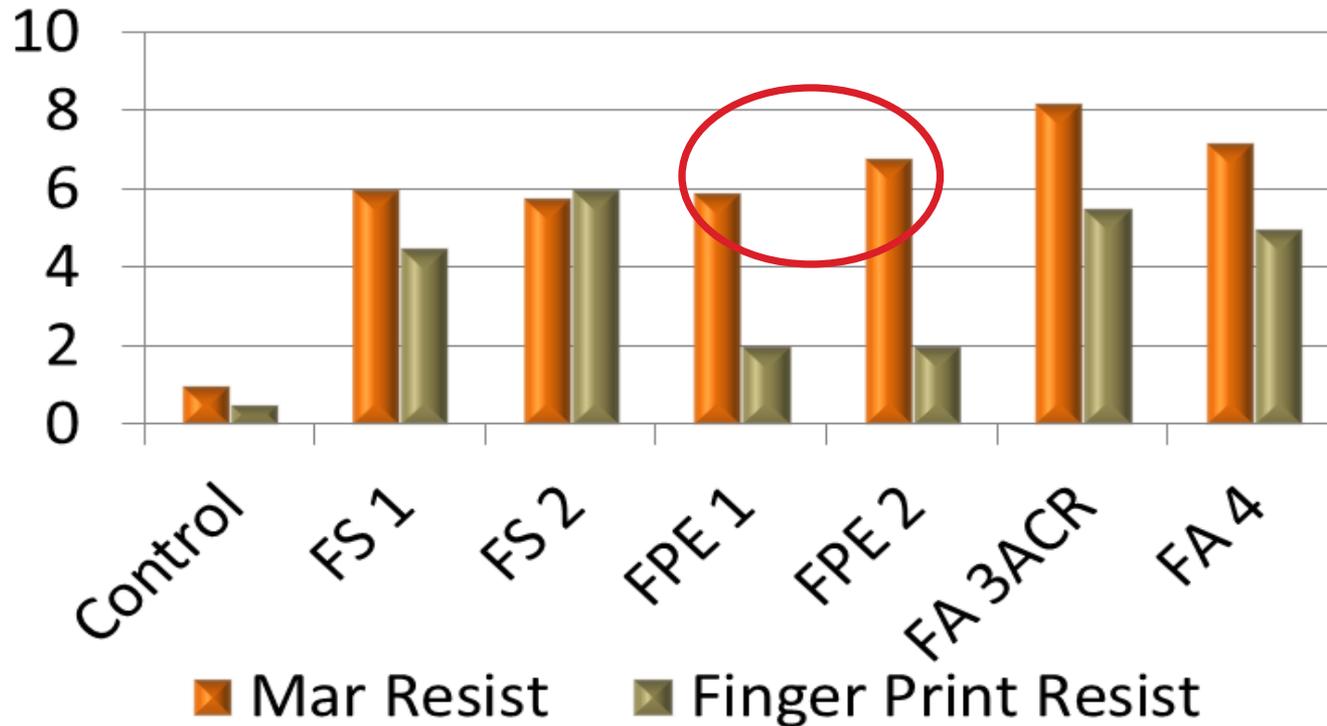
	60° Gloss	Stain Resist	Mar Resist	Static COF	Kinetic COF	Finger Print Resist	Surface appearance
Control	93.2	1.7	1.0	1.99	2.18	0.5	Some craters
FS 1	54.6	4.0	6.0	0.93	0.93	4.5	Patches
FS 2	76.5	6.7	5.8	1.37	1.26	6.0	Patches
FPE 1	92.4	7.6	5.9	1.25	1.56	2.0	Smooth
FPE 2	92.9	7.6	6.8	1.31	1.34	2.0	Smooth
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 II: UV cured



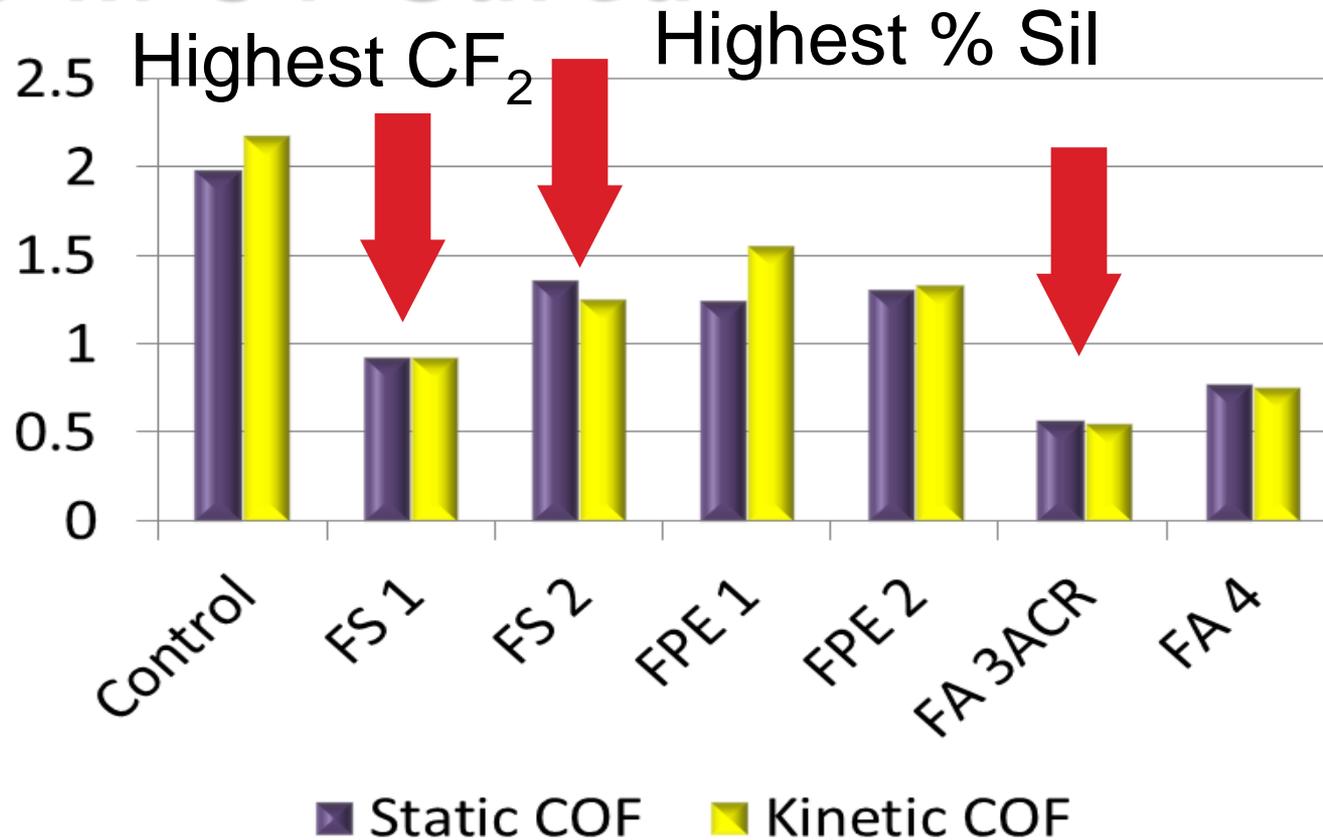
- FPE are most miscible, keep gloss
- FA and FS types decrease gloss

Mar and Finger print II: UV cure



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

Slip II: UV Cured

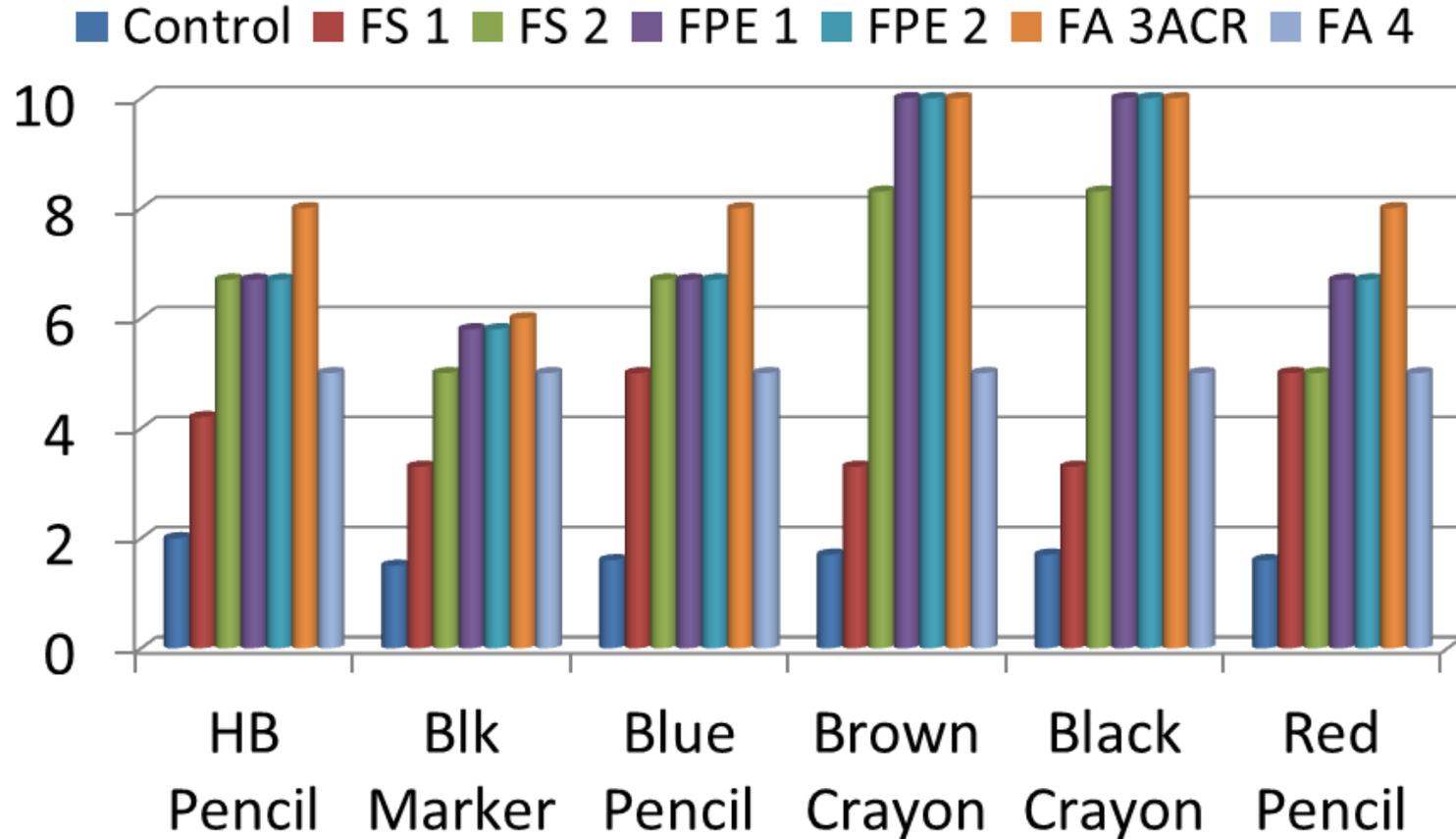


- All improve COF
- More with $>$ wt% CF_2

Stain Resist II: UV cured

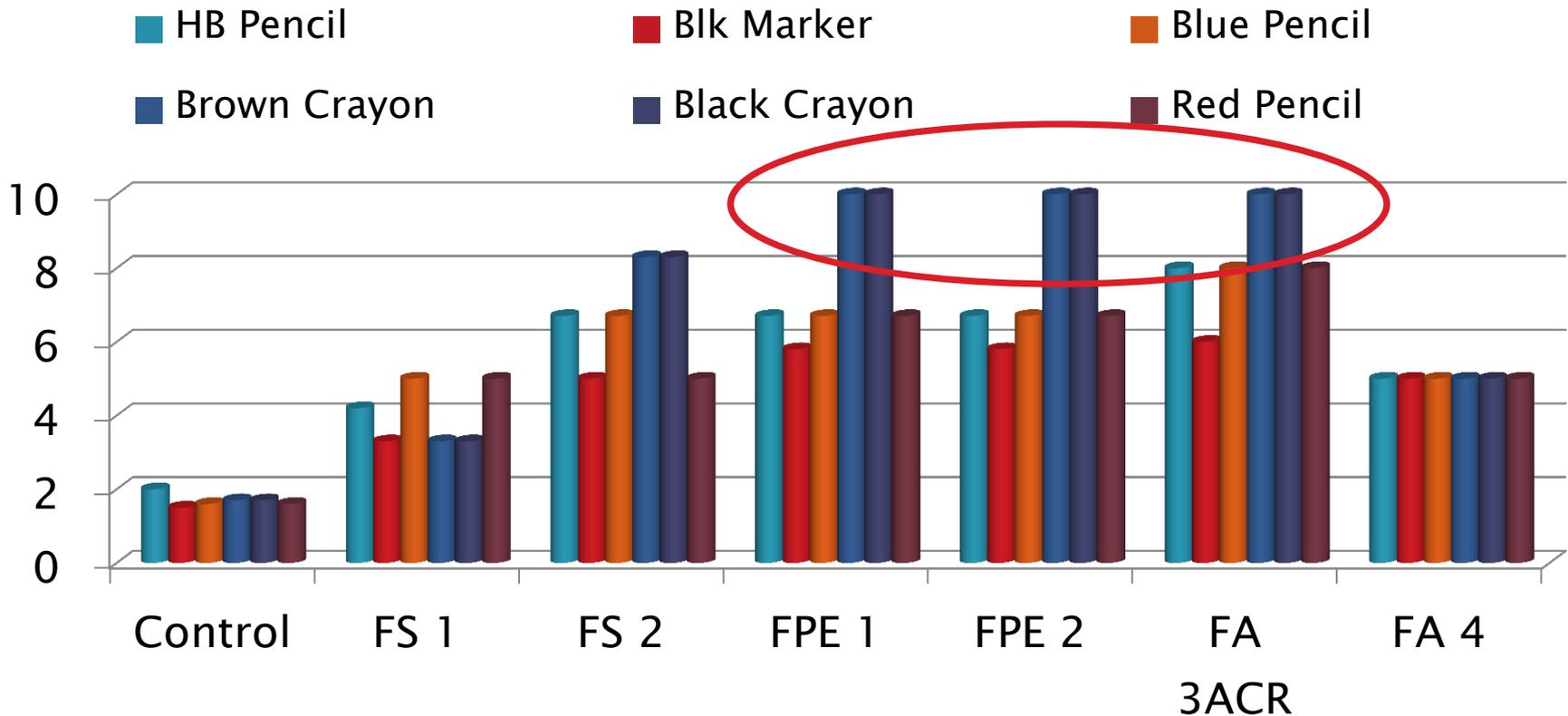
	HB Pencil	Black Crayons	Brown Crayon	Red pencil crayon	Blue pencil crayon	Black permanent marker	Average
Control	2.0	1.7	1.7	1.6	1.6	1.5	1.7
FS 1	4.2	3.3	3.3	5.0	5.0	3.3	4.0
FS 2	6.7	8.3	8.3	5.0	6.7	5.0	6.7
FPE 1	6.7	10.0	10.0	6.7	6.7	5.8	7.6
FPE 2	6.7	10.0	10.0	6.7	6.7	5.8	7.6
FA 3ACR	8.0	10.0	10.0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



- Crayons are effectively blocked by several

Stain Resist II: UV Cured



- FA 3 ACR and FPEs are effective

Results System II UV cured

- ▶ All FAS additives improve mar resistance and to a lesser degree fingerprint resistance
- ▶ FS 2, FA 4 and FA 3ACR give the best fingerprint resistance.
- ▶ Stain resistance is best for crayons and with FA 3 ACR
- ▶ FPE most compatible and good slip, mar and anti stain, but weak finger print resist
- ▶ All reduced COF

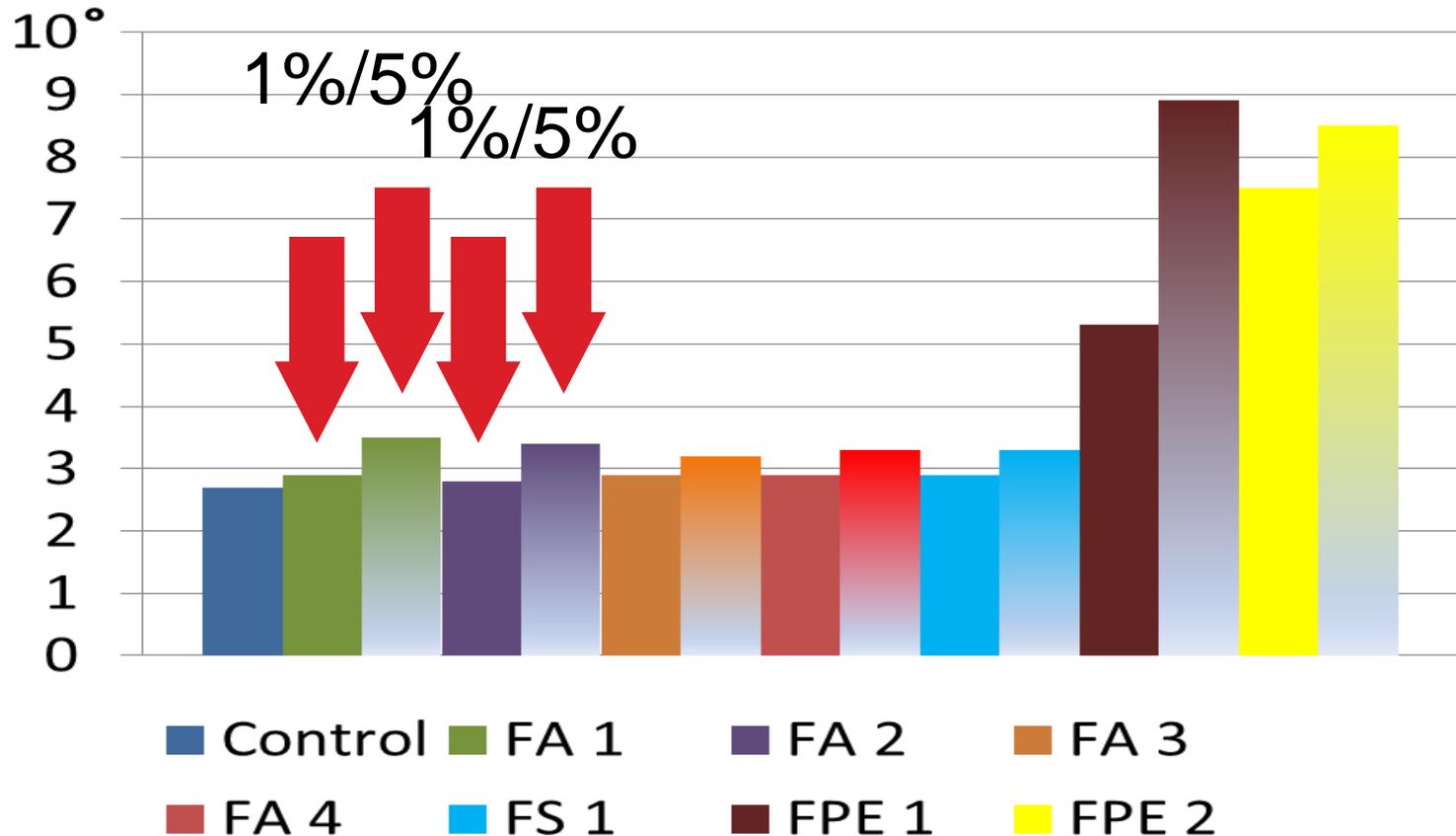
System III: commercial paint

- ▶ Retail Behr 1050 flat white paint.
- ▶ Post-added 1% and 5% FAS samples.
- ▶ Drawn down on Leneta paper in a 1 mil thickness using a # 10 rod .
- ▶ Dried/ conditioned at ambient for seven days.

Film Properties III: post add

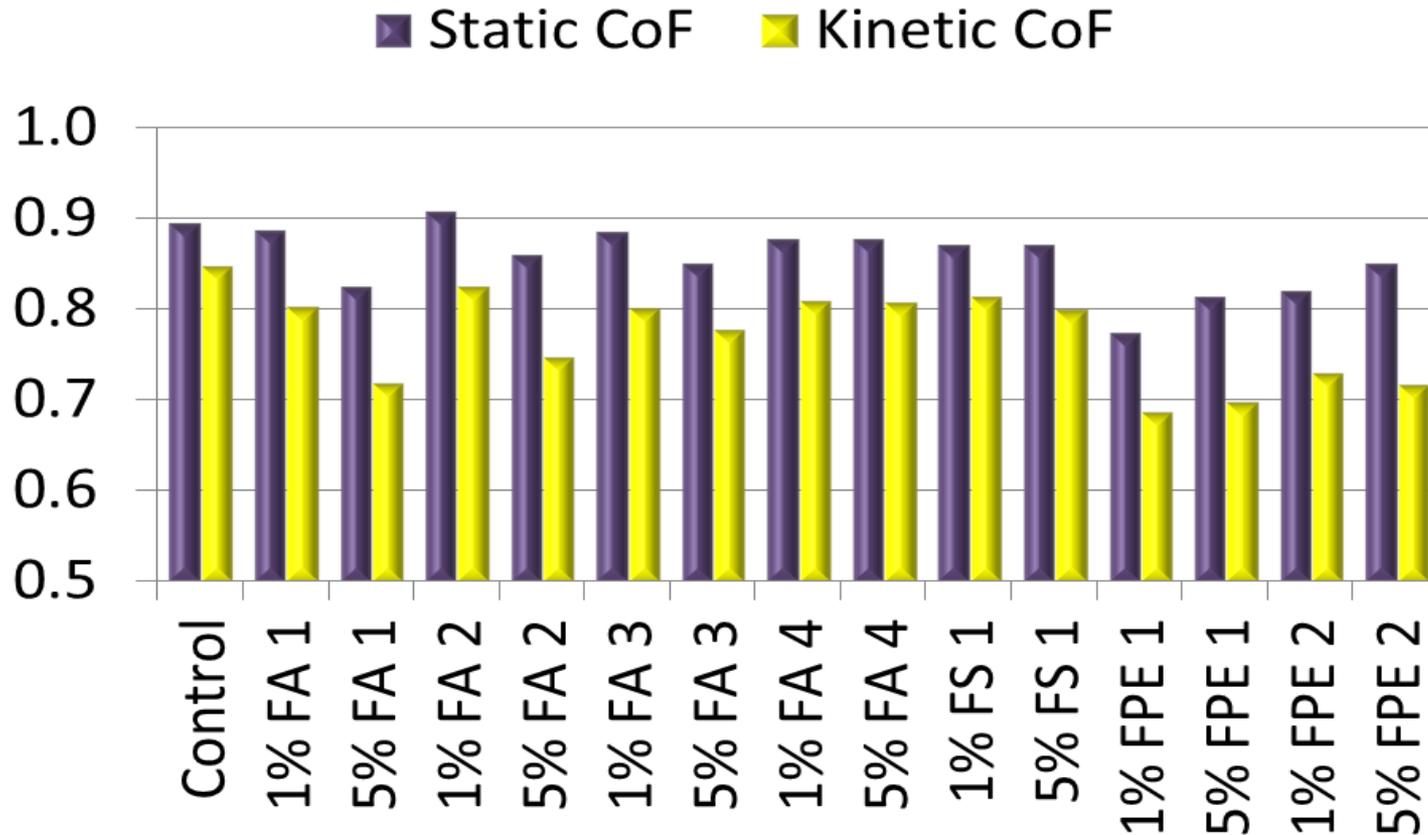
	%	Static CoF	Kinetic CoF	60° Gloss	Mar Resist	Stain Resist	Film Appearance
Control	0%	0.896	0.847	2.7	1.1	1.9	Smooth
FA 1	1%	0.887	0.803	2.9	5.5	2.5	Fisheyes
	5%	0.826	0.719	3.5	7.8	3.5	Fisheyes
FA 2	1%	0.908	0.826	2.8	5.6	3.0	Fisheyes
	5%	0.860	0.748	3.4	5.6	4.5	Fisheyes
FA 3	1%	0.886	0.801	2.9	6.7	3.0	Fisheyes
	5%	0.851	0.778	3.2	7.8	4.6	Fisheyes
FA 4	1%	0.878	0.810	2.9	7.8	2.0	Fisheyes
	5%	0.877	0.808	3.3	8.9	3.6	Fisheyes
FS 1	1%	0.872	0.814	2.9	6.7	2.5	Fisheyes
	5%	0.871	0.800	3.3	7.8	3.0	Fisheyes
FPE 1	1%	0.774	0.688	5.3	3.3	1.8	Smooth
	5%	0.815	0.698	8.9	5.6	2.7	Smooth
FPE 2	1%	0.821	0.730	7.5	3.3	1.7	Smooth
	5%	0.851	0.717	8.5	6.7	3.0	Smooth

Gloss III: post add



- All improve gloss/ more at 5%
- FPEs are best

Slip III: Post add



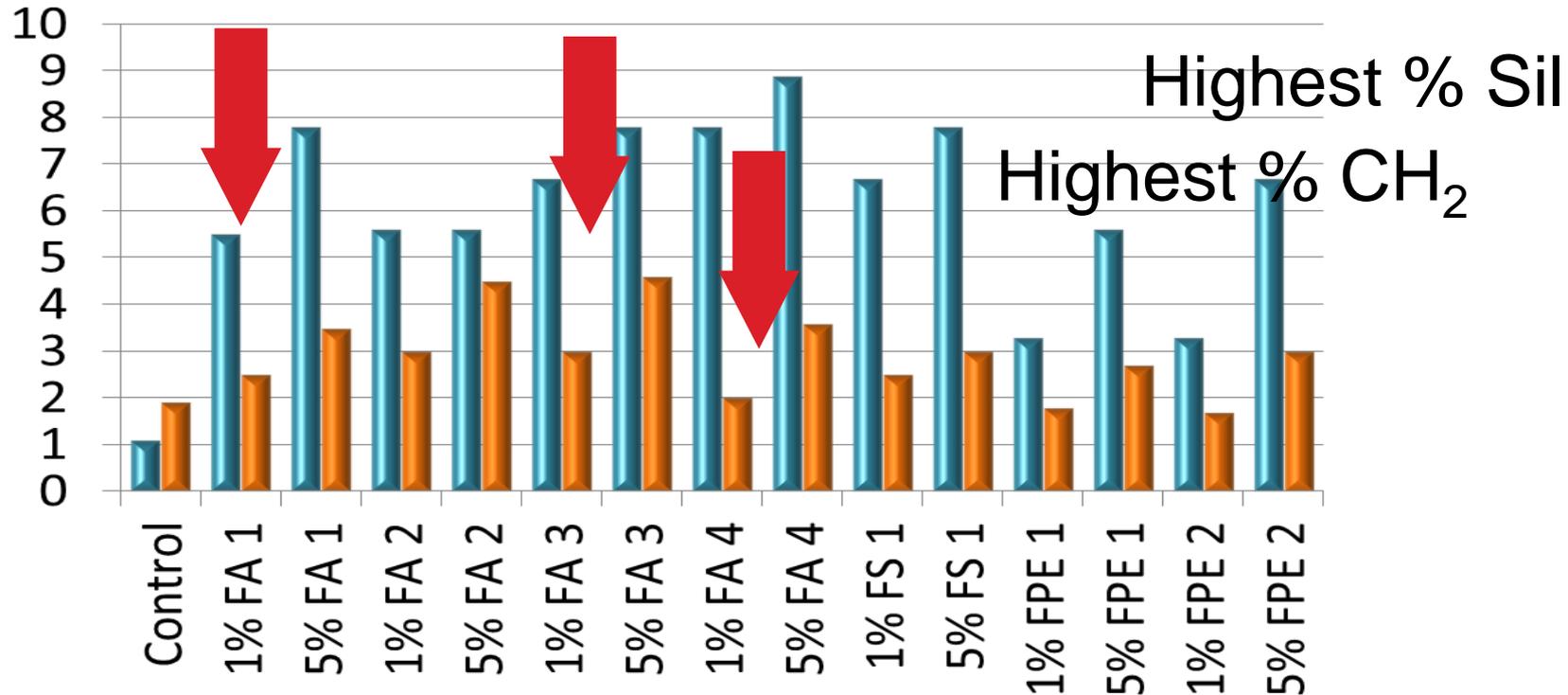
- All improve COF, more at 5%
- FPEs are very good

Mar and Stain III: post add

Highest CF_2

■ Mar Resistance

■ Stain Resistance

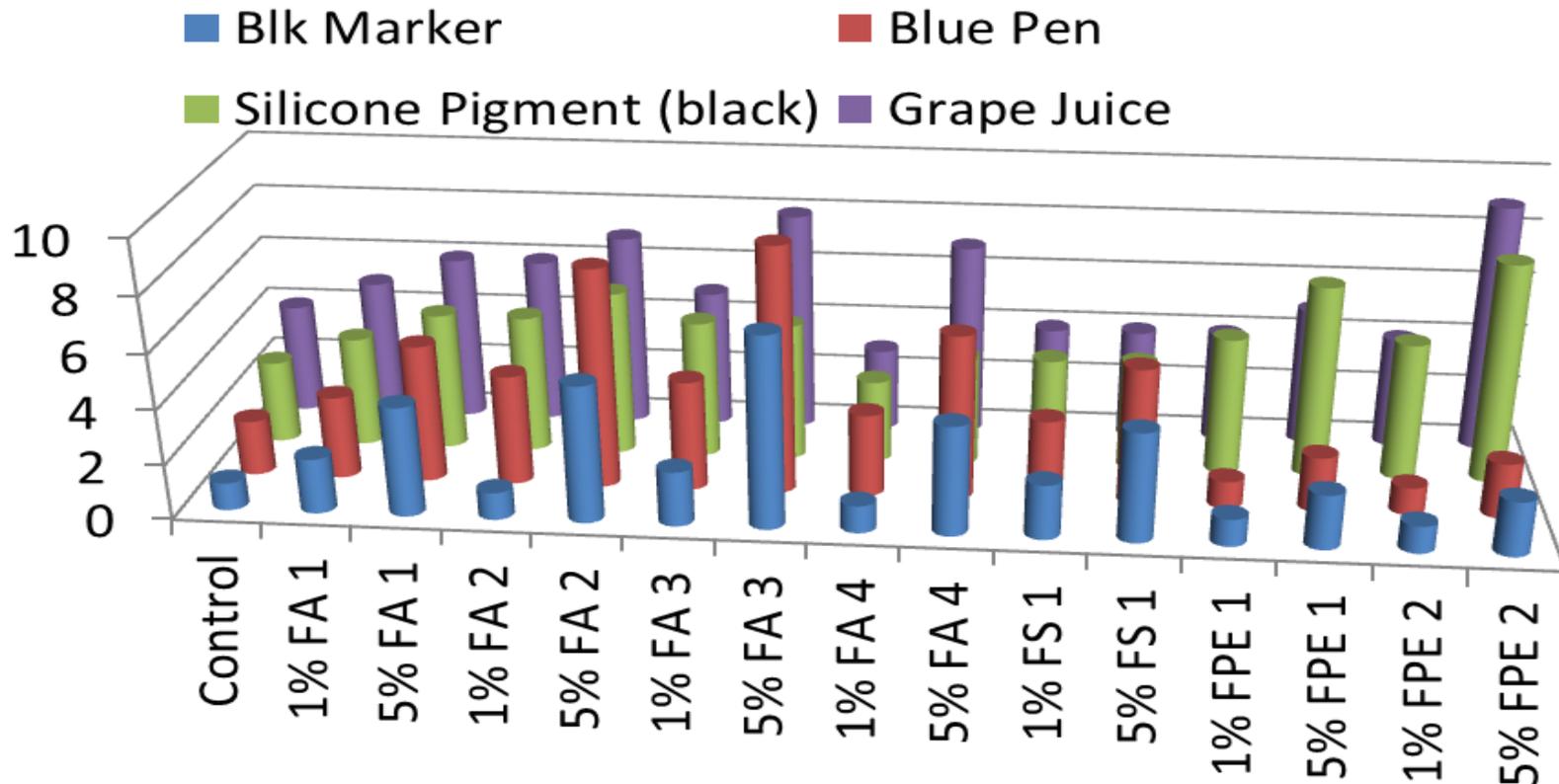


- All improve mar resistance/ more at 5%
- Both % CF_2 and %Sil help
- Lesser improvement in stain/ 5% better

Stain Resist III: Post Add

	Use level	Blue Ball Pen	Permanent Marker (black)	Silicone Pigment (black)	Grape Juice
Control	0%	2	1	3	4
FA 1	1%	3	2	4	5
	5%	5	4	5	6
FA 2	1%	4	1	5	6
	5%	8	5	6	7
FA 3	1%	4	2	5	5
	5%	9	7	5	8
FA 4	1%	3	1	3	3
	5%	6	4	4	7
FS 1	1%	3	2	4	4
	5%	5	4	4	4
FPE 1	1%	1	1	5	4
	5%	2	2	7	5
FPE 2	1%	1	1	5	4
	5%	2	2	8	9

Summary Stain III: Post add

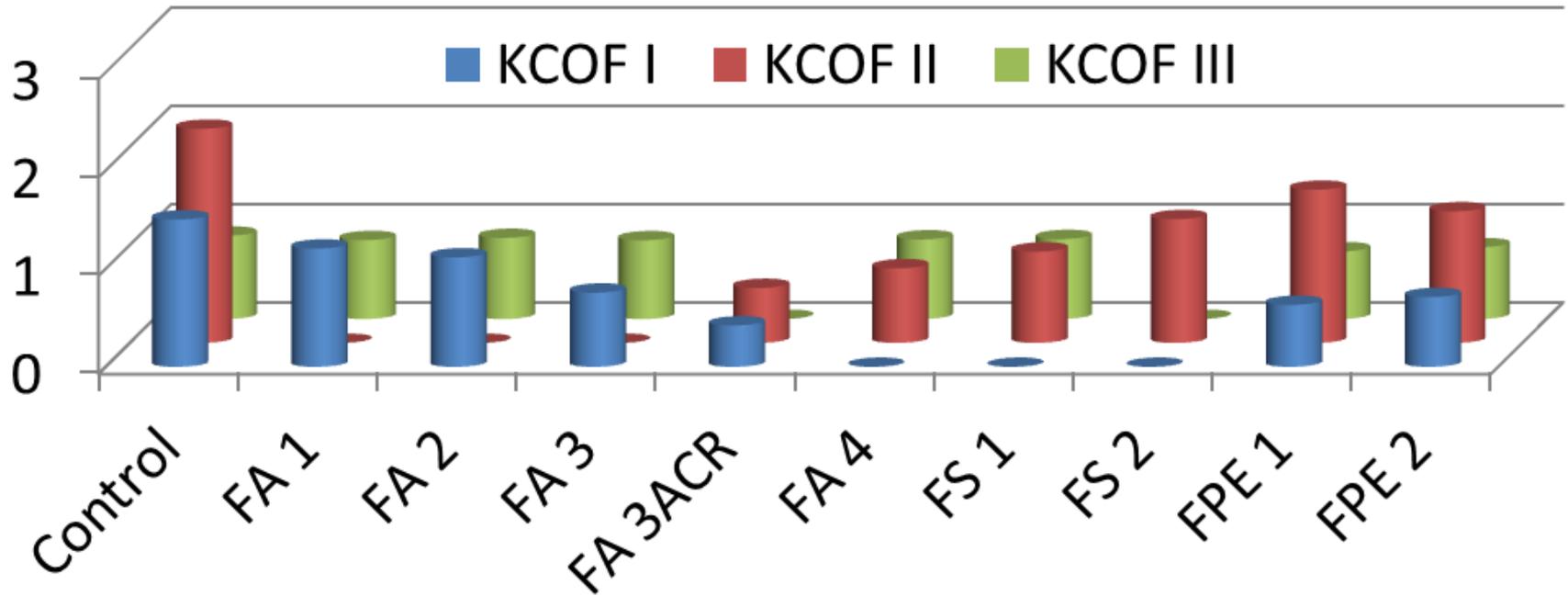


- Many improve stain resistance/ more at 5%
- FPEs good against grape and silicone pigment
- FA 2, FA 3 good on all

Summary post add paints

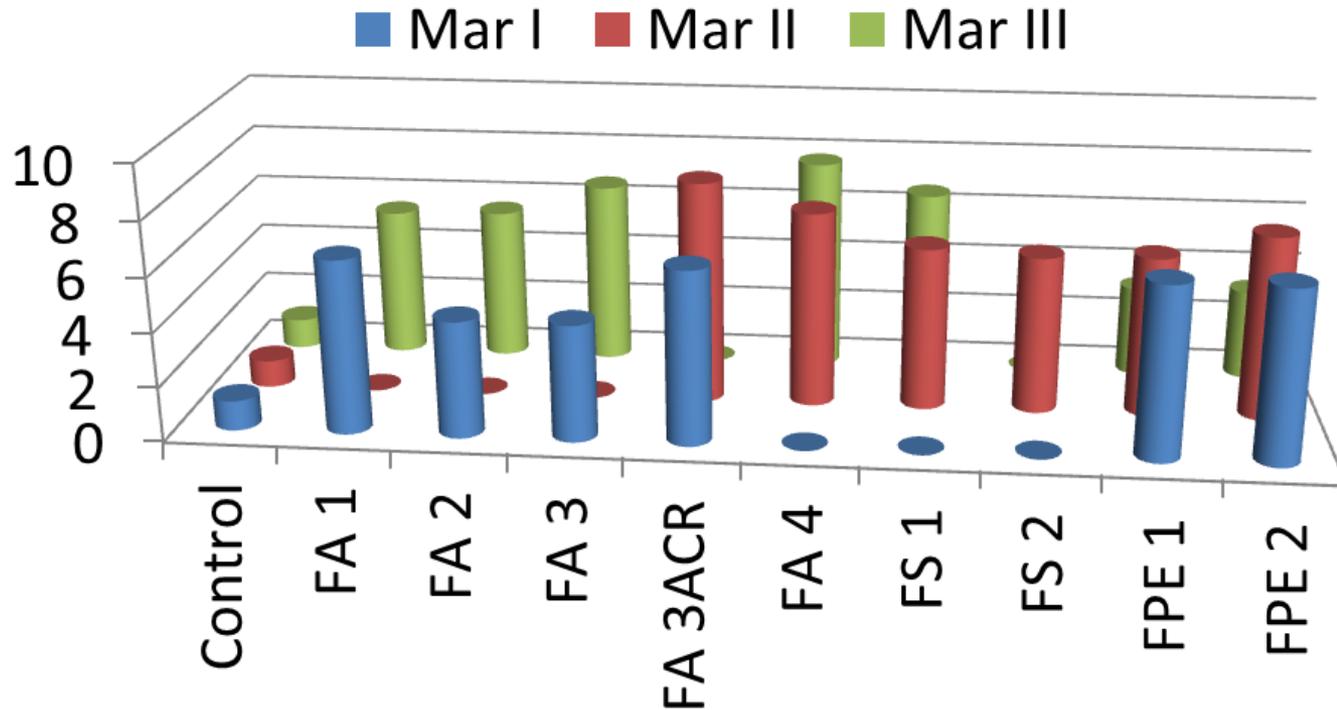
- ▶ Post-added FAS have little effect on slip and gloss but do affect mar and stain resistance.
- ▶ FPEs are only compatible.
- ▶ Mar resist is easy
- ▶ Stain resist is a mix of different factors but FAS seem better than Silicone alone.
- ▶ More is better for mar and stain.

Summary Slip



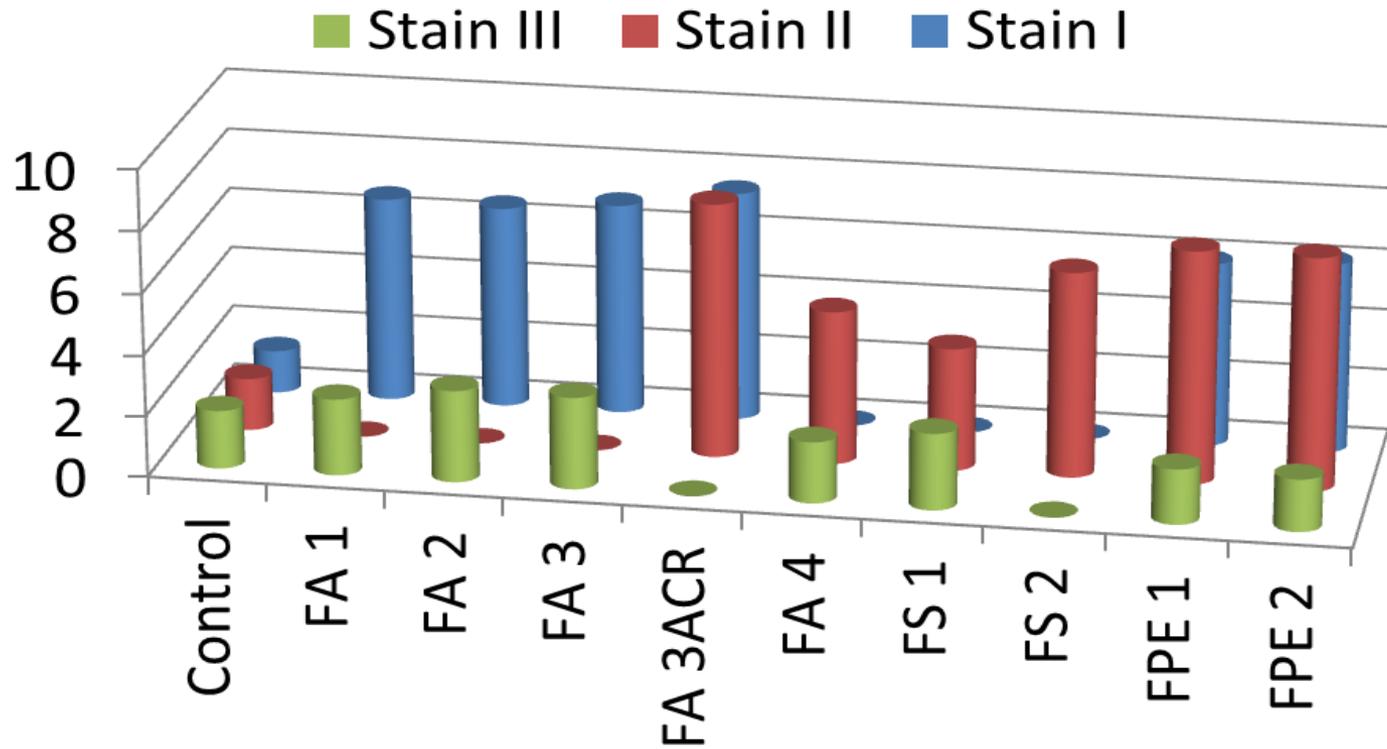
- FA 3 with moderate %CF₂ content is best
- FPEs are very good for low %Sil and CF₂

Summary Mar

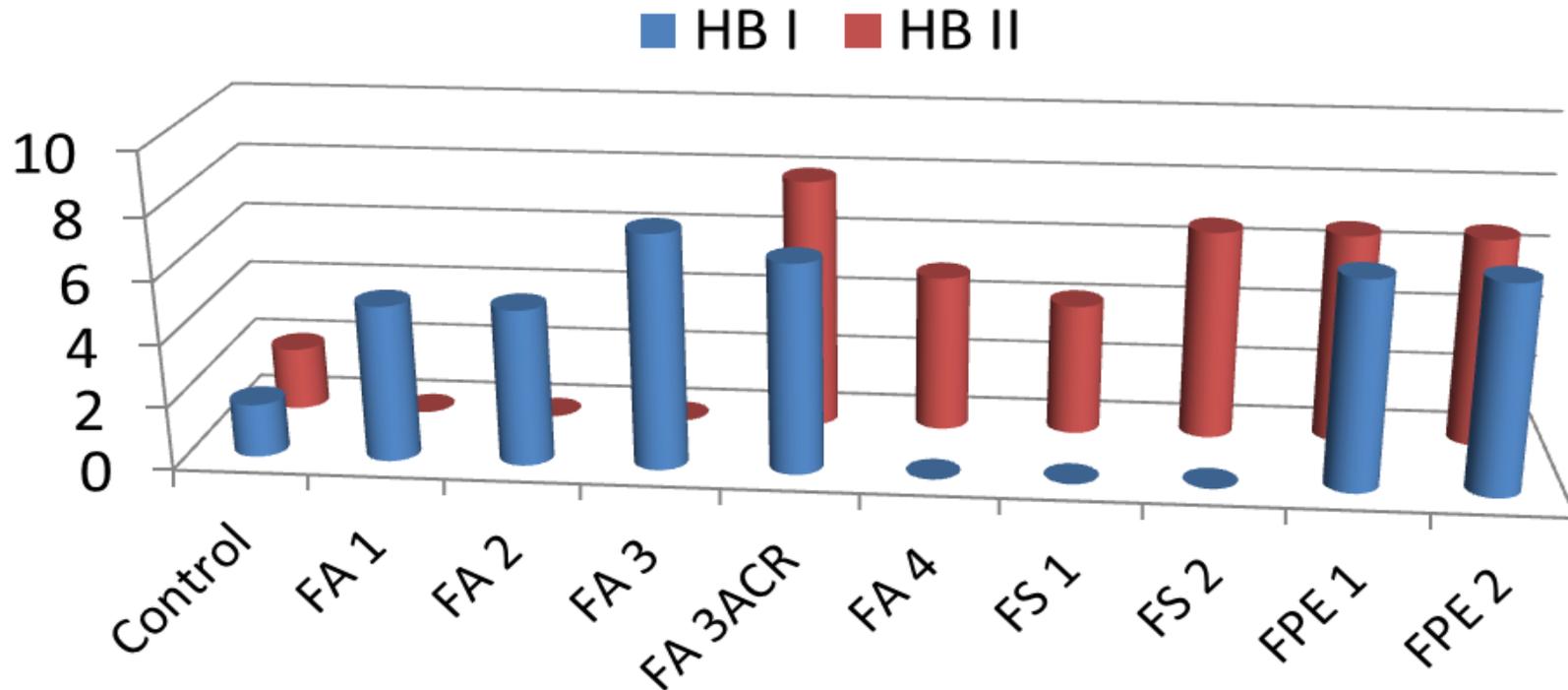


- %Sil and %CF₂ both work
- FA 3 ACR (reactive) is very good
- FPEs are very good for low %Sil and CF₂

Summary Average Stain

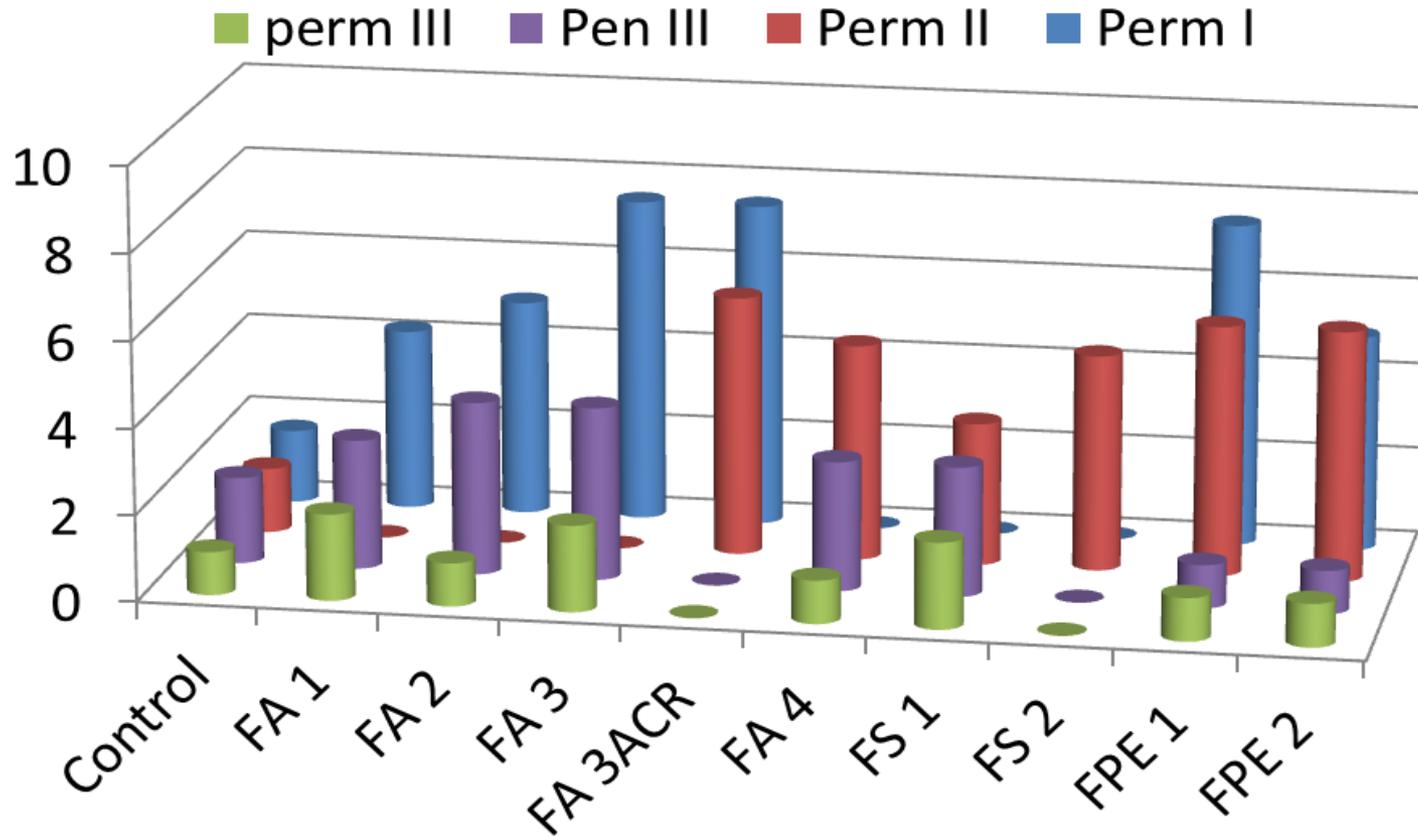


HB Pencil: graphite



- FA 3, FS 2 (high % Si) & FPE (high % CH₂)
- FS 1, FA 1 (high %CF₂) not as good
- FA 2 (high MW) not as good

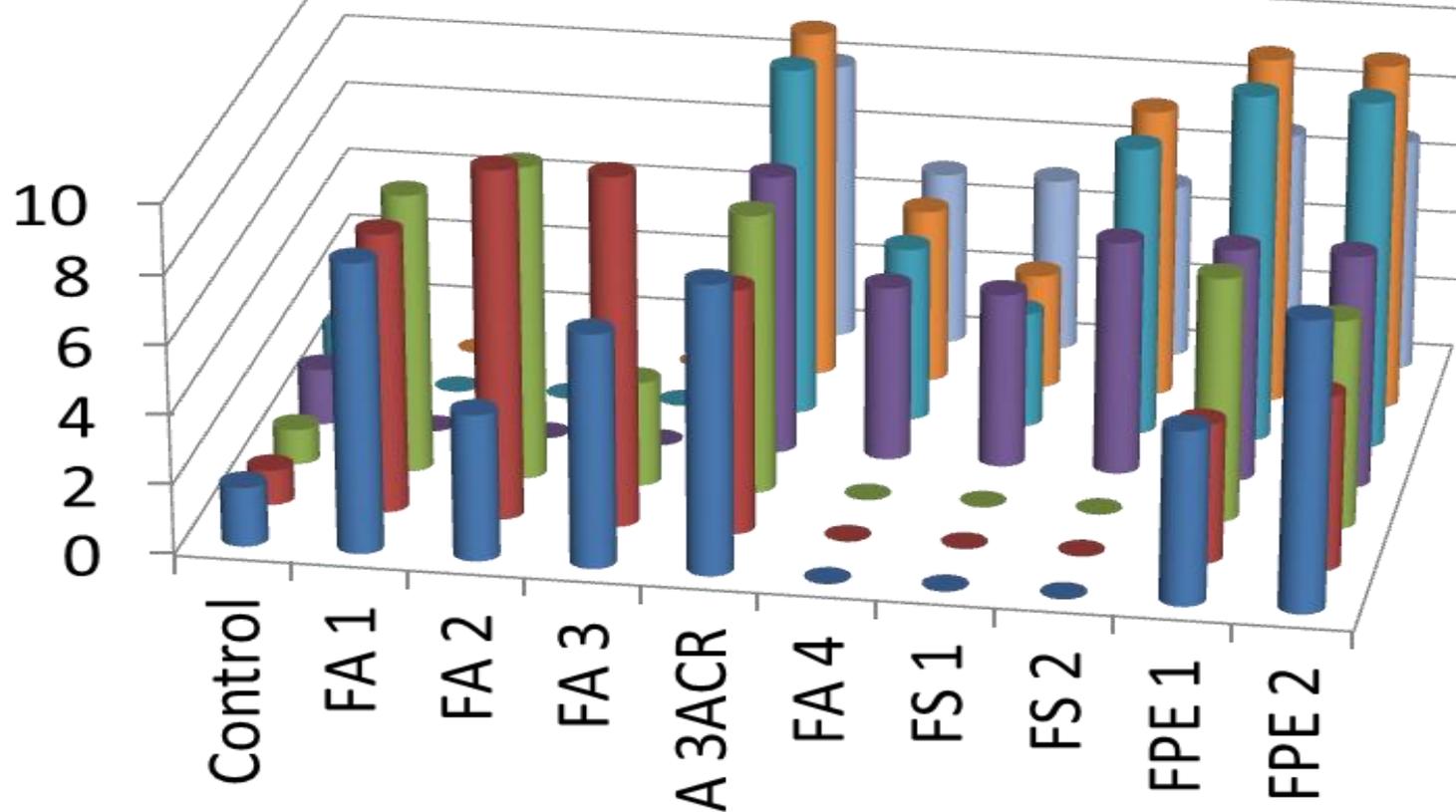
WB Stains



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

Waxy stains

■ Blue I ■ Brown I ■ Black I ■ Blue II ■ Brown II ■ Black II ■ Red II



- FA 3, FS 2 (high % sil) & FPE (high % CH₂)
- FA 1, FS 2 (high %CF₂) does better
- FA 2 (high MW) does better

Stain summary

- ▶ High % Silicone FAS materials are best on Graphite, WB and Waxy stains
- ▶ High % CF₂ 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		
	SB	UV	Paint	SB	UV	Paint	SB	UV	Paint	SB	UV	Paint
FPE 1	+++	+++	+++	+++	+	-	+++	+	+	+	+++	-
FPE 2	+++	+++	+++	+++	+	-	+++	+	+	+	+++	-
FS 1		-	-		++	-		+	+		+	-
FS 2		-			+			+			++	
FA 1	-		-	-		-	++		++	++		-
FA 2	+		-	+		-	+		++	++		-
FA 3	+		-	+		-	+		++	++		-
FA 3ACR	-	+		++	++		++	++		++	++	
FA 4		-	-		++	-		++	++		+	-

Stain Resistance Summary

	WB Inks			Waxy Crayon			Black Silicone			Grape Juice		
	SB	UV	Paint	SB	UV	P	SB	UV	P	SB	UV	P
FPE 1	++	++	-	+	++				++			-
FPE 2	+	++	-	+	++				++			++
FS 1		-	+		-				-			-
FS 2		+			+							
FA 1	+		+	++					-			+
FA 2	+		++	++					+			++
FA 3	++		++	+					+			++
FA 3 ACR	++	++		++	++							
FA 4		+	+		+				-			++

THANK YOU

