NOVEL ORGANOSILICONE FLUORO-FREE ANTI-GRAFFITI AGENTS

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Abstract

A new composition of non-fluoro containing organomodified silicone has been developed. Early testing shows strong anti-stain properties when compared to fluorochemical controls. We present data comparing this class of compounds in some standard formulations.

Introduction

Three families of organo-modified silicones, two newly conceived, were evaluated for slip, mar and stain resistance. We used our best fluoroalkyl silicones and a commercial, competitive organosilicone as controls and evaluated these in a waterborne and solventborne 2 part polyurethane heat cured coatings.

Traditional approaches to stain release and anti-graffiti involve fluoroalkyl compounds. These low surface energy, immiscible materials are considered the best approach to stain release and anti-graffiti. The negatives of these products are high cost and recent concerns about their impact on the environment[i]. Recent, notable results on organomodified silicones from our labs have compelled us to re-examine this paradigm and evaluate some fluoroalkyl free organo-modified silicones.

In this previous work[ii] we saw surprisingly good anti-stain performance from a line of our non-fluoroalkyl containing organo-silicone products. These compounds have a short alkyl chain and one hydroxyl group. This unexpected behavior included a synergistic effect when fluoroalkyl groups are incorporated allowing us to achieve the best behavior with minimal fluoroalkyl content[iii]. We wondered how effective these hydroxyl alkyl silicones were and how adding similar chains with multiple hydroxyls would affect the stain resistance.

Experimental

Formulations.

The experimental additives were screened at 1% or 2% in a waterborne, 2 part polyurethane (WB 2K PU) or a solventborne (SB 2K PU) model systems. The details of these formulations are shown in Table 1.

Table 1 - Formulations

2K WB PU formulation		**2K SB PU formulation**	
Part A		**Part A**	
Bayhydrol A145	54.55%	Desmophen A870 BA	31.84%
Surfynol 104 DPM	1.30%	Desmophen VPLS 2388	21.19%
Borchigel PW 25	0.19%	Dabco T-12 (Durastab LT-2)	0.05%
Water (Distilled)	23.23%	n-BA (used Tert Butyl Acetate)	5.72%
Part B		PMA (Glycol Ether PM Acetate)	7.62%
Desmodur I	9.32%	EEP (Ester EEP)	9.14%
Bayhydur VP LS 2150/1	7.24%	**Part B**	
Exxate 600	4.15%	Desmodur N-3390A BA/SN	24.45%
Total	100%	**Total**	100%

Test Panel Preparation

Samples were drawn down on 4”x 6” aluminum Q-Panels using a #10 wire wound rod. The Q-Panel was then transferred to an oven at 110°C for 60 minutes to effect curing. The samples were left at ambient to condition for a minimum of 24 hours before testing.

Stain Resistance (Marker Removal) Test

Stain resistance is measured using a Sutherland 2000 Ink Rub Tester - Dry Rub method to remove marker stain. The following settings are applied for the test: 100 rubs and 84 rpm stroke speed. Two thick black marks and green marks are applied on the test panel with a Papermate permanent marker, Super Sharpie marker and Berol Liquid TIP marker. Rubbings are done using a 4 lb test block which is attached with a 2”x 4” nylon scrubbing pad. The degree of difficulty of marker to write on the coating and the degree of easiness to remove the marker from the coating are recorded. The rating is estimated by visual inspection. 10 is the best and 0 is the worst.

Note: Rub Tester does not have enough force to remove marker whether wet or dry. IPA removes marker easily for all samples. Hard rubbing by hand with paper towel was used for Marker removal dry and wet results.

Mar Resistance Test

Mar resistance is measured using a Sutherland 2000 Ink Rub Tester - Dry Rub method with the following settings: 100 rubs and 84 rpm stroke speed. Rubbings are done using a 4 lb test block which is attached with a 2”x 4” nylon scrubbing pad. The rating is calculated based on the percentage change in gloss reading before and after the rubbing test, and rating from visual inspection. The above rub test is then replied with 10 rubs at 40 rpm, using a 4 lb test block attached with a 2”x4” P1000 sand paper. The second rating is calculated based on percentage change in gloss reading before and after the rubbing test and from visual inspection.

Rating 10 is the best; 0 is the worst.

Coefficient of Friction - COF (Slip)

Slip is measured with ChemInstruments Coefficient of Friction -500. (Test speed: 15 cm/min; travel length: 15 cm; Sled weight: 200 grams and Sled surface which is covered with ASTM-specified rubber). Static coefficient of friction is 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 (200 grams). Kinetic coefficient of friction is 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 (200 grams). The greater the value, the higher the friction is for the substrate.

Gloss:

Gloss is measured with BYK-Gardner 60 micro-glossmeter before and after mar resistance test. The value is directly recorded from the micro-glossmeter.

Anti-graffiti

Anti-graffiti is rated based on the following parameters:

- Degree of difficulty to put on black marks with permanent marker on coating. (Marker resistance with weighting factor = 0.4)
- Degree of difficulty to remove black marks without damaging the coating, (Marker removal with weighting factor=0.4)
- Mar and stain resistance according to the aforementioned procedure (Mar resistance with weighting factor = 0.2)
- Visual inspection

Rating 10 is the best; 0 is the worst.

Three types (labeled A, B and C) of hydroxyalkyl silicone compounds were synthesized with standard hydrosilation techniques. These were made in either linear or pendant molecular architectures. See Figure 1: Silicone Structures, Figure 2: Organic Groups and Table 2: Structural Details.

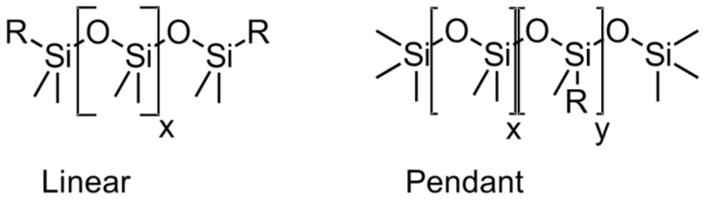

Figure 1: Silicone Structures

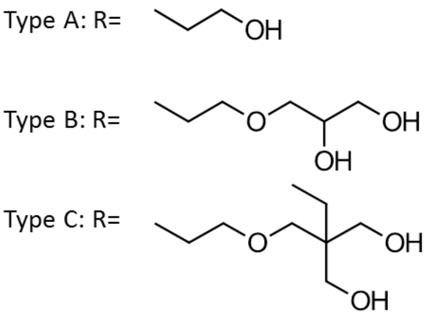

Figure 2: Organic Groups

Table 2: Structural Details

code	MW	Hydroxy Alkyl Type	Architecture
LA 10	1000	A	Linear
LB 10	1000	B	Linear
LC 10	1000	C	Linear
LA 50	4000	A	Linear
LB 50	4000	B	Linear
LC 50	4000	C	Linear
LA 100	8000	A	Linear
LC 100	8000	C	Linear
PA 48	3000	A	Pendant
PB 48	3000	B	Pendant
PC 565	5000	C	Pendant
PA 10100	9000	A	Pendant
PB 10100	9000	B	Pendant
PC 10100	9000	C	Pendant
PA 350	12000	A	Pendant
PA 460	18000	A	Pendant

Results

In a quick screen we evaluated Type A and Type C silicones against a Fluoroalkyl silicone with high CF_2 content and a commercial anti-graffiti product from a competitor. Both Static and Kinetic COF, generally required for stain resistance and anti-graffiti performance, was reduced relative to both controls. Likewise the anti-graffiti behavior was improved especially in the solventborne system. The Type C product was better than the Type A material and the linear structure was better than the non-linear one. These results were what we were hoping for so we proceeded with other analogues. See Figure 3: COF screen and Figure 4: Resistance Screen

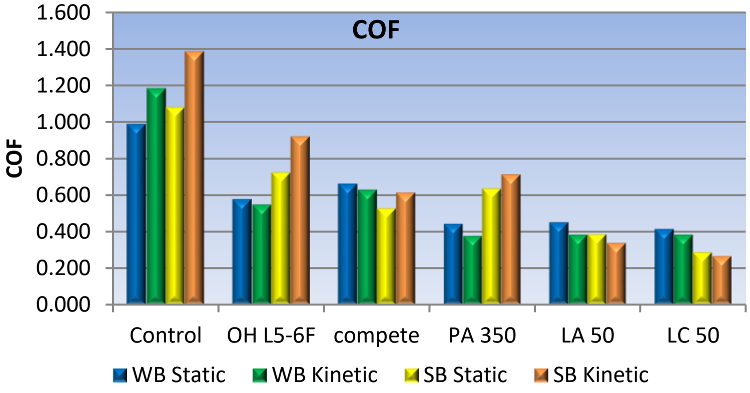

Figure 3: COF screen

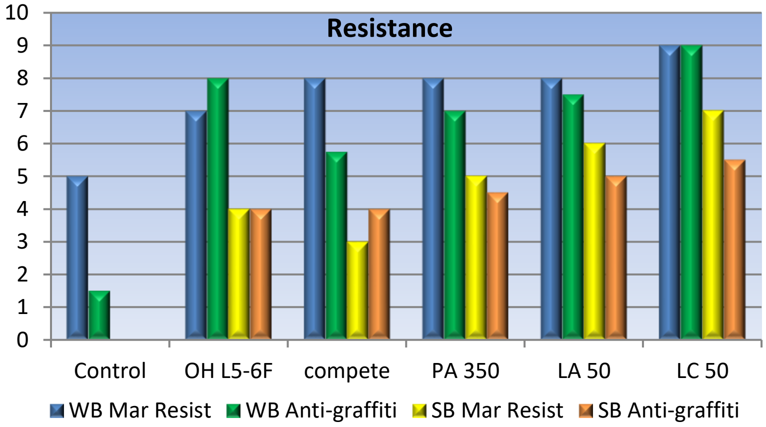

Figure 4: Resistance Screen

Next we evaluated Type A and Type B materials at 1% in both WB and SB PU system using the competitive silicone as a control. The structures evaluated were five examples of Type A silicones and three corresponding (same values of x,y) Type B silicones. All of the raw data are show in Table 3: 1% Additive WB PU through Table 6.

Relative to the controls only the lowest molecular weight species, labeled PA 48 and PB 48 did not show improved properties over the competitive control. The proportional relationship between silicone molecular weight and COF/ release properties is expected, and seems to be a dominant factor. PA 350 and PA 460 are the highest molecular weight materials. See Figure 5 and Figure 6.

Within the three pairs of Type A and Type B, performance was very similar across types. Comparing PA 48 with PB 48; LA 10 with LB 10; and LA 50 with LB 50 these types perform very similarly against each other.

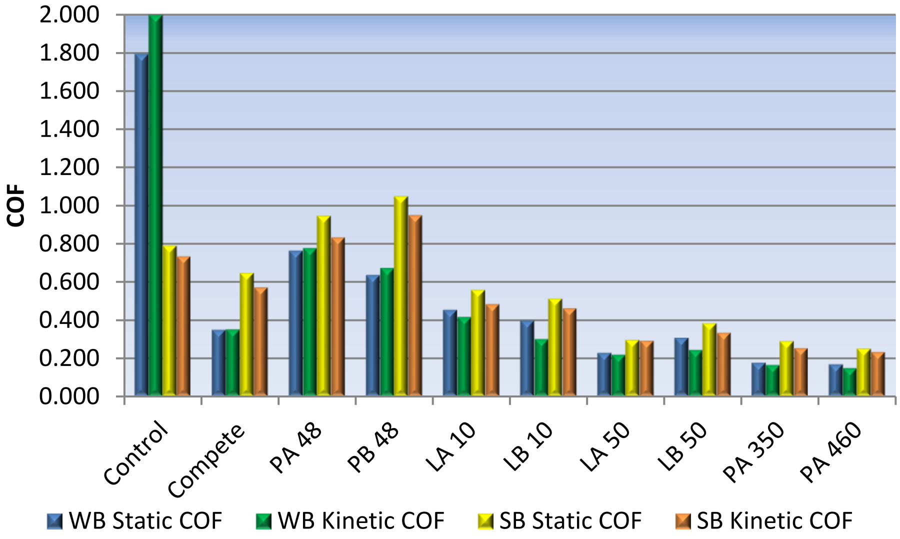

Figure 5: 1% Additive

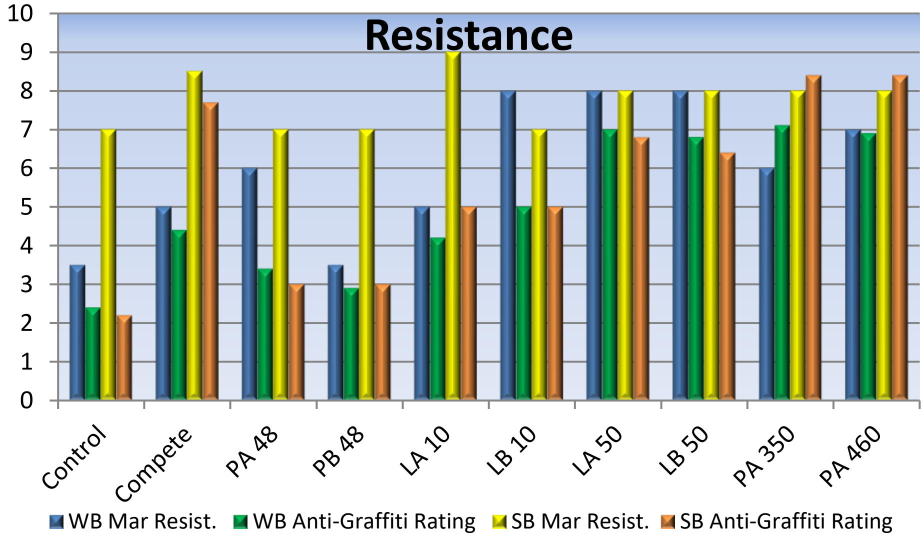

Figure 6: 1% Additive

We then examined a broader range of silicones including the newest Type C derivatives using our Fluorosil products which have demonstrated efficacy in this area as well as the competitive silicone based anti-stain ingredient. In these experiments we used them at a higher use level of 2%. All of these were better than the control without an additive. The best of these products showed performance as good as, or even better than the fluorosilicone controls which were better than the competitive product. See Figure 7and Figure 8.

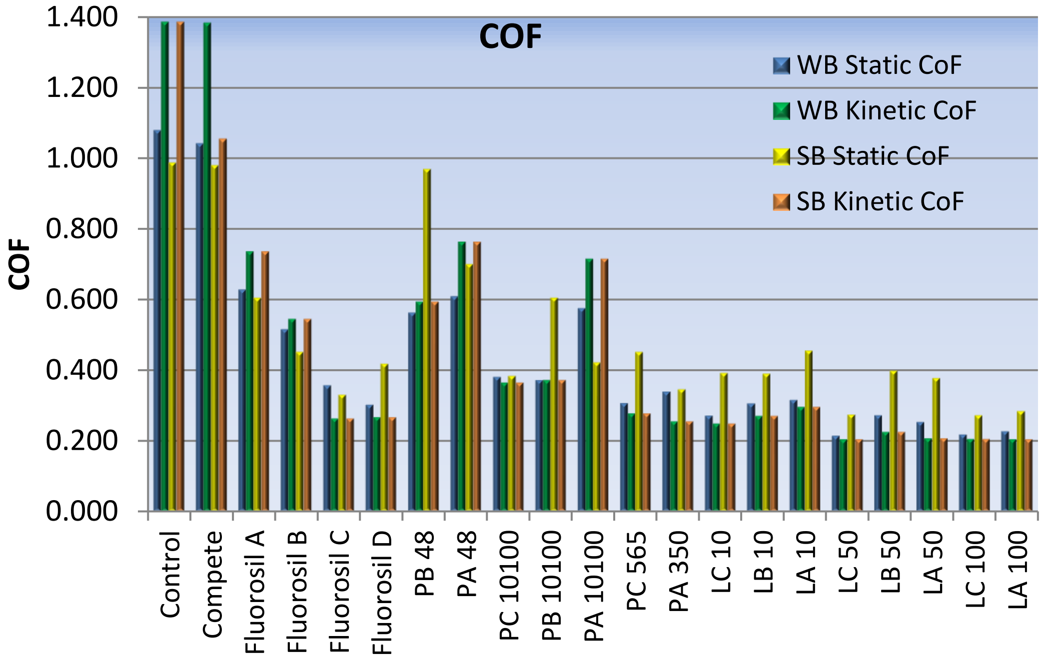

Figure 7: 2% Additive COF

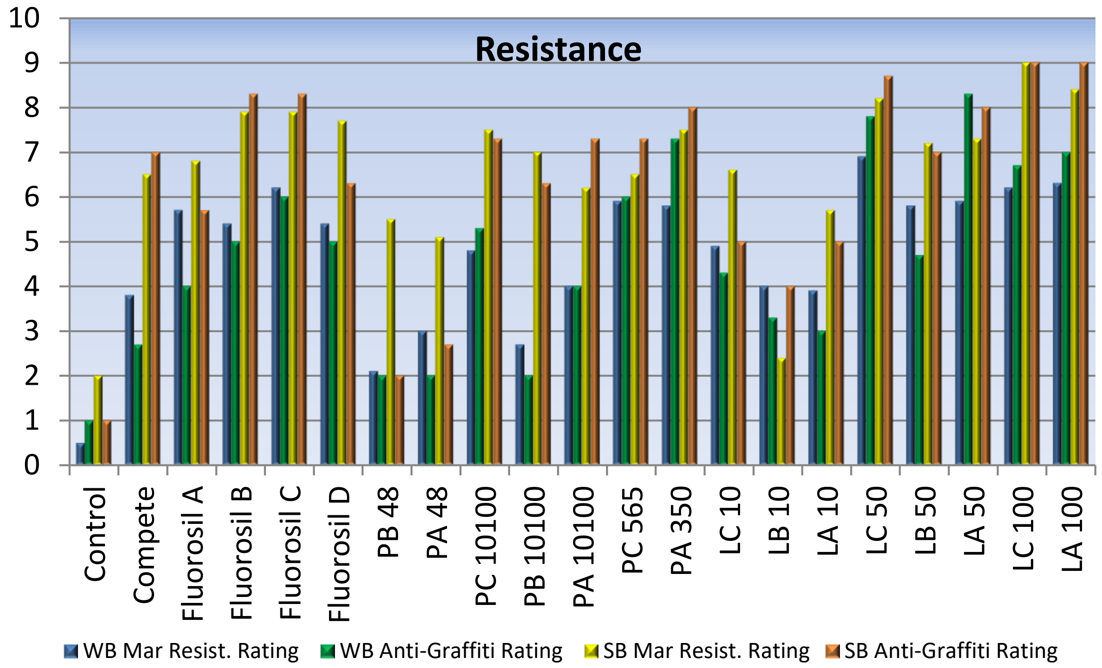

Figure 8: 2% Additive Resistance

Within each analogous series, the Type C structures showed the best performance and the Type B structures showed less performance than Type A. However, the key parameters seem to be that the linear structures perform better than the pendant materials. Also, the higher molecular weight improves performance.

Table 3: 1% Additive WB PU

1% Silicone: WB/PU	Static COF	% Change in Static COF	Kinetic COF	% Change in Kinetic COF	Initial Gloss	Gloss % change after rubbing	Mar Resist Rating	Anti-Graffiti Rating	Coating Appearance
LB 10	0.398	-77.8%	0.300	-85.0%	122	-11.7%	8	5	Blotchy, Grainy
LA 10	0.453	-74.8%	0.416	-79.2%	107	-9.3%	5	4.2	Slight Grainy
LB 50	0.307	-82.9%	0.244	-87.8%	111	-21.6%	8	6.8	Smooth, Similar to Compete
LA 50	0.229	-87.2%	0.219	-89.0%	111	-14.0%	8	7	Smooth, Similar to Compete
LA 350	0.176	-90.2%	0.164	-91.8%	103	-11.7%	6	7.1	Smooth, Grainier than LA 50
LA 460	0.168	-90.6%	0.147	-92.6%	95	-13.8%	7	6.9	Smooth, Grainier than LA 50
LB 48	0.635	-64.6%	0.673	-66.3%	90	-17.2%	3.5	2.9	Blotchy with fisheyes
LA 48	0.763	-57.5%	0.776	-61.1%	118	-9.0%	6	3.4	Blotchy with fisheyes
Compete	0.349	-80.6%	0.350	-82.5%	90	-16.7%	5	4.4	Smooth with fine blotches
Control	1.794	0.0%	1.997	0.0%	131	-39.2%	3.5	2.4	Smooth

Table 4: 1% Additive SB PU

1% Silicone in SB/PU	Static COF	% Change in Static COF	Kinetic COF	% Change in Kinetic COF	Initial Gloss	Gloss % change after rubbing	Mar Resist. Rating	Anti-Graffiti Rating	Coating Appearance
LB 10	0.511	-35.2%	0.460	-37.1%	126	-4.8%	7	5	Smooth

LA 10	0.557	-29.3%	0.482	-34.1%	132	-1.8%	9	5	Smooth
LB 50	0.383	-51.5%	0.333	-54.4%	121	-1.9%	8	6.4	Smooth
LA 50	0.296	-62.5%	0.290	-60.3%	120	-2.8%	8	6.8	Smooth with Slight mottling
LA 350	0.288	-63.5%	0.252	-65.6%	122	-3.8%	8	8.4	Smooth with Slight mottling
LA 460	0.250	-68.3%	0.232	-68.3%	123	-3.8%	8	8.4	Smooth with Slight mottling
LB 48	1.046	32.7%	0.946	29.3%	130	-2.8%	7	3	Smooth
LA 48	0.944	19.7%	0.830	13.4%	127	-3.7%	7	3	Smooth
Compete	0.646	-18.1%	0.569	-22.2%	133	-2.5%	8.5	7.7	Smooth
Control	0.789	0.0%	0.732	0.0%	133	-4.3%	7	2.2	Smooth

Table 5: 2% Additive WB PU

2% Additive in WB/PU	**Static CoF**	**% Change Static CoF**	**Kinetic CoF**	**% Change Kinetic CoF**	**Initial Gloss**	**% Gloss Change after rubbing with nylon pad**	**% Gloss Change after rubbing with P1000**	**Mar Resist. Rating**	**Anti-Graffiti Rating**	**Coating Appearance**
LC 100	0.218	-79.8%	0.205	-85.2%	94	-10.9%	-58.4%	6.2	6.7	Smooth
LA 100	0.227	-79.0%	0.204	-85.3%	92	-4.0%	-61.4%	6.3	7	Smooth
LC 50	0.214	-80.2%	0.204	-85.3%	102	-7.1%	-46.6%	6.9	7.8	Smooth
LB 50	0.272	-74.8%	0.225	-83.8%	92	-11.1%	-56.4%	5.8	4.7	Smooth
LA 50	0.253	-76.6%	0.207	-85.1%	101	-5.2%	-57.4%	5.9	8.3	Smooth
PA 350	0.339	-68.6%	0.255	-81.6%	106	-4.7%	-61.3%	5.8	7.3	Smooth
LC 10	0.271	-74.9%	0.249	-82.0%	80	-9.1%	-66.9%	4.9	4.3	Slight Grainy
LB 10	0.306	-71.7%	0.270	-80.5%	71	-13.9%	-60.2%	4	3.3	Blotchy with fisheyes
LA 100	0.316	-70.8%	0.296	-78.6%	81	-12.4%	-63.5%	3.9	3	Slight Grainy
PC 10100	0.381	-64.7%	0.365	-73.6%	80	-15.7%	-53.7%	4.8	5.3	Smooth
PB 10100	0.372	-65.5%	0.372	-73.2%	70	-16.3%	-65.3%	2.7	2	V. Grainy
PA 10100	0.576	-46.6%	0.715	-48.4%	104	-17.7%	-69.7%	4	4	Smooth
PC 565	0.307	-71.5%	0.278	-79.9%	89	-9.6%	-55.2%	5.9	6	Smooth
PB 48	0.563	-47.8%	0.594	-57.1%	85	-30.7%	-69.0%	2.1	2	Blotchy with fisheyes
PA 48	0.609	-43.5%	0.763	-44.9%	79	-26.2%	-74.1%	3	2	Blotchy with fisheyes
Fluorosil B	0.516	-52.2%	0.545	-60.6%	102	-9.0%	-56.2%	5.4	5	Smooth
Fluorosil C	0.357	-66.9%	0.263	-81.0%	102	-3.2%	-53.1%	6.2	6	Smooth
Fluorosil D	0.302	-72.0%	0.267	-80.7%	98	-13.4%	-63.9%	5.4	5	Smooth
Fluorosil A	0.628	-41.8%	0.736	-46.8%	91	-12.7%	-56.3%	5.7	4	Smooth
Compete	1.042	-3.4%	1.383	-0.1%	95	-34.8%	-60.6%	3.8	2.7	Smooth with pinholes
Control	1.079	0.0%	1.385	0.0%	124	-56.6%	-84.9%	0.5	1	Smooth

Table 6: 2% Additive SB PU

2% Additive in SB/PU	**Static CoF**	**% Change Static CoF**	**Kinetic CoF**	**% Change Kinetic CoF**	**Initial Gloss**	**% Gloss Change after rubbing with nylon pad**	**% Gloss Change after rubbing with P1000**	**Mar Resist. Rating**	**Anti-Graffiti Rating**	**Coating Appearance**
LC 100	0.272	-72.4%	0.230	-80.6%	120	-0.8%	-25.5%	9	9	Smooth
LA 100	0.284	-71.2%	0.230	-80.6%	122	-2.9%	-30.3%	8.4	9	Smooth
LC 50	0.274	-72.2%	0.256	-78.4%	123	-2.6%	-34.3%	8.2	8.7	Smooth
LB 50	0.398	-59.7%	0.358	-69.7%	125	-3.6%	-43.4%	7.2	7	Smooth
LA 50	0.377	-61.8%	0.295	-75.1%	124	-2.6%	-43.7%	7.3	8	Smooth
PA 350	0.346	-65.0%	0.279	-76.4%	124	-3.5%	-42.5%	7.5	8	Smooth
LC 10	0.392	-60.3%	0.353	-70.2%	125	-5.5%	-36.8%	6.6	5	Smooth
LB 10	0.390	-60.5%	0.424	-64.2%	125	-7.9%	-50.6%	2.4	4	Smooth
LA 100	0.455	-54.0%	0.415	-64.9%	127	-5.8%	-35.9%	5.7	5	Smooth
PC 10100	0.384	-61.1%	0.370	-68.7%	123	-3.4%	-35.7%	7.5	7.3	Smooth

PB 10100	0.605	-38.8%	0.554	-53.2%	123	-3.8%	-42.9%	7	6.3	Smooth
PA 10100	0.422	-57.2%	0.375	-68.3%	121	-4.7%	-36.8%	6.2	7.3	Smooth
PC 565	0.452	-54.3%	0.403	-66.0%	125	-4.1%	-49.0%	6.5	7.3	Smooth
PB 48	0.969	-1.8%	0.925	-21.8%	127	-7.2%	-42.4%	5.5	2	Smooth
PA 48	0.700	-29.1%	0.705	-40.5%	126	-9.4%	-37.4%	5.1	2.7	Smooth
Fluorosil B	0.452	-54.3%	0.418	-64.7%	122	-2.5%	-39.2%	7.9	8.3	Smooth
Fluorosil C	0.330	-66.6%	0.285	-75.9%	125	-2.3%	-39.4%	7.9	8.3	Smooth
Fluorosil D	0.418	-57.7%	0.384	-67.5%	123	-2.3%	-41.9%	7.7	6.3	Smooth
Fluorosil A	0.605	-38.7%	0.676	-42.9%	124	-5.5%	-45.2%	6.8	5.7	Smooth
Compete	0.980	-0.7%	1.055	-10.9%	134	-8.2%	-49.4%	6.5	7	Smooth
Control	0.987	0.0%	1.183	0.0%	134	-17.4%	-60.4%	2	1	Smooth

Conclusion

The original premise, that non-fluoro containing organomodified silicones can perform as good or better than fluoroalkyl materials is validated. Additionally many of the products screened are better than the commercially available silicone in these limited tests.

Within the types of silicones, Type B is not a strong player. The performance of these products is at best similar to that of the Type A family which are already commercial. The Type C family is much more interesting. The premise that as we add more hydrocarbon chain and/or hydroxyls; anti-stain performance will increase is supported by these results.

The main variables in anti-stain performance were not a surprise. As noted previously, the linear silicones were better than the pendant materials and the higher the molecular weight the better the performance.

Footnotes and References.

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[i] EPA factsheet; “Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)”, www.EPA.gov, **May 2012**

[ii] Ruckle, R.E., Cheung, T.; “Properties of Silicone Modified UV Cured Acrylate and Epoxy Coatings Films”, *Proceedings of the Waterborne Symposium*, **2013**, University of Southern Mississippi.

[iii] Ruckle, R.E., Cheung, T.; “Incorporation of Fluoro-Silicones in Coatings Films and the Resulting Properties”, *Proceedings of the Waterborne Symposium*, **2014**, University of Southern Mississippi.