An Exploration of Novel and Uncommon Organosilicone Additives in Various Coatings Films.

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Introduction

At Siltech we focus on differentiation and specialization. We strive to create and apply unique silicone structures to old and new problems. In this paper we explore the properties of some of these more notable silicones. First monofunctional, reactive silicones are compared to more traditional di-functional and multi-functional analogues; secondly the effect of some small molecular weight alkylquaternary ammonium silicones are examined; and finally the characteristics of unique, non-PFOS based fluoroalkyl silicone in some standard coatings formulations are shown.

Monofunctional silicones are difficult to synthesize as acid or based-catalyzed redistribution of the Si-O-Si bonds, the standard methodology for making silicones, results in a broad distribution of polymers. While this broad distribution may average one reactive site, much of the polymer distribution will have no or many more sites.

Trisiloxane materials have been the exception to this problem, because the requisite silicone is small enough to be distilled to mono-dispersity. However, there is also a well-known kinetic process discovered in academia[1] that has been available commercially on a limited scale. The acrylated versions of these materials are used in extended wear contact lens manufacture where the free radical cascade requires monofunctional to prevent cross linking, but few other applications have been identified. In this paper we will examine a few of these for their possible uniqueness in coatings.

Quaternized aminoalkyl silicones have been available commercially. In this paper we will look at the properties of some small molecular weight commercial materials from our portfolio.

Fluoroalkyl modified silicones have been available for many years. Offering additional properties over simple polydimethylsiloxanes, these have efficacy 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[2]. 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.

Experimental and Methodology:

The functionalized silicones were evaluated in some of the following coating systems; a two part solvent borne heat cured urethane system, a UV cured acrylate system, a cationic epoxy UV formula and/or a condensation cured silicone system.

In the first study, a series of monofunctional silicones of approximately 1200 g/mol molecular weight were compared to similarly sized linear, di-functional and pendant multifunctional silicones. The functional groups of hydroxyl, acrylate and trimethyl silane were chosen to react with the polyurethane, UV cured acrylate or condensed silicone resin systems.

Table A: Functional Silicone Information

Sample name	*Functional group*	*MW*	*Type*
Silmer OH Mo-1000	Hydroxyl	1200	Monofunctional Reactive Silicone
Silmer ACR Mo-1000	Acrylate	1200	
Silmer TMS Mo-1000	Trimethoxy Silane	1200	
Silmer OH Di-10	Hydroxyl	1000	Di-functional Reactive Silicone
Silmer ACR Di-10	Acrylate	1000	
Silmer OH D2	Hydroxyl	1300	Multi-functional Reactive Silicone
Silmer ACR D2	Acrylate	1300	

In the second study, commercially available silicone alkyl quaternary ammonium salts were selected due to their small size which gives higher compatibilization, better wetting and higher charge density.[3]

Table B: Quaternary Ammonium Silicone Information

Sample name	*Surface Resistivity* Ω/sq.*	*MW*	*Type*
Silquat A0	2.88×10^{6} (Dissipative)	500	Monofunctional
Silquat Di-10	1.58×10^{7} (Dissipative)	1300	Di-functional
Silquat D2	9.40×10^{6} (Dissipative)	1900	Multi-functional

*measured on Lenetta paper deposited from IPA

In the final study, several fluoroalkyl silicone backbone materials used were modified with fluoroalkyl alone; fluoroalkyl and polyether; or fluoroalkyl and alkyl using well known hydrosilylation procedures.

The fluoroalkyl silicones designated as Fluorosil OH G2-F, Fluorosil OH E3.5-F, Fluorosil OH C7-F, Fluorosil 2010 and Fluorosil 2110 are primary hydroxyl functional and can therefore react with the PU system. The material designated as Fluorosil ACR C7-F is an acrylate ester analogue of Fluorosil OH C7-F and can therefore react into the UV cured acrylate system.

Fluorosil D2 and Fluorosil J15 additives offer a high (44%) and a low (14%) CF_2 content material for comparison but are expected to have compatibility issues.

Fluorosil 2010 and Fluorosil 2110 have low CF_2 and high organic contents so going into the study we expected them to offer little in terms of slip or mar and stain resistance. They should be compatible and offer wetting and leveling.

Fluorosil OH G2-F, Fluorosil OH E3.5-Fand Fluorosil OH C7-F series offer moderate CF_2 contents at low, medium and high silicone contents for comparison. The Fluorosil H418 brings moderate organic, silicone and fluoroalkyl contents but no reactive sites.

Table C: Fluoroalkyl Silicone Information

Sample name	*Wt % Silicone*	*Wt % Fluoroalkyl*	*Wt % Organic*	*MW*	*Type*
Fluorosil 2010	38%	7%	55%	3000	fluoroalkyl polyether silicone
Fluorosil 2110	33%	3%	64%	7000	
Fluorosil D2	56%	44%	0%	2000	fluoroalkyl silicone
Fluorosil J15	86%	14%	0%	14000	
Fluorosil OH G2-F	75%	9%	16%	3000	alkyl, fluoroalkyl silicone
Fluorosil OH E3.5-F	80%	9%	11%	3000	
Fluorosil OH C7-F	86%	9%	5%	2000	
Fluorosil ACR C7-F	86%	9%	5%	2000	
Fluorosil H418	63%	16%	21%	5000	

Procedures and Coatings Systems

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

Table D: 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	0.04-0.10%
Silicone Additive	Siltech	1.0%
n-BA		5.52%
PMA		7.27%
EEP		8.84%
Part B:		
Desmodur N-3390 BA/SN Part A/B:	Bayer	75/25

Preparation of System I: The silicone to be evaluated was added to the A side at 1% of the final weight. Parts A and B were mixed in the 75/25 ratio with minimum adjustments for each experiment noted in results. 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, B and C**, UV cured acrylate formulations were modified with various silicones at 1% use level and evaluated.

Table E: Formulation System II, a UV curable acrylate system

Component	***Supplier***	***Wt%(A)***	***Wt%(B)***	***Wt%(C)***
CN910A70 (difunctional urethane acrylate)	Sartomer	74.26%		
CN2282 (tetrafunctional polyester acrylate)	Sartomer			64.04%
Proprietary Epoxy Acrylate UV Resin Blend	Customer		66.0%	
SR 355 (TMPTA)	Sartomer	4.95%		
DPHA				12.76%
Irgacure 184	Ciba	4.95%		1.93%
Silicone Additive	Siltech	0.99%	1.0%	1.0%
Butyl Acetate		3.71%	8.25%	10.24%
Toluene		3.71%	8.25%	
Methyl Isobutyl Ketone		4.46%	9.9%	
Methyl Ethyl Ketone		2.97%	6.6%	10.24%

Preparation of System II: 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.

In **System IIIA**, a UV cured, cycloaliphatic epoxy system was used based on adding the silicone additive at 1% level into a basic starting formulation.

Table F: Formulation of UV curable cycloaliphatic epoxy system

Component	***Supplier***	***Wt%(A)***	***Wt% (B)***
UVA Cure 1500	Cytec/Allnex	75.1%	
Silmer EPC E9 as Resin	Siltech		94.5-99.3%
Silicone Additive	Siltech	1.0%	0.2-5.0%
Irgacure 150	CIBA	4.0%	
UV 9380C	Momentive		0.5%
Castor Oil		19.9%	

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.

In **System IIIB** 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 fluoroalkyl silicone (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 G: Formulations of System IIIB – Cationic UV Epoxy Silicone with various FAS additives

	Epoxy Silicone	*Catalyst*	*Fluorosil D2*	*Fluorosil OH C7-F*	*Fluorosil OH G2-F*	*Fluorosil OH E3.5-F*
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.

In **System IV**, a silanol and silicone were condensed in the presence of alkoxy silanes and the trialkoxy silane functional mono silicone. The formula is below.

Component	*Supplier*	*Wt%*
Silanol (20,000 cps)	Siltech	24.4%
Siltech F-10 (PDMS 10 cps)	Siltech	8.3%
Silmer TMS Mo-1000	Siltech	1.0%
Ethyl Triacetoxy Silane		2.5%
OS-3000 Tetra Oximino Silane	Honeywell	2.0%
Butyl Acetate		61.8%

After thorough mixing, each sample is drawn down on Leneta paper in a 1 mil thickness coating using a wirewound rod # 10. Each paper is allowed to dry at room temperature for approximately one day before testing.

Stain Resistance ASTM D3450:

For Systems I, II and IIIA: 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 I (Silicone quaternary compounds only) and System IIIB 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.

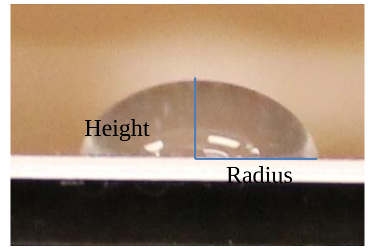
Gloss:

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).

Water Repellence



A droplet of water is placed on the coated panel. A camera is placed on the same horizon as the water droplet. A photo of the droplet is taken and enlarged. The height/radius ratio of the drop is measured and recorded. Higher ratios of height/ radius represent better water repellence and higher contact angles.

Surface Resistivity

Surface resistivity was determined on both the silicone quaternary ammonium salts and the uncured coatings systems with silicone quat included. The silicones were evaluated by wetting the surface of Leneta paper with 5% silicone quat. in IPA and then drying the paper in a 100°C oven for 15 minutes. The uncured coatings systems were done similarly with 1% silicone and the inherent solvents of the system.

Surface resistance for each panel was measured using Extech Megohmmeter. The surface resistivity was then calculated according to the following equation:

Surface resistivity (Ω/square) = (Surface Resistance * Film Width) / (Distance between Electrodes)

For surface resistivity higher than $1x10^{10}$ Ω/sq, 1000 volts was applied with the following settings: Film Width = 6.5” and Distance between Electrodes = 0.025”
For surface resistivity less than $1x10^{10}$ Ω/sq, 250 volts was applied with the following settings: Film Width = 4” and Distance between Electrodes = 5”

As per AINSI/ EIA-541 specifications[4], the classifications of surface resistivity are:

Resistivity	*EIA-541 Designation*
$<1x10^4$	Conductive
$>1x10^4$ and $<1x10^{12}$	Dissipative (Antistatic)
$>1x10^{12}$	Insulative

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 and Discussion:

Reactive Monofunctional materials

Table H: Mono, di- and Multi-functional reactive species

		control	***Mono- 1200 MW***	***Di- 1100 mw***	***Multi- 1200 mw***
System II C UV Acrylate	Gloss	132	132	132	130
	Avg. Stain Resistance*	6	8	8	7.8
	Mar Resistance	93%	93%	97%	97%
	Static COF	0.815	0.415	0.377	0.735
	Kinetic COF	0.856	0.320	0.317	0.535
	Contact Angle (H/L)	0.39	0.58	0.59	0.72
System I PU NCO/OH 1.1	Gloss	136	131	134	136
	Avg. Stain Resistance*	5.8	7.4	7.3	7
	Mar Resistance	69%	91%	84%	83%
	Static COF	0.588	0.221	0.245	0.251
	Kinetic COF	0.523	0.218	0.216	0.272
	Contact Angle (H/L)	0.59	0.74	0.75	0.69
System IV Silicone Resin	Gloss	107	107	106	104
	Avg. Stain Resistance*	7	6.9	7.3	7.8
	Mar Resistance	89%	85%	91%	90%
	Static COF	0.943	0.853	0.919	1.014
	Kinetic COF	0.843	0.807	0.827	0.835
	Contact Angle (H/L)	0.72	0.77	0.73	0.61
System I repeat SB PU NCO/OH 1.1	Gloss	134	126	134	
	Avg. Stain Resistance*	6.8	9.6	8	
	Mar Resistance	90%	97%	91%	
	Static COF	1.064	0.351	0.903	
	Kinetic COF	1.165	0.330	0.910	
	Contact Angle (H/L)	0.63	0.81	0.66	

*Blue pen ink, black marker ink, black sharpie ink, stamp ink and inkjet printer ink

None of these silicone polymer architectures was consistently or remarkably better than the others. All three materials evaluated improved the properties over the controls in the directions expected for silicone additives.

In the polyurethane (System I two experiments) the mono-OH functional is significantly better than the other two at lowering slip, increasing contact angle, mar resistance and stain resistance. There is some reduction in gloss. The di-functional material is a close second.

The silicone resin (System IV) also shows the Silmer TMS Mo-1000 is the best material for slip and water repellence but not for mar and stain resistance.

In the UV cured acrylate (System IIC), the higher number of reactive sites of the multi-functional Silmer ACR D2 gave it the best mar resistance and highest water repellence. Here the di-functional material gave the lowest slip but the mono-material was close.

We consider these very promising results for early screening of these un-optimized monofunctional reactive silicones.

Silicone Quaternary Ammonium Salts

Table I: Silicone Quaternary Ammonium Salts in System I: SB PU

	Gloss	*Static COF*	*Kinetic COF*	*Mar Resist*	*Stain Resist**	*Surface Resistivity** Ω/sq.*	*Water Resistance 5 days*	*Appearance*
Silquat A0	96	1.997	2.172	3.2	5	1.56E+10	Pass	Smooth, Glossy
Silquat D2	93	1.936	1.806	0.6	4	1.90E+10	Pass	Smooth, Pinholes
Silquat Di 10	96	1.793	1.473	2	4	5.39E+10	Pass	Smooth
Control	96	1.953	1.951	0.4	2.5	>5.20E+11	Pass	Smooth, Craters

*HB pencil, black & brown crayons, red & blue pencil crayons, and black permanent marker
**Measured on the coating containing 1% Silquat dried onto Lenetta paper.

In the polyurethane (System I) which was mixed with an NCO/OH ratio of 1.05:1, most of the Silicone quaternary ammonium materials did not provide reduction in COF. They did provide flow and leveling and conductivity lowering the resistivity down into the dissipative or antistatic range.

The Silquat A0, monofunctional trisiloxane type material, performed the best in this system and improved the flow and leveling and increased both the mar and stain resistance. The di-functional material was next best.

Table J: Silicone Quaternary Ammonium salts in System IIIA: UV cured cycloaliphatic epoxy

	Gloss	*Static COF*	*Kinetic COF*	*Mar Resist*	*Stain Resist**	*Surface Resistivity** Ω/sq.*	*Water Resist 5 days*	*Flow(mm)*	*Appearance*
Silquat A0	79	2.341	2.315	1.1	3	1.41E+11	Pass	53	Smooth
Silquat D2	55	1.964	2.409	0	2	1.24E+11	Pass	43	Orange peel
Silquat Di 10	87	2.017	2.364	3.7	5	4.27E+10	Pass	43	Smooth, few lines
Control	94	1.937	2.038	1.1	3	>5.20E+11	Pass	53	Many Craters

*HB pencil, black & brown crayons, red & blue pencil crayons, and black permanent marker
**Measured on the coating containing 1% Silquat dried onto Lenetta paper.

In the UV cured cycloaliphatic epoxy system similar performanced were seen with conductivity and flow but in this system the di-functional Silquat Di-10 may be the better choice than the mono quat.

Fluoroalkyl Silicones

Table K: Film properties of system I: 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
Fluorosil OH G2-F	1.274	1.204	120	95.0%	6.4	Fisheyes
Fluorosil OH E3.5-F	0.940	1.115	123	86.2%	4.3	Smooth
Fluorosil OH C7-F	0.794	0.756	113	87.1%	4.3	Smooth
Fluorosil ACR C7-F	0.405	0.422	107	93.1%	6.4	Fisheyes
Fluorosil 2010	0.577	0.631	130	96.7%	6.4	Smooth
Fluorosil 2110	0.681	0.711	128	96.4%	6.4	Smooth

Table L: Stain Resistance of system I: 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
Fluorosil OH G2-F	5.0	4.2	8.3	8.0	8.0	6.7
Fluorosil OH E3.5-F	5.0	5.0	4.2	10.0	9.0	6.6
Fluorosil OH C7-F	7.5	7.5	6.7	10.0	3.0	6.9
Fluorosil ACR C7-F	6.7	7.5	8.3	7.0	8.0	7.5
Fluorosil 2010	6.7	7.5	5.0	4.0	7.0	6.0
Fluorosil 2110	6.7	5.0	8.3	5.0	6.0	6.2

Table M: Film properties of System II A: 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
Fluorosil D2	54.6	4.0	6.0	0.93	0.93	4.5	Patches
Fluorosil J15	76.5	6.7	5.8	1.37	1.26	6.0	Patches
Fluorosil 2010	92.4	7.6	5.9	1.25	1.56	2.0	Smooth
Fluorosil 2110	92.9	7.6	6.8	1.31	1.34	2.0	Smooth
Fluorosil ACR C7-F	68.3	8.3	8.2	0.58	0.56	5.5	Smooth
Fluorosil H418	79.5	5.0	7.2	0.78	0.76	5.0	Wavy

Table N: Stain resistance of System IIA: UV cured 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
Fluorosil D2	4.2	3.3	3.3	5.0	5.0	3.3	4.0
Fluorosil J15	6.7	8.3	8.3	5.0	6.7	5.0	6.7
Fluorosil 2010	6.7	10.0	10.0	6.7	6.7	5.8	7.6
Fluorosil 2110	6.7	10.0	10.0	6.7	6.7	5.8	7.6
Fluorosil ACR C7-F	8.0	10.0	10.0	8.0	8.0	6.0	8.3
Fluorosil H418	5.0	5.0	5.0	5.0	5.0	5.0	5.0

Table O: Film properties of System IIB: UV cured acrylate coating with 1% Fluoroalkyl Silicone

	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
Fluorosil D2	85.5	4.2	3.5	2.32	2.06	5.5	Patches
Fluorosil H418	91.2	5.0	3.1	1.88	1.80	6.5	Matte
Fluorosil J15	90.8	6.7	3.8	1.96	1.61	6.0	Patches
Fluorosil 2010	92.7	7.6	4.8	2.08	2.33	3.5	Smooth
Fluorosil 2110	92.7	7.6	6.0	2.26	2.76	4.0	Smooth
Fluorosil ACR C7-F	88.3	8.3	8.5	0.52	0.51	7.0	Smooth

Table P: Stain resistance of System IIB: UV cured acrylate with 1% Fluoroalkyl Silicone

	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
Fluorosil D2	5.0	5.0	5.0	4.0	4.0	2.3	4.2
Fluorosil H418	6.0	5.5	5.5	5.0	5.0	3.0	5.0
Fluorosil J15	7.0	8.0	8.0	6.0	6.0	5.4	6.7
Fluorosil 2110	7.5	9.0	9.0	8.0	8.0	4.0	7.6
Fluorosil 2010	7.5	9.0	9.0	8.0	8.0	4.0	7.6
Fluorosil ACR C7-F	10.0	9.0	6.0	8.0	8.0	9.0	8.3

The Fluoroalkyl silicones improved the properties in all of the coatings systems we evaluated. Across all systems, the materials without organic modification showed incompatibility as evidenced by loss of gloss, increase in defects, and poor appearance of the cured coating.

As expected the polyether modified materials Fluorosil 2010 and Fluorosil 2110 gave the best compatibility and the unmodified fluoroalkyl silicones gave the worst compatibility. We were somewhat surprised to see such strong performance from the fluorosilicone polyether materials in slip, mar and stain resistance.

The fluoroalkyl materials were borderline compatible with compatibility decreasing from "G2" to "E3.5" to "C7" as organic content is replaced with silicone content. This is evidenced in some loss of gloss and appearance. In system I, we see these three materials all do well for slip, mar and stain resistance with the ACR version of the C7-F product being the best. We are uncertain why the ACR and OH versions of this molecule behave differently in the PU system but it is consistent and probably related to the fact that the hydroxyl but not the acrylate version should react into the film.

In the UV cured systems we screened only the acrylate of these four and it was consistently better than the other materials for slip, mar and stain resistance.

The Fluorosil H418 with a good balance of silicone, fluoroalkyl and organic content gave good performance in all systems.

Fingerprint resistance is improved most with Fluorosil J15, Fluorosil H418 and Fluorosil ACR C7-F materials.

In system IIIB we examined use level as well as additive structure evaluating four of them at 0.2-5%.

System IIIB – Cationic UV Epoxy Cured Silicone

Table Q: Film properties of System IIIB – 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
Fluorosil D2	0.2%	0.782	0.758	76.3	28.4%	2.8	2.4	Smooth
Fluorosil D2	0.5%	0.639	0.648	76.5	26.2%	2.6	2.8	Smooth
Fluorosil D2	1.0%	0.549	0.545	75.2	26.2%	2.6	3.6	Smooth
Fluorosil D2	3.0%	0.528	0.508	74.8	39.0%	3.9	4.7	Smooth
Fluorosil D2	5.0%	0.582	0.583	71.2	27.1%	2.7	6.1	Smooth
Fluorosil OH C7-F	0.2%	0.977	0.789	76.5	18.0%	1.8	2.7	Smooth
Fluorosil OH C7-F	0.5%	1.221	1.084	76.5	18.0%	1.8	2.8	Smooth
Fluorosil OH C7-F	1.0%	1.182	1.001	75.9	28.3%	2.8	4.3	Smooth
Fluorosil OH C7-F	3.0%	0.955	0.905	75.3	28.7%	2.9	5.3	Smooth
Fluorosil OH C7-F	5.0%	1.256	1.236	75.9	18.9%	1.9	5.9	Smooth
Fluorosil OH G2-F	0.2%	1.147	1.005	75.8	54.5%	5.4	2.9	Smooth
Fluorosil OH G2-F	0.5%	1.149	0.883	75.7	64.8%	6.5	3.3	Smooth
Fluorosil OH G2-F	1.0%	0.764	0.656	73.7	18.9%	1.9	4.1	Smooth
Fluorosil OH G2-F	3.0%	1.257	1.128	67.3	32.9%	3.3	4.8	Smooth
Fluorosil OH G2-F	5.0%	1.265	1.262	63.3	28.9%	2.9	6.0	Smooth
Fluorosil OH E3.5-F	0.2%	1.262	1.12	77.0	43.5%	4.4	3.1	Smooth
Fluorosil OH E3.5-F	0.5%	1.158	1.129	76.4	35.1%	3.5	3.6	Smooth
Fluorosil OH E3.5-F	1.0%	0.791	0.754	76.5	43.9%	4.4	4.4	Smooth
Fluorosil OH E3.5-F	3.0%	1.179	1.114	71.6	33.3%	3.3	5.3	Smooth
Fluorosil OH E3.5-F	5.0%	1.215	1.093	69.2	25.7%	2.6	5.8	Smooth

Table R: 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
Fluorosil D2	0.2%	6.5	6	2.5	5.5	2	2	1.5	2	2
Fluorosil D2	0.5%	10	6	2.5	6.5	2	2	1.5	2.5	2.5
Fluorosil D2	1.0%	10	4.5	3	6.5	3	3.5	3.5	2.5	2.5
Fluorosil D2	3.0%	10	5.5	3	7.5	3.5	4.5	6	3	3.5
Fluorosil D2	5.0%	10	5.5	2.5	9	4.5	5.5	6	5.5	6
Fluorosil OH C7-F	0.2%	4.5	6	3	6	2	2	2	2	2
Fluorosil OH C7-F	0.5%	6.5	5.5	3	6	2	2.5	2	2	2.5
Fluorosil OH C7-F	1.0%	7.5	6	2.5	6	4.5	2.5	4	3.5	5
Fluorosil OH C7-F	3.0%	7.5	5	2	7.5	4.5	5.5	5	4	5
Fluorosil OH C7-F	5.0%	7.5	6	2.5	7.5	6.5	5	5	5.5	6
Fluorosil OH G2-F	0.2%	6.5	6	3	6.5	2.5	3	2.5	2	1.5
Fluorosil OH G2-F	0.5%	6	6	3	6.5	4.5	3	2.5	2	1.5
Fluorosil OH G2-F	1.0%	6.5	6	2.5	6.5	4.5	4	3.5	3	3
Fluorosil OH G2-F	3.0%	7	6	3	6.5	6	4.5	5	3.5	3
Fluorosil OH G2-F	5.0%	8	5	3.5	6.5	7.5	5.5	5.5	5.5	5.5
Fluorosil OH E3.5-F	0.2%	7.5	6.5	3	6	3.5	3	2.5	2	2
Fluorosil OH E3.5-F	0.5%	7.5	6.5	2.5	6.5	4.5	3.5	3	2	2
Fluorosil OH E3.5-F	1.0%	7	6	3	6.5	4.5	3.5	3	4	5
Fluorosil OH E3.5-F	3.0%	7	5.5	4.5	7.5	4.5	5	4	5.5	5
Fluorosil OH E3.5-F	5.0%	7	5.5	4.5	8	5.5	5	5	5.5	5.5

Summary of System IIIB - UV Epoxy Silicone – Silmer EPC E9:

All tested Fluoroalkyl silicones are compatible with the silicone epoxy resin. In all cases, 60° gloss is only slightly reduced and no surface defects are seen. Increasing the use level of fluoroalkyl silicone does lower the gloss indicating the compatibility isn't complete.

Stain resistance in all cases improved as use levels increased.

Improved mar resistance is seen for all of the materials evaluated. This mar resistance improvement is seen at the lowest use levels, improves and plateaus usually barely improved or somewhat lost at the highest use levels. We have seen this concentration behavior before.[5]

Only the high CF_2 content Fluorosil D2 shows the dramatic lowering of COF that one usually sees with silicone or fluoroalkyl additives. That is because the silicone resin itself has a low COF and the fluoro content is needed to decrease it.

We are very excited about the high level of performance of these reactive, low fluoroalkyl content fluoroalkyl silicones. The low CF_2 content needed allows us to keep prices low.

These unique silicones are showing a great deal of promise, but more understanding and testing is needed.

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