Fluoro-Free Anti-Graffiti Properties From A Novel OrganoSilicone

Tom Seung-Tong Cheung, Bob Ruckle, Steve Wilkowski
Siltech Corp, Canada

Introduction

A new composition of non-fluoro containing organomodified silicone has been developed. These products show strong anti-graffiti properties without the presence of environmentally problematic Fluoroalkyl groups. This performance will be demonstrated in some standard formulations.

Three families of organo-modified silicones were evaluated for slip, mar and stain resistance. We used several fluoroalkyl silicones and a commercial, competitive organosilicone as controls and evaluated all of these in a waterborne and a 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 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 terminated with an 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

An array of organomodified silicones were evaluated for slip, gloss, defects, and several types of release properties. These were evaluated in basic waterborne and a solvent borne polyurethane coatings systems at the same use level of commercial fluoroalkyl silicones (labeled Fluorosil A,B, etc.), a commercially available material from another supplier (labeled compete), and against the base coating without any additives (labeled control).

Three types (labeled A, B and C respectively) of hydroxyalkyl silicone compounds were synthesized with standard hydrosilation techniques. These were made in either linear or pendant molecular architectures.

Figure 1: Silicone Structures

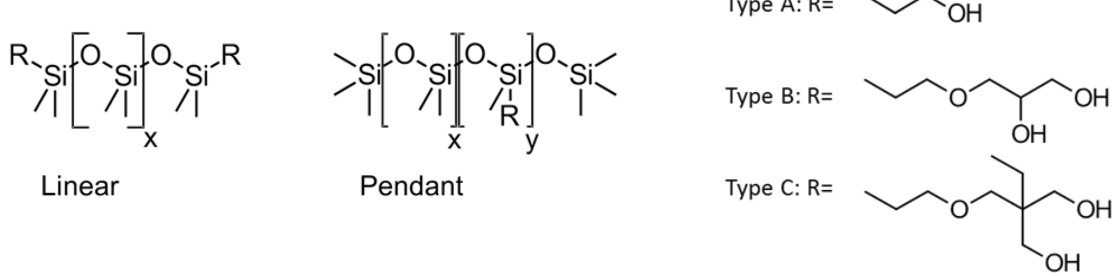


Table 1: Structural Details

Label	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

The formulations prepared 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 and left at ambient conditions for a minimum of 24 hours before testing. The panels are evaluated as below and generally rated on a scale of 1 to 10 (best) for ease of plotting.

Mar Resistance Test

Mar resistance is measured using the dry rub method and Sutherland 2000 Ink Rub Tester with settings: 100 rubs and 84 rpm stroke speed. Rubbings are done using a 4 lb test block which is attached to 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 repeated 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 change in gloss reading before and after the rubbing test and from visual inspection.

Coefficient of Friction: COF or Slip

Slip is measured as COF with the ChemInstruments Coefficient of Friction 500. The following conditions are used: Test speed of 15 cm/min; travel length of 15 cm; Sled weight of 200 grams and Sled surface 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, the lower the value the more slip is improved.

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.

Stain Resistance: Marker Removal Test

Marker Removal was measured by first marking the coating panels with a hand drawn line approximately 2.5 cm long and 0.5 cm thick using a sharpie pen in up to eight colors. The marker stains were allowed to dry at ambient conditions for 10 minutes. We found the Sutherland 2000 Ink Rub Tester does not have enough force to remove the marker whether wet or dry. Using IPA removed the marks too easily, so differences were evaluated by hard hand rubbing with paper towel without solvent.

Stain Resistance Rating is given based on visual inspection with respect to; the degree of difficulty of marker to write on the coating and the degree of easiness to remove the marker from the coating.

Anti-graffiti

Anti-graffiti is evaluated for marks created with a permanent black marker. The results are rated based on the ratings for degree of difficulty to put on black marks on coating (marker resistance); degree of difficulty to remove black marks without damaging the coating (marker removal); and mar resistance as described above. The formula used to obtain the total rating is 0.4 marker resistance + 0.4 marker removal + 0.2 mar resistance.

Iodine Stain Resistance Test

2.5% Iodine Solution is used for this test. 10µL of the Iodine solution is applied on the surface of aluminum panel using a micro-syringe and then the stain is covered with a 22mm by 22mm watch glass. The iodine solution is allowed to contact with the coating for 5 seconds and 10 seconds. The watch glass is then removed. The surface is dried with dry paper towel. The rating is estimated by visually inspection.

Other Stains

The test procedure for other types of stains is the same as Iodine Stain Resistance Test except that all of the stains are allowed to be in contact with the coating for 4 hours at ambient conditions covered with a 22mm by 22mm watch glass. The following stains are using for the current experiment: Black coffee, Red wine, Red Kool-Aid, Black printer ink, Red printer ink, Motor oil, Vegetable oil, Yellow mustard, and Potassium permanganate.

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 2.

Table 2 - 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%		t-BA (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%

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 2 and Figure 2.

Figure 2: COF screen

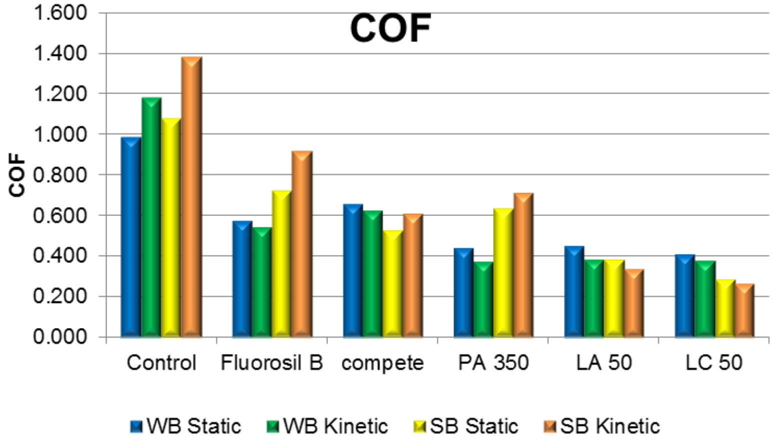
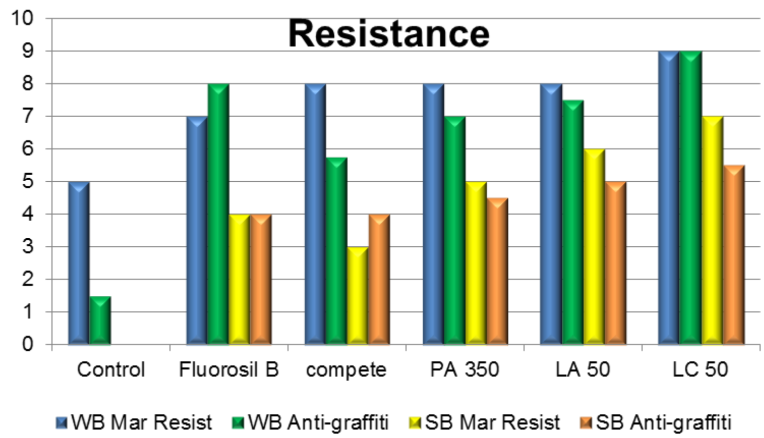


Figure 3: Resistance Screen



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 Tables 3 - 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 4 and Figure 5.

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 to each other.

Figure 4: 1% Additive COF

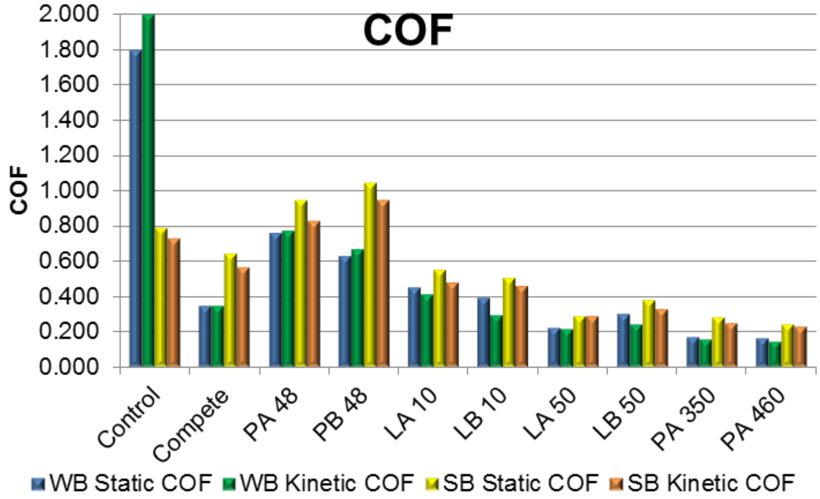
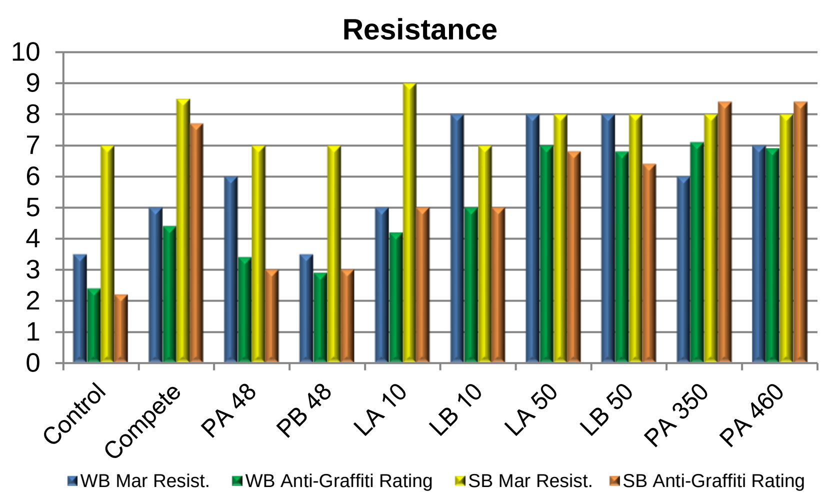


Figure 5: 1% Additive Resistance



We then examined a broader range of silicones including the newest Type C derivatives using our fluorosilicone products which have demonstrated efficacy in this area as well as the competitive silicone based anti-stain ingredient as positive controls. In these experiments we used the additives 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 6.

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 are that the linear structures outperform the pendant materials and that higher molecular weight improves performance.

Figure 6: 2% Additive Resistance

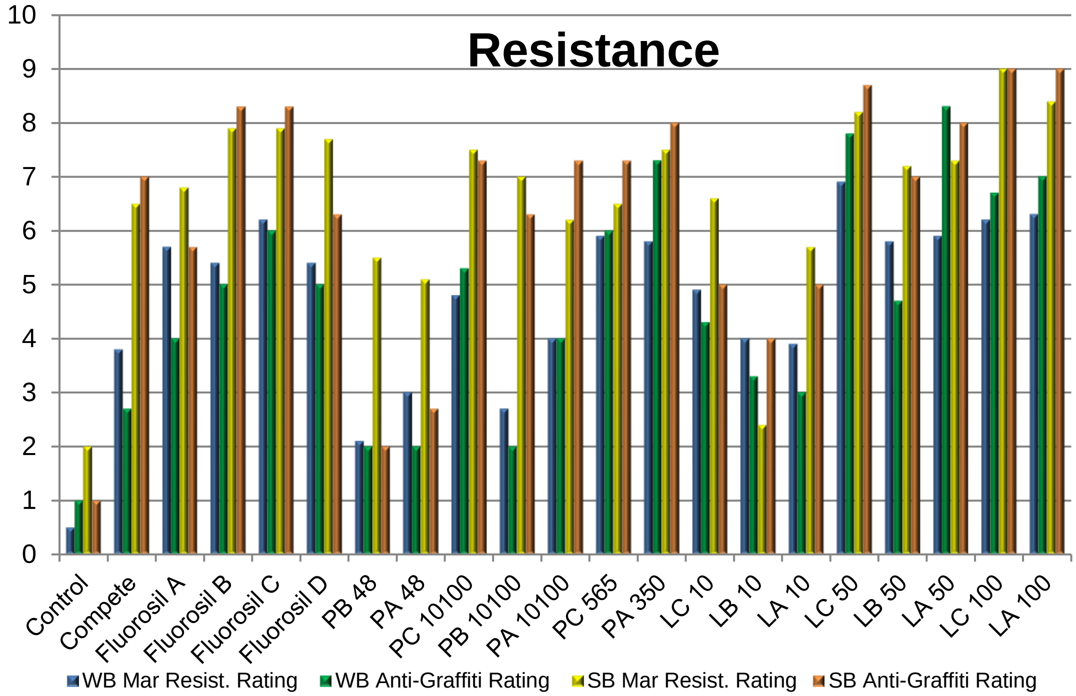


Table 3: 1% Additive WB PU

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 with nylon pad	Gloss Change 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 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	Very 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 fisheyes
PA 48	0.609	-43.5%	0.763	-44.9%	79	-26.2%	-74.1%	3	2	Blotchy 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 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

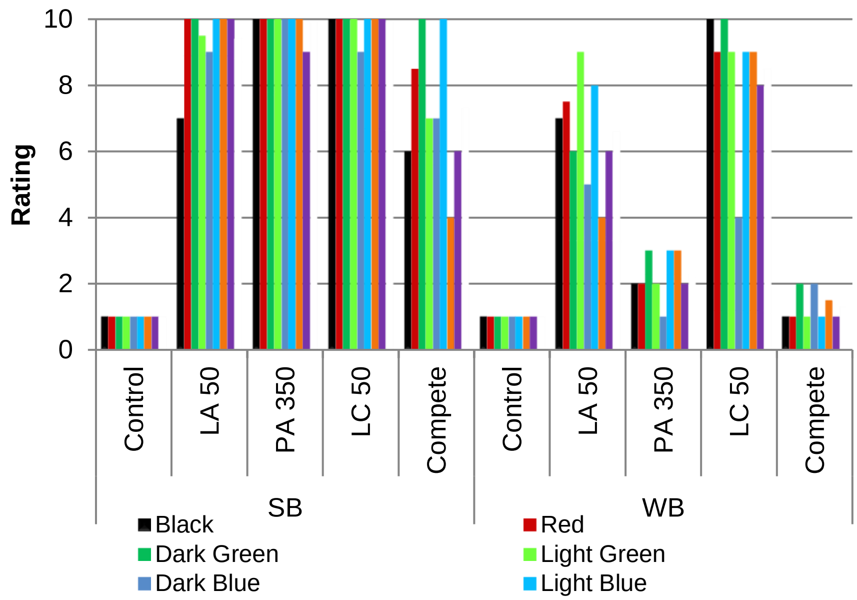
2% Additive in SB/PU	Static CoF	Change Static CoF	Kinetic CoF	Change Kinetic CoF	Initial Gloss	Gloss Change with nylon pad	Gloss Change with P1000	Mar Resist. Rating	Anti-Graffiti Rating	Coating Appearance
LC 100	0.272	-72.4%	0.230	-80.6%	120	-0.8%	-25.5%	9	9	Smooth
LA 100	0.284	-71.2%	0.230	-80.6%	122	-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

Some of the better products were subjected to more comprehensive stain resistance testing. In Table 7 and Figure 7 results are shown for three products with 10 different colored sharpie pens. In this test, dramatically improved marker release is seen for each silicone compared to the control and the competitive benchmark (especially in the WB system).

Table 7.

		Black	Red	Dark Green	Light Green	Dark Blue	Light Blue	Orange	Purple	Average Marker Removal
1% additive in SB PU	Control	1	1	1	1	1	1	1	1	1
	LA 50	7	10	10	9.5	9	10	10	10	9.4
	PA 350	10	10	10	10	10	10	10	9	9.9
	LC 50	10	10	10	10	9	10	10	10	9.9
	Fluorosil	10	10	9.5	9.5	9	10	10	9	9.6
	Compete	6	8.5	10	7	7	10	4	6	7.3
1% additive in WB PU	Control	1	1	1	1	1	1	1	1	1
	LA 50	7	7.5	6	9	5	8	4	6	6.6
	PA 350	2	2	3	2	1	3	3	2	2.3
	LC 50	10	9	10	9	4	9	9	8	8.5
	Fluorosil	1	1	1	1	1	2	1	2	1.3
	Compete	1	1	2	1	2	1	1.5	1	1.3

Figure 7. Marker Release from colored sharpie pens.



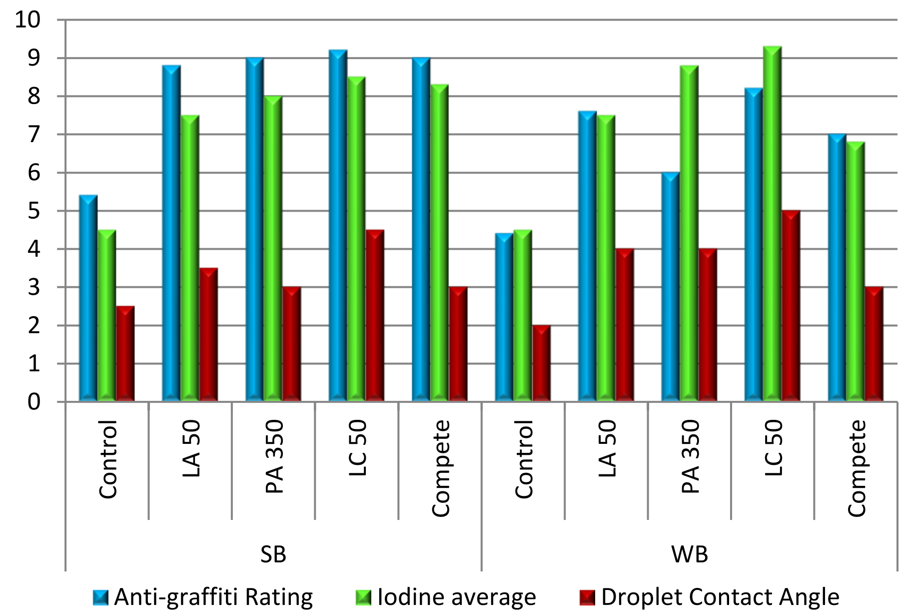
The same abbreviated series was evaluated for anti-graffiti, iodine stain resistance and contact angle. Table 8 and Figure 8 show a significant improvement especially for the LC 50 sample.

Table 8.

	Rating	Difficulty of Marker Application	Average Dry Marker Removal	Mar Resistance	Anti-graffiti	5 sec Iodine	10 sec Iodine	Average Iodine Stain	Droplet Contact Angle
1% additive in SB PU	Control	10	1	5	5.4	5	4	4.5	2.5
	LA 50	8	10	8	8.8	8	7	7.5	3.5
	PA 350	8.5	10	8	9	8.5	7.5	8	3
	LC 50	8.5	10	9	9.2	9	8	8.5	4.5
	Fluorosil	8.5	10	7	8.8	8	7.5	7.8	5
	Compete	8.5	10	8	9	8.5	8	8.3	3

1% additive in WB PU	Control	10	1	0	4.4	5	4	4.5	2
	LA 50	9	7	6	7.6	8	7	7.5	4
	PA 350	8	4.5	5	6	9	8.5	8.8	4
	LC 50	9	8	7	8.2	9.5	9	9.3	5
	Fluorosil	8	4.5	4	5.8	8.5	8	8.3	5
	Compete	9	7	3	7	7	6.5	6.8	3

Figure 8: Anti-graffiti, Iodine Resistance and Contact Angle Ratings.

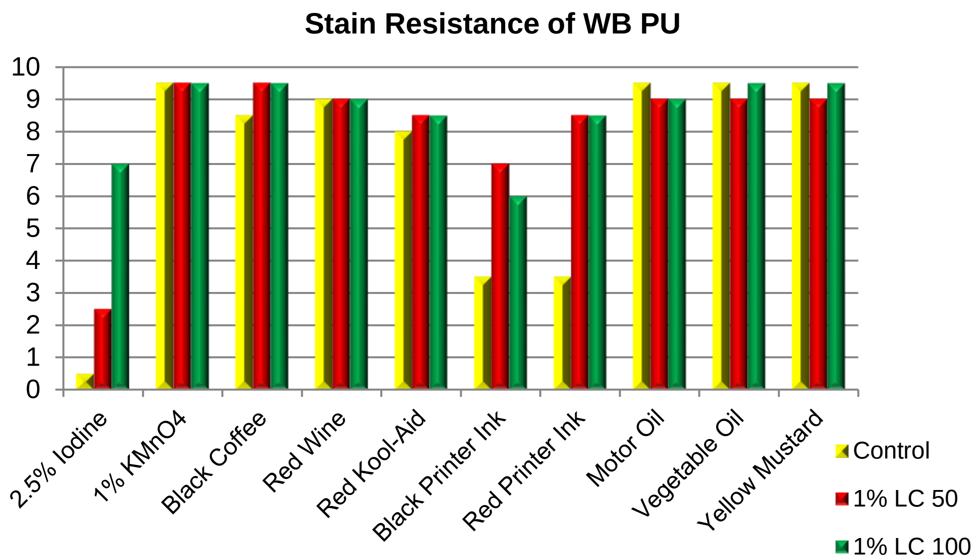


Finally, a small set of samples was evaluated for other stains. The data is shown in Table 9 and Figure 9. While many of the stains are adequately protected against by the control formulation without additives, some stains such as Iodine, $KMNO_4$, and the printer inks do show significant improvement.

Table 9: Other Stains

		Iodine	$KMnO_4$	Black Coffee	Red Wine	Red Kool-Aid	Black Printer Ink	Red Printer Ink	Motor Oil	Vegetable Oil	Yellow Mustard	Average
WBPU	Control	0.5	9.5	8.5	9	8	3.5	3.5	9.5	9.5	9.5	7.1
	1% LC 50	2.5	9.5	9.5	9	8.5	7	8.5	9	9	9	8.2
	1% LC 100	7	9.5	9.5	9	8.5	6	8.5	9	9.5	9.5	8.6
	2% LC 50	8	9.5	9.5	9	8.5	7	9	9	9.5	9.5	8.9
	2% LC 100	3	9.5	9.5	9	9	7	9	9	9.5	9.5	8.4
SBPU	Control	1.5	9.5	9	9	8	3.5	3.5	9	9	9.5	7.2
	1% LC 50	4	9.5	9.5	9	9	7	9	9	9.5	9	8.5
	1% LC 100	4	9.5	9	9	9	7	9	9	9.5	9.5	8.5
	2% LC 50	5	9.5	9.5	9	9	7	8.5	9	9.5	9	8.5
	2% LC 100	5	9.5	9.5	9	9	8.5	9.5	9	9.5	9	8.8

Figure 9: Stain Resistance in WB PU at 1% additive



Conclusion

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

Endnotes.

[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.