Fluoro- Silicones in UV cured Coatings Films.

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Abstract

A series of our non-PFOS fluoroalkyl silicones will be examined in UV cured coatings films for their impact on coatings properties such as appearance, COF reduction, and mar, stain and fingerprint release. Both reactive and non-reactive fluoroalkyl silicones will be examined. Earlier results of reactive silicones in films have shown interesting results on stain release and the hope is that the fluoroalkyl group will enhance these properties in particular.

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 UV cured systems; a urethane acrylate, an epoxy acrylate and a cationic UV cured epoxy silicone resin. We will then examine the effects of these products.

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, FPE 1 and FPE 2 are primary hydroxyl functional. 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.

The FS 1 and FS 2 additives offer a high (44%) and a low (14%) CF_2 content material for comparison. Likewise the FA 1, FA 2, FA 3 series offers CF_2 contents at low, medium and high for comparison. FA 3 ACR will show the effect of reacting when compared to FA 3.

The FPE 1 and FPE 2 have very low CF_2 contents and going into the study we expect them to offer little in terms of slip or mar and stain resistance. Likewise the FA 4 can be compared to FA 3 and FS 2 to see the impact of including CH_2 content.

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

Stain Resistance ASTM D3450:

For Systems I and II, 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 remain 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 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 III 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, 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. A final 60° gloss value is recorded again. Mar resistance is quantified by percent remaining gloss after rubbing. Qualitative scores are also recorded from 1-10. (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 (Kinetic) 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:

In **system I**, a UV cured urethane acrylate formulation was modified with various fluoroalkyl silicones (FAS) at 1% use level and evaluated.

Table B: Formulation System I, 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 I: 0.5 ml of the coating above is drawn on a 4"X6.5" white Leneta 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.

Series I: UV Curable Urethane Acrylate Coating System:

Table C: 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 1: Film properties of UV cured urethane acrylate coating treated with 1% Fluoroalkyl silicone

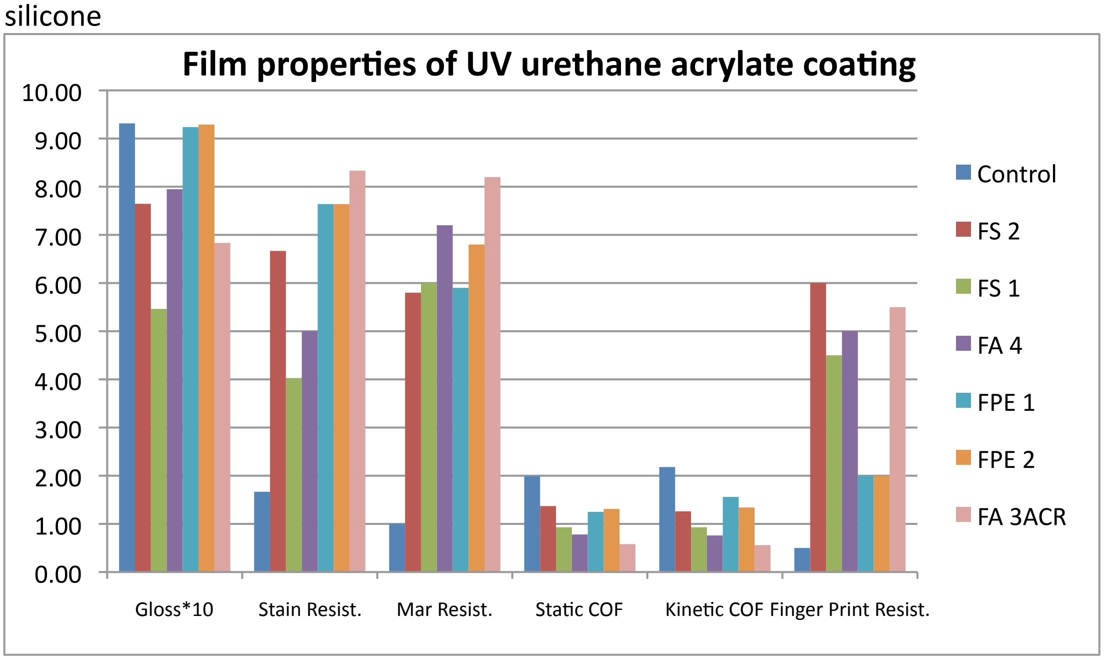
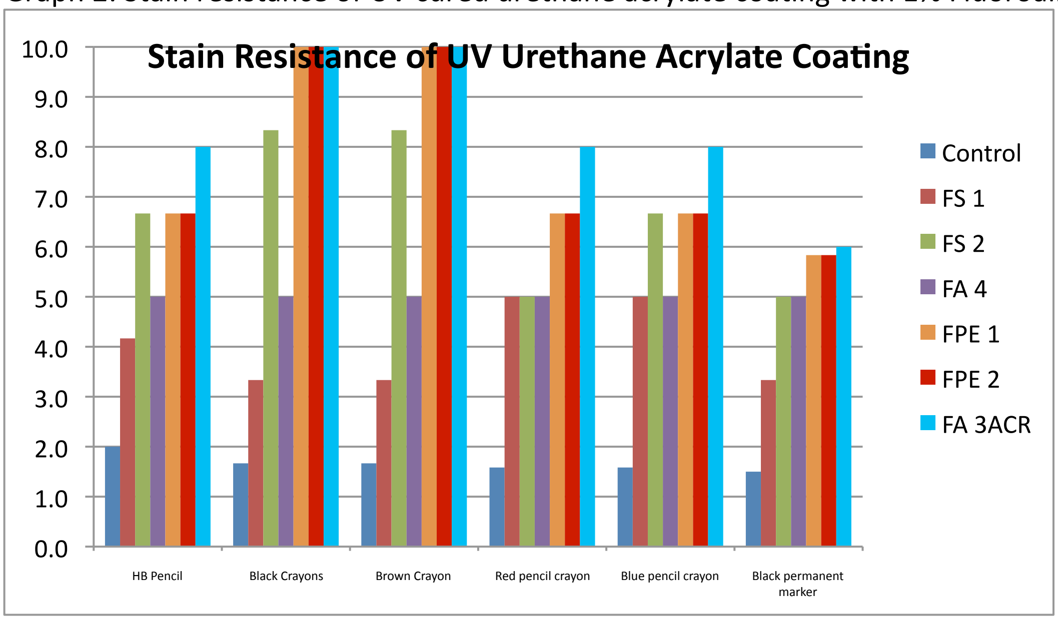


Table D: Stain resistance of UV cured urethane acrylate coating with 1% Fluoroalkyl silicone

	HB Pencil	Black Crayon	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 2: Stain resistance of UV cured urethane acrylate coating with 1% Fluoroalkyl silicone



Summary of Series I - UV Urethane Acrylate

1. The coatings prepared with fluoroalkyl silicones all had reduced COFs and increased mar resistance.
2. Gloss is reduced by all FS and FA types but not FPE types, indicating a compatibility issue for those.
3. Performance in stain resistance is similar in all but seems more dependent on stain than additive.
4. FA 3ACR, FPE 1 and FPE 2 give relatively high ratings for gloss, mar and stain resistance.
5. FS 2, FA 4 and FA 3ACR give the best finger print resistance. The better performance of FS 2 to FS 1 is surprising because the latter has higher CF_2 content and was expected to perform the best.

6. FA 4 - which has a balance of % silicone, %CF_2, and %CH_2 contents in the structure - gives a very good balance of properties.

Series II: UV Curable Epoxy Acrylate Coating System

All epoxy acrylate coatings prepared were based on adding the FAS additive at 1% level into the resin manufacturer's starting formulation.

Table E: Formulation of UV curable epoxy acrylate system

Butyl Acetate	8.25%
Toluene	8.25%
Methyl Isobutyl Ketone	9.9%
Methyl Ethyl Ketone	6.6%
Epoxy Acrylate UV Resin Blend (Pesiff)	66.0%
FAS additive (Siltech)	1.0%

Each sample is drawn down on a Leneta paper using a wire-wound rod #10 to create a 1 mil thickness coating. That film was then cured for at least 1 hour in a 10 mW/cm^2 UV box.

Table F: Film properties of UV cured epoxy acrylate coating treated with 1% FAS

	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

Table G: Stain resistance of UV cured epoxy acrylate coating treated with 1% FAS

	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

Summary of Series II - UV Epoxy Acrylate

1. Gloss and defects confirm the only fully compatible materials are the FPE types.
2. FA 3ACR, FPE 1 and FPE 2 again give relatively high ratings for gloss, mar and stain resistance.
3. FA 4 - which has a balance of % silicone, %CF_2, and %CH_2 contents in the structure - again gives a very good balance of properties.
4. FS 2, FA 4 and FA 3ACR again give the best finger print resistance.

Series III – Cationic UV Epoxy Cured Silicone

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:

Table H: Formulations of Series III – Cationic UV Epoxy Silicone with various FAS additives

	Epoxy Silicone	Catalyst	FS 1	FA 3	FA 1	FA 2
Control	99.5%	0.5%				
A	99.3%	0.5%	0.2%			
B	99%	0.5%	0.5%			
C	98.5%	0.5%	1.0%			
D	96.5%	0.5%	3.0%			
E	94.5%	0.5%	5.0%			
F	99.3%	0.5%		0.2%		
G	99%	0.5%		0.5%		
H	98.5%	0.5%		1.0%		
I	96.5%	0.5%		3.0%		
J	94.5%	0.5%		5.0%		
K	99.3%	0.5%			0.2%	
L	99%	0.5%			0.5%	
M	98.5%	0.5%			1.0%	
N	96.5%	0.5%			3.0%	
O	94.5%	0.5%			5.0%	
P	99.3%	0.5%				0.2%
Q	99%	0.5%				0.5%
R	98.5%	0.5%				1.0%
S	96.5%	0.5%				3.0%
T	94.5%	0.5%				5.0%

The above formulations are mixed, and then drawn down on Leneta paper in a 1 mil thickness coating using a wire-wound rod #10. Each paper is then placed in a 10 mW/cm^2 UV box for 1 hour to cure, and then kept at room temperature for at least one day before testing.

Table I: Film properties of Series III – Cationic UV Epoxy Silicone with various FAS additives.

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

Table J: Stain resistance ratings of epoxy silicone treated with various FAS

Additive	% FAS	Ball Pen	Silicone pigment	Black Sharpie	Blue High lighter	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

Summary of Series VIII - UV Epoxy Silicone – Silmer EPC E9:

1. All tested FAS are compatible with the tested silicone epoxy resin.
2. Stain resistance in all cases studied increased as use level of FAS increased.
3. All FAS show improvements to mar resistance. This mar resistance is seen at low use levels and barely improved or somewhat lost at higher use levels. This is consistent with our previous results.[2]
4. 60° Gloss is slightly reduced and no surface defects are seen. More FAS does lower gloss more.
5. Only FS 1 – with the highest CF_2 content - shows the dramatic lowering of COF that one usually sees with silicone or fluoroalkyl additives.

Conclusions:

The results are charted below as "++" for best results; "+" for moderate results; or "-" for no or very little 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. The FS series, which is the least soluble, gives good properties but often give defects and gloss reduction. The FA (alkyl, fluoroalkyl) series are sometimes compatible and generally give better properties than the FPE type. In particular fingerprint resistance is improved with this type.

	compatible I	compatible II	compatible III	Slip I	Slip II	Slip III	Mar I	Mar II	Mar III	Stain I	Stain II	Stain III	Fingerprint I	Fingerprint II
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 fluoroalkylsilicones give good results but have defect problems, and the FA alkyl fluoroalkyl type is often the best balance.

Sample name	**Blue ink III**	**Black marker I**	**Black marker II**	**Black marker III**	**Crayons I**	**Crayons II**	**Black silicone III**	**Pencil Crayon I**	**Pencil Crayon II**	**Pencil Crayon III**
FPE 1		++	+		++	++		++	++	
FPE 2		++	+		++	++		++	++	
FS 1	++	-	-	-	-	++	-	+	+	++
FS 2		+	+		++	++		+	+	
FA 1	+			-			+			++
FA 2	+			-			++			++
FA 3	+			+			+			++
FA 3ACR		++	++		++	++		+	++	
FA 4		+	+		+	+		+	+	

Worthy of more thought and experimentation is the consistently very good behavior of FA 3, FA 3ACR and FS 2 – which have a smaller amount of %CF_2 than the other FASs studied. We expected the highest CF_2 content materials to provide the most slip, stain resistance and fingerprint resistance due to the lipophobic nature of perfluoroalkyl materials. That is not the case in this study, the presence of CF_2 groups helps this behavior, but maximizing the amount of CF_2 is not the optimum, in fact the best FAS additives have a little CF_2 content and very high (80%) silicone content.

We have seen this same behavior in non-UV systems as well.[3] This observation may indicate that only a little perfluoroalkyl is needed, an important fact for cost considerations.

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.
3. Ruckle; Cheung, Proceedings of the Waterborne Symposium, 2014.