Incorporation of Fluoro-Silicones in Coatings Films and the Resulting Properties.

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Abstract

A series of several non-PFOS fluoroalkyl silicones will be examined in various coatings films for their impact on coatings properties such as COF reduction, tape release and stain release. Earlier results of reactive silicones in films have shown interesting results on stain release and the expectation is that the fluoroalkyl group will enhance these properties.

Introduction

Fluoroalkyl modified silicones have been available for many years. Offering additional properties over simple polydimethylsiloxanes, these have found utility in coatings for slip, COF, mar resistance, stain resistance, lubricity, hydrophobicity and oleophobicity.

Regulatory and safety concerns over perfluorooctyl's persistence in the environment have put pressure in recent years on these systems[1]. In general, chemical manufacturers have responded with shorter chains to obtain the unique properties of fluoroalkyls while eliminating this environmental concern.

Fluoroalkyl silicones used in this study are based on a three-carbon chain and so are not affected by current regulatory actions.

In this paper, we have modified some coatings systems with our fluoroalkyl silicones and examined the effect on the cured film properties.

Experimental and Methodology:

The overall design is to evaluate multiple fluoroalkyl silicones in three coating systems; a two part solvent borne heat cured urethane system, a UV cured urethane acrylate system and a commercial paint to examine the effects of these products in broad strokes.

To synthesize the fluoroalkyl silicone materials used herein, several silicone backbones were modified with fluoroalkyl alone; fluoroalkyl and polyether; or fluoroalkyl and alkyl using well known hydrosilylation procedures.

The fluoroalkyl silicones designated as FA 1, FA 2, FA 3, FSE 1 and FSE 2 are primary hydroxyl functional and can therefore react with the PU system. The material designated as FA

3ACR is an acrylate ester analogue of Sample FA 3 and can therefore react into the UV cured acrylate system.

Table A: Fluoroalkyl silicone information:

Sample name	Wt %Sil	Wt % CF_2	Wt % organic	MW	Type
FPE 1	38%	7%	55%	3000	fluoroalkyl polyether silicone
FPE 2	33%	3%	64%	7000	
FS 1	56%	44%	0%	2000	fluoroalkyl silicone
FS 2	86%	14%	0%	14000	
FA 1	57%	41%	2%	3000	alkyl, fluoroalkyl silicone
FA 2	68%	30%	2%	3000	
FA 3	81%	17%	2%	2000	
FA 3ACR	81%	17%	2%	2000	
FA 4	63%	16%	21%	5000	

Procedures

In **system I**, a solvent-borne 2 part heat cured polyurethane is modified with various fluoroalkyl silicones at 1% use level and evaluated for appearance, slip, mar resistance, and stain resistance.

Table B: Formulation of system I, a 2K SB/PU formulation.

Component	Supplier	Wt%
Part A:		
Desmophen A870 BA	Bayer	46.92%
Desmophen 670A-80	Bayer	31.35%
Dabco T-12	Air Products	0.10%
n-BA		5.52%
PMA		7.27%
EEP		8.84%
Part B:		
Desmodur N-3390 BA/SN	Bayer	36.35%
PartA/PartB = 73.34%/26.66%		

Preparation of System I: The fluoroalkyl silicone was added to the A side at 1% of the total weight. Part A and B were mixed in the ratio above. Five minutes later a 1 mL sample was drawn down on an aluminum panel with a #10 wire wound rod. The panel was heated to 110°C for 1 hour and then cooled/conditioned in ambient for two hours before testing.

In **system II**, a UV cured epoxy acrylate formulation was modified with various fluoroalkyl silicones at 1% use level and evaluated for the properties listed in System I and also finger print resistance.

Table C: Formulation System II, a UV curable urethane acrylate system

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 of System II: 0.5 ml of the coating above is drawn on a 4"X6.5" white Leneta Byko-Chart paper with a #5 wire wound rod. The wet film was immediately cured in a UV box using a 15 watt UVP bench lamp with two long-wave tubes. The entire panel was exposed to the UV tubes at a distance of 3" from the tubes for one hour.

In System III, commercial Behr 1050 flat white paint was obtained from a retail store and the fluoroalkylsilicone samples were post-added. After thorough mixing, each paint sample was drawn down on Leneta paper in a 1 mil thickness coating using a wirewound rod # 10. Each paper is allowed to dry at ambient conditions for approximately seven days before testing.

Stain Resistance ASTM D3450:

For Systems I and III, one drop of test fluid stain was carefully applied to the test surface. Creation of an indentation was avoided when using a marker or pen because this would reduce the rub tester's effectiveness. The solution was allowed to settle for one hour before being wiped with paper towel. Any staining is observed and recorded from 1-10 (1 being the worst, and 10 being completely clean.) Next a Sutherland 2000 rub tester is then used to wipe the stain with a Kimwipe saturated with water for 25 cycles (50 wipes) at 84 rpm. The remaining stain is evaluated qualitatively again from 1-10.

System II differed in that only 42 rubs were used on the rub tester and a 64:1 diluted solution of commercial cleaner was used instead of water.

Test fluids used: Blue pen ink, black marker ink, silicone pigments (by Dispersion Technologies Inc. and Smooth-On Inc.,) black sharpie ink, red sharpie ink, graphite pencil, printer ink, concentrated grape juice, crayon, and pencil crayon.

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.

Gloss:

Gloss is measured with a BYK-Gardner 60° micro-glossmeter. Gloss value is directly recorded from the micro-glossmeter display. 0 is the lowest possible score.

Mar Resistance:

First, the initial 60° gloss is measured using a BYK-Gardner 60° micro-glossmeter. The gloss value is read directly from the micro-glossmeter display. Afterwards, the sample is rubbed for 500 rubs at 84 rpm using a 4 lb test block attached to a nylon scrubbing pad. Final 60° gloss value is recorded again. Mar resistance is quantified by percent remaining gloss after rubbing. For low gloss paint sample, mar resistance rating is qualitatively determined by visual inspection of the panel after rubbing (10 is the best).

Coefficient of Friction: Slip was measured with ChemInstruments Coefficient of Friction -500. (Test speed: 15 cm/min; travel length: 15 cm; Sled weight: 200 grams. The Sled surface is covered with ASTM-specified rubber). Static coefficient of friction was directly obtained from the equipment, representing the ratio of the horizontal component of the force (required to overcome the initial friction) to the vertical component of the object weight. Dynamic coefficient of friction was also directly obtained from the equipment, representing the ratio of the horizontal component of the force (required to cause the object to slide at a constant velocity) to the vertical component of the object weight. The greater the value, the higher the friction is for the substrate.

Results:

Series I: Two part solvent borne polyurethane (2k SB/PU)

Table D: Film properties of system I, a 2K SB/PU coating with 1% Fluoroalkyl silicones

1% Fluoroalkyl silicone	Static COF	Kinetic COF	Initial 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

Graph 1: Film properties of 2K SB/PU System with 1% Fluoroalkyl silicone

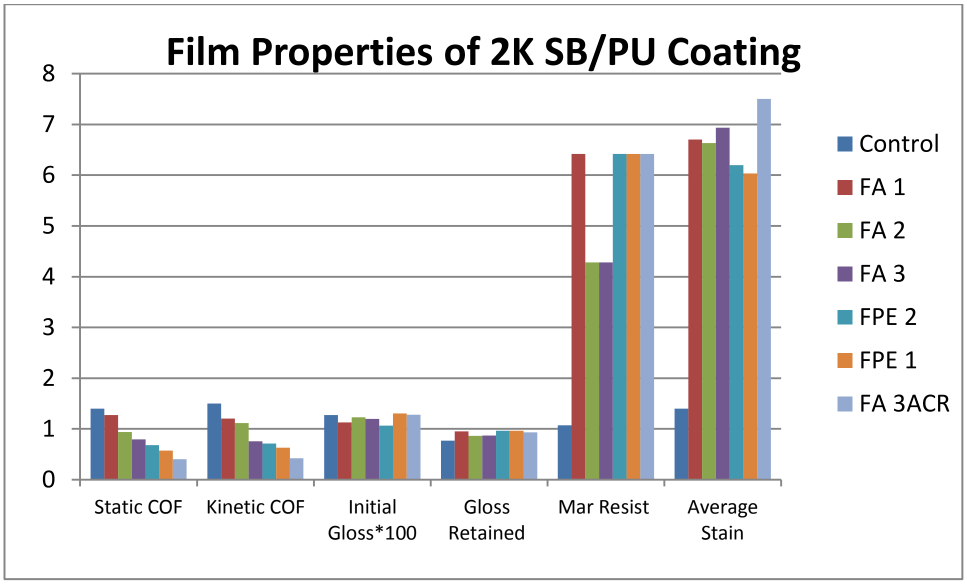
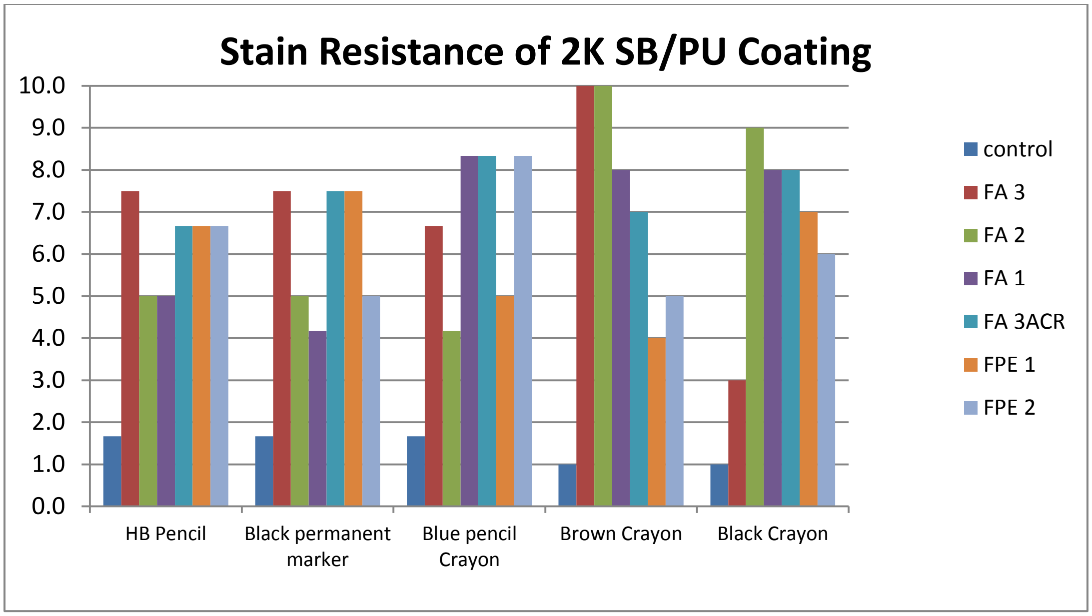


Table E: Stain Resistance of 2K SB/PU System with 1% Fluoroalkyl silicone

	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

Graph 2: Stain Resistance of 2K SB/PU System with 1% Fluoroalkyl silicone



Summary of Series I – 2K Heat Cured SB/PU coating system

1. The samples prepared with FA 3ACR and FA 1 have some fisheyes, indicating incompatibility. FA 1 with its highest CF_2 content, is the most likely to cause defects, but the FA 3 ACR defects, especially since FA 3 was defect free, is surprising.
2. FA 3, FA 2 and both FPE fluoroalkyl silicones give smooth appearance with 2K SB/PU coating system.
3. The gloss of FPE 1 and FPE 2 samples remains unchanged over the control indicating that these are the most compatible species used.
4. The coatings prepared with fluoroalkyl silicones all had reduced COFs and increased mar resistance. The surprisingly poor performance of FA 1, FA 2 and FA 3 could be explained by their reacting into the PU film which we have shown affects this property.[2]
5. Performance in stain resistance is similar in all but seems more dependent on stain than additive.

Series II, a UV Curable Urethane Acrylate Coating System:

Table F: Film properties of UV cured acrylate coating with 1% Fluoroalkyl silicone

	60° Gloss	Stain Resistance	Mar Resistance	Static COF	Kinetic COF	Finger Print Resistance	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

Graph 5: Film properties of UV cured urethane acrylate coating treated with 1% Fluoroalkyl silicone

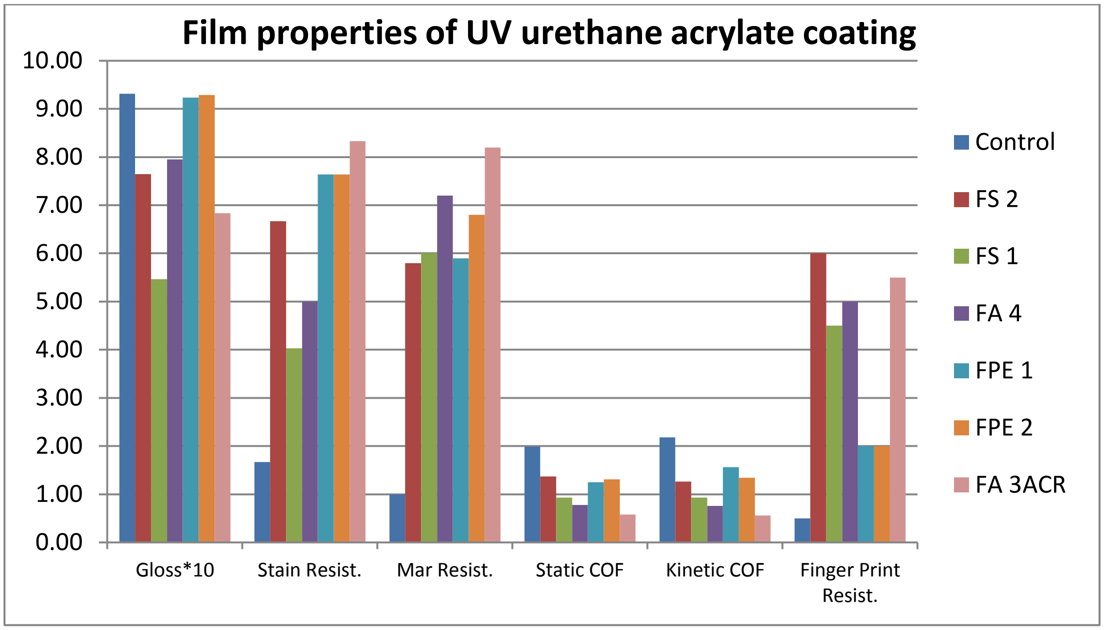
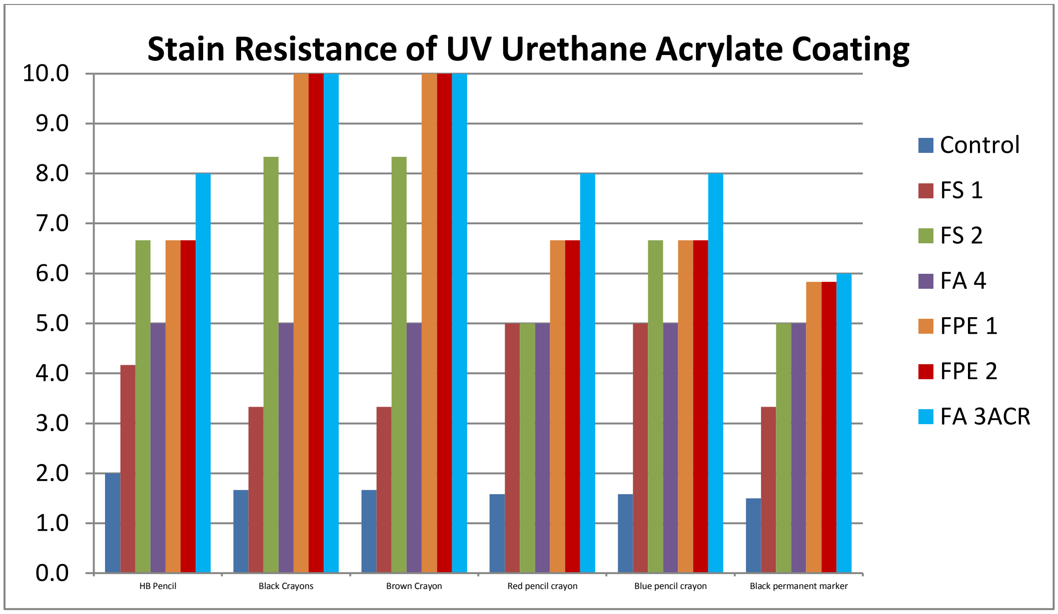


Table G: Stain resistance of UV cured urethane acrylate coating with 1% Fluoroalkyl silicone

	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

Graph 6: Stain resistance of UV cured urethane acrylate coating with 1% Fluoroalkyl silicone



Summary of Series II - UV Urethane Acrylate

1. The coatings prepared with fluoroalkyl silicones all had reduced COFs and increased mar resistance.
2. Performance in stain resistance is similar in all but seems more dependent on stain than additive.
3. The samples prepared with FA 4, FS 1 and FS 2 have defects and gloss reduction indicating incompatibility.
4. The gloss of FPE 1 and FPE 2 samples remains unchanged over the control indicating that these are the most compatible species used.
5. Fluoroalkyl silicone FA 4 gives a good balance of properties.
6. FS 2, FA 4 and FA 3ACR give the best finger print resistance.

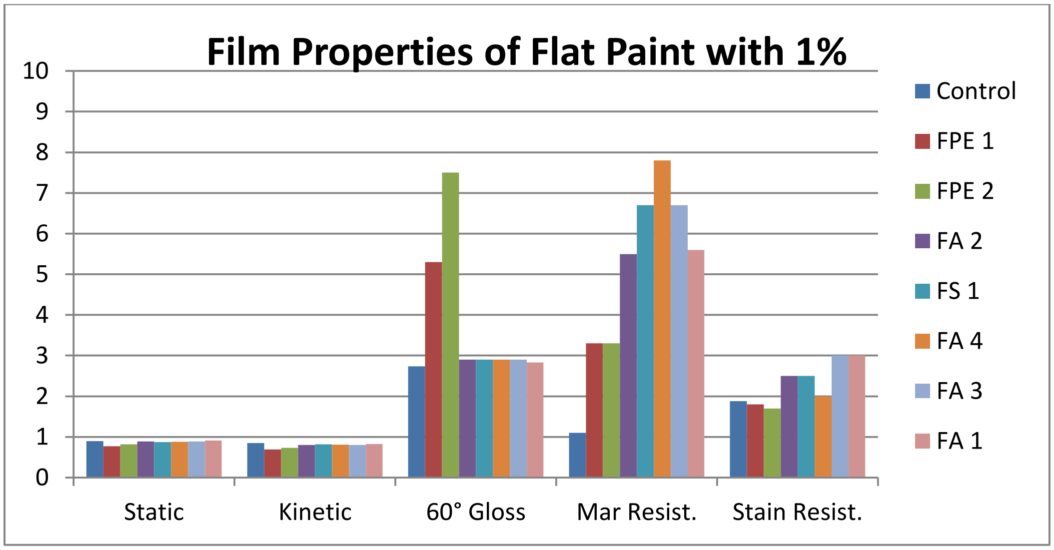
Series III: Flat Paint – Treated with Various Fluoroalkyl silicones

Table H: Film properties of flat white paint treated with various fluoroalkyl silicones

	%	Static CoF	Kinetic CoF	60° Gloss	Mar Resistance	Stain Resistance	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

Graph 7: Film properties of Flat Paint with 1% Fluoroalkyl silicone



Graph 8: Film properties of Flat Paint with 5% Fluoroalkyl silicone

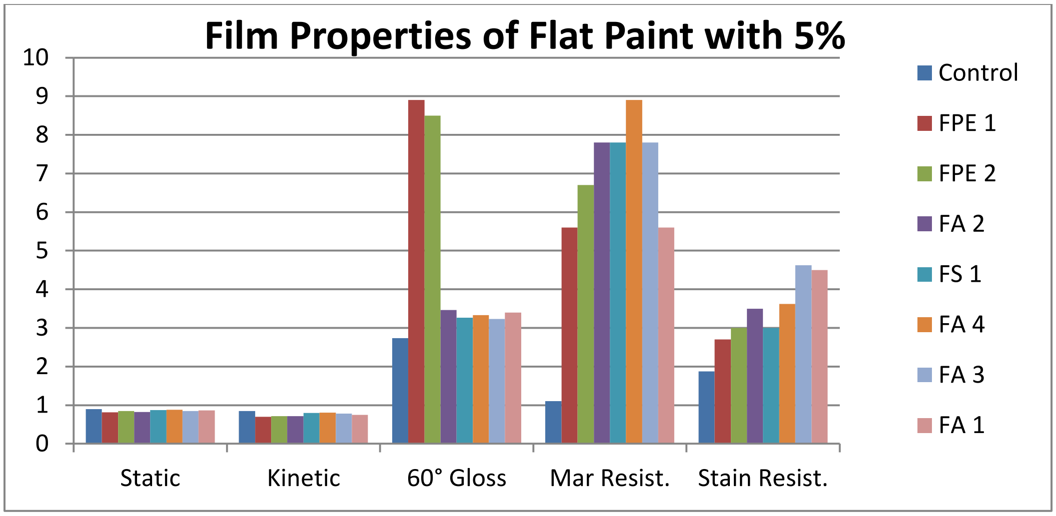


Table I: Stain resistance of Flat Paint with various Fluoroalkyl silicones

Fluoroalkyl silicone	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 of Series III - Flat Paint Treated with Various Fluoroalkyl silicones

1. Post-added Fluoroalkyl silicones have no significant effect on slip and gloss for flat paint but do affect mar and stain resistance.
2. Fluoroalkyl silicone FA 3 and FA 2 give the best overall stain resistance.
3. Except for FPE 1 and FPE 2, the Fluoroalkyl silicones are not compatible with this white flat paint.

Conclusions:

Charting results below as "++" for best results; "+" for moderate results; or "-" for no improvement, one can see that the FPE type products are always compatible resulting in few or no defects or reduction in gloss and generally give good improvements in the properties (Long confusing sentence). The FS series, which is the least soluble, gives good properties but always give defects. The alkyl, fluoroalkyl series are sometimes compatible and generally give better properties than the FPE type.

	compatible I	compatible II	compatible II	Slip I	Slip II	Slip III	Mar I	Mar II	Mar III	Stain I	Stain II	Stain III
FPE 1	++	++	++	++	+	-	++	+	+	+	++	-

FPE 2	++	++	++	++	+	-	++	+	+	+	++	-
FS 1		-	-		++	-		+	+		+	-
FS 2		-			+			+			++	
FA 1	-		-	-		-	++		++	++		-
FA 2	+		-	+		-	+		++	++		-
FA 3	+		-	+		-	+		++	++		-
FA 3ACR	-	+		++	++		++	++		++	++	
FA 4		-	-		++	-		++	++		+	-

Using a similar analysis to look at stain resistance in more detail, the same overall conclusions are supported. The compatible FPE type products give good results, the FS fluorosilicones give good results but have defect problems, and the alkyl fluoroalkyl type is often the best balance.

Sample name	Blue Ink I	Blue ink II	Blue ink III	Black marker I	Black marker II	Black marker III	Crayons I	Crayons II	Crayons III	Black Silicone I	Black Silicone II	Black silicone III	Grape juice I	Grape juice II	Grape Juice III
FPE 1			-	++	++	-	+	++				++			-
FPE 2			-	+	++	-	+	++				++			++
FS 1			+		-	+		-				-			-
FS 2					+			+							
FA 1			+	+		+	++					-			+
FA 2			++	+		++	++					+			++
FA 3			++	++		++	+					+			++
FA 3ACR				++	++		++	++							
FA 4			+		+	+		+				-			++

References:

1. EPA factsheet; "Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)", www.EPA.gov, May 2012
2. Ruckle; Cheung, Proceedings of the Waterborne Symposium, 2013.