A NEW TIN-FREE SILICONE GUM DISPERSION FOR USE AS A HIGH SLIP AGENT FOR COATINGS AND LEATHER

Tom Seung-Tong Cheung, Bo Qi, <u>Bob Ruckle</u>
Siltech Corp
Toronto, ON M4H 1G5



Why do this work?

- Silicone Gum Dispersions are used extensively for stain, mar resistance, feel, slip and COF reduction in leather treatments and coatings.
- These materials are hard to stabilize and manufacture.
- In-situ increase of the silicone MW with tinbased condensation catalysts is the norm.
- Regulatory and market forces make Tin unusable in new products
- Solvents in COMP



Experimental

The experimental additives were screened at 0.5% or 1.25% in

- Solvent based acrylic clear coating
- Acrylic latex paint
- 2K Waterborne polyurethane clear coating
- 1K Waterborne polyurethane coating
- 2K Solventborne polyurethane clear coating
- 1K Solventborne polyurethane coating
- WB HG Black Enamel
- SB HG Black Enamel



Experimental

Developmental additives started from 40A, our best offering at the time. (Tin catalyzed)

Variations included silicone oil MW, dispersants, silica and condensation catalyst.

Two control experiments were conducted in each case.

- Comparable use level of the commercially available competitive product labeled COMP.
- No additive labeled CONTROL.



Test Panel

- For most, 1 ml coating liquid was drawn on a 4"
 x 6.5" Leneta paper with wire-wound rod #30.
 The films are dried at ambient for 4 days.
- For 1K waterborne polyurethane coating, wirewound rod #5 is used to cast about 0.5 mil wet liquid on Leneta paper.
- The wet film prepared with 2K waterborne polyurethane clear coating is dried in a 110°C oven for 30 minutes or in an 80°C oven for 60 minutes.

Mar Resistance

Mar resistance is measured using a Sutherland 2000 Ink Rub Tester. We used the Dry Rub method with the following settings: 100 to 500 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 panels are rated based on percentage change in gloss reading before and after the rubbing test. Rating 10 is the best; 0 is the worst.



Slip

Slip or Coefficient of Friction (COF) 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 and Kinetic coefficients of friction are obtained directly from the equipment

The greater the value, the higher the friction is for the substrate.





Initial WB Acrylic

		WB Acrylic						
	40A COMP CONTROL							
Static COF	3.135	3.218	3.637					
Kinetic COF	0.931	0.977	1.480					
Gloss Before	46.2	42.2	47.1					
Gloss After	43.1	39.2	10.6					
% Change	-6.7%	-7.0%	-77.5%					
Surface Appearance	Many craters	Many craters	Smooth					

Initial SB Acrylic

	SB Acrylic								
	40A	40A COMP CONTROL							
Static COF	0.650	0.691	1.389						
Kinetic COF	0.437	0.320	1.262						
Gloss Before	72.9	76.2	84.9						
Gloss After	65.6	64.4	18.4						
% Change	-10.1%	-15.4%	-78.4%						
Surface Appearance	Mild wave	Smooth							

Initial WB PU 1K

	WB/PU-1K							
	40A COMP CONTROL							
Static COF	0.631	0.695	0.922					
Kinetic COF	0.328	0.372	0.648					
Gloss Before	14.4	14.5	15.0					
Gloss After	13.9	14.0	14.3					
% Change	-3.6%	-3.2%	-4.7%					
Surface Appearance	5 craters	Smooth	Smooth					

Initial WB PU 2K

		WB/PU-2K				
	40A	40A COMP				
Static COF	0.801	0.723	1.372			
Kinetic COF	0.638	0.401	1.925			
Gloss Before	22.8	39.4	90.8			
Gloss After	21.5	35.9	69.7			
% Change	-5.7%	-8.8%	-23.2%			
Surface	Orange	Orange	Some			
Appearance	peel Many	•				
	craters	peel	craters			

40 A,B,C

 40A performance is similar to COMP, but less compatible in some formulations.

Next variations:

- A,B,C dispersed with organic surfactants
- A,B silicone phase is high viscosity fluid
- C silicone phase contains silicone gum



WB Acrylic

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
<u>ပ</u>	40B	0.696	0.644	5.0	5.1	1.0%	Droplets
	40C	0.741	0.645	4.5	5.3	16.2%	Droplets
Acı	40A	0.812	0.659	5.2	5.6	9.0%	Droplets
B	COMP	0.810	0.706	5.6	5.8	4.8%	Smooth
_	CONTROL	0.791	0.754	4.6	4.5	-2.5%	Smooth



SB Acrylic

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
ပ	40B	0.658	0.413	34.9	20.0	-42.8%	Smooth
\ <u>\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\</u>	40C	0.713	0.300	33.4	21.3	-36.0%	Smooth
	40A	0.506	0.320	30.0	17.2	-42.7%	Smooth
m	COMP	0.576	0.390	34.6	23.4	-32.5%	Smooth
S	CONTROL	1.020	0.883	31.2	4.4	-85.8%	Smooth



WB PU 1K

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
Y	40B	0.526	0.363	20.2	19.1	-5.4%	Smooth
1-1	40C	0.450	0.261	20.2	18.8	-6.8%	Smooth
WB/PU	40A	0.408	0.271	20.6	19.2	-6.6%	Smooth
VB/	COMP	0.450	0.308	19.5	18.1	-7.3%	Smooth
 	CONTROL	0.538	0.391	19.5	18.0	-7.5%	Smooth



SB PU 1K

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
	40B	0.747	0.510	16.3	15.1	-7.4%	Smooth
SB/PU	40C	0.817	0.421	19.8	19.7	-0.6%	Smooth
3B/	40A	0.782	0.477	19.1	19.0	-0.1%	Smooth
×	COMP	0.694	0.323	18.3	18.3	-0.1%	Smooth
_	CONTROL	1.012	1.218	18.7	15.4	-17.5%	Smooth



WB PU 2K

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
	40B	0.452	0.485	77.8	73.0	-6.2%	Lots of
							craters
	40C	0.369	0.295	65.9	59.2	-10.3%	Lots of
2K							craters
WB/PU-2K	40A	0.347	0.265	86.9	78.7	-9.5%	Few
3/F							craters
\$	COMP	0.343	0.193	69.2	61.8	-10.7%	Smooth,
							no crater
	CONTROL	1.227	1.609	91.9	81.0	-12.0%	Smooth,
							no crater

SB PU 2K

	Sample	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Delta	Surface Appear- ance
	40B	0.389	0.314	37.5	31.8	-15.2%	Orange peel
X	40C	0.265	0.184	66.0	56.2	-14.8%	Orange peel
SB/PU-2K	40A	0.255	0.194	55.9	47.8	-14.5%	Orange peel
SE	COMP	0.264	0.165	66.9	58.3	-12.9%	Rough surface
	CONTROL	1.198	1.527	98.5	81.3	-17.4%	Few craters

40 D-F

- 40A,B,C not compatible enough
- 40A,C close in performance
- 40B not performing

Next Variations:

- 40 D–F silicone phase is high viscosity
- Silicone polyether emulsifier
- 40F has silica added



WB Acrylic

	Sample	Static	Kinetic	%	Mar	Stain	Surface
		COF	COF	Gloss	Resist	Resist	Appear-
				Delta			ance
ပ	40D	0.253	0.168	-27.4%	1.9	6.5	Droplets
Acrylic	40E	0.263	0.167	-27.6%	1.9	5.5	Droplets
Ac	40F	0.273	0.173	-25.8%	2.5	7.5	Droplets
WB	COMP	0.533	0.292	-26.4%	2.3	5	Smooth
>	CONTROL	0.543	0.357	-28.8%	1.4	1.5	Smooth



SB Acrylic

	Sample	Static COF	Kinetic COF	% Gloss Delta	Mar Resist	Stain Resist	Surface Appear- ance
O	40D	0.335	0.184	-27.1%	2.0	6.5	Smooth
∑	40E	0.319	0.186	-18.7%	5.1	7	Smooth
Acrylic	40F	0.340	0.180	-20.0%	4.6	5.5	Smooth
SB	COMP	0.431	0.194	-17.9%	5.4	7.5	Smooth
	CONTROL	0.673	0.763	-32.8%	0.0	1.5	Smooth



WP PU 1K

	Sample	Static COF	Kinetic COF	% Gloss Delta	Mar Resist	Stain Resist	Surface Appear- ance
	40D	0.298	0.167	-10.8%	8.0	6.5	Droplets
PU	40E	0.304	0.148	-12.7%	7.3	5.5	Droplets
左	40F	0.260	0.152	-10.2%	8.2	7.5	Droplets
WB	COMP	0.381	0.205	-11.8%	7.6	5	Smooth
>	CONTROL	0.641	0.435	-14.7%	6.6	1.5	Smooth



SB PU 1K

	Sample	Static COF	Kinetic COF	% Gloss Delta	Mar Resist	Stain Resist	Surface Appear- ance
	40D	0.532	0.248	-27.5%	1.9	5.5	Smooth
P	40E	0.610	0.258	-23.6%	3.3	5.5	Smooth
大	40F	0.666	0.253	-17.6%	5.5	6.5	Smooth
SB	COMP	0.677	0.335	-18.8%	5.1	6.5	Smooth
	CONTROL	1.014	0.845	-28.4%	1.6	1.5	Smooth



40 G-J

 40D-F are performing better and have better compatibility

Next Variations:

- G-J silicone phase is a mix of high viscosity fluid and gum, with silicone and organic emulsification
- 40I added film former
- 40J added film former and silica



WB Acrylic

	Sample	Static	Kinetic	% Gloss	Mar	Surface
	Sample	COF	COF	Delta	Resist.	Appearance
	40G	0.854	0.322	-14.5%	3.2	Smooth
Acrylic	40H	0.899	0.314	-15.0%	2.8	Smooth
CL	40 l	0.889	0.326	-13.8%	3.5	Smooth
M W	40J	0.784	0.304	-14.6%	3.1	Smooth
WB	COMP	0.900	0.383	-13.2%	3.9	Smooth
	CONTROL	0.922	0.590	-15.1%	2.8	Smooth



SB Acrylic

	Sample	Static COF	Kinetic COF	% Gloss Delta	Mar Resist.	Surface Appear- ance
	40G	0.791	0.313	-12.1%	4.6	Smooth
0	40H	0.669	0.282	-13.8%	3.6	Smooth
ylic	401	0.641	0.279	-10.2%	5.7	Smooth
Acr	40J	0.714	0.294	-10.6%	5.5	Smooth
SB Acrylic	COMP	0.592	0.242	-10.8%	5.4	Minor Lines
	CONTROL	0.994	0.752	-19.6%	0	Smooth



WB PU 1K

	Sample	Static	Kinetic	Gloss	% Gloss	Mar	Surface
	Sample	COF	COF	Before	Delta	Resist.	Appearance
	40G	0.686	0.304	19.0	-8.8%	6.6	Minor Lines
PU	40H	0.650	0.293	18.5	-7.8%	7.2	Smooth
	40 l	0.729	0.324	20.0	-6.8%	7.8	Minor Lines
WB	40J	0.649	0.283	19.2	-7.7%	7.3	Smooth
关	COMP	0.765	0.312	17.1	-8.7%	6.7	Craters
	CONTROL	0.948	0.678	20.8	-9.1%	6.4	Smooth



SB PU 1K

	Sampla	Static	Kinetic	% Gloss	Mar	Surface
	Sample	COF	COF	Delta	Resist.	Appearance
	40G	1.396	0.371	-4.9%	9	Mild Wave
PU	40H	1.355	0.364	-4.9%	9	Smooth
SB F	40 l	1.228	0.362	-8.7%	6.7	Smooth
	40J	1.063	0.355	-4.2%	9.4	Smooth
7	COMP	1.266	0.393	-9.1%	6.5	Smooth
	CONTROL	1.427	0.653	-9.3%	6.3	Smooth



WB PU 2K

	Sample	Static	Kinetic	Gloss	% Gloss	Mar	Surface
	Sample	COF	COF	Before	Delta	Resist.	Appearance
	40G	1.182	1.249	85.4	-8.4%	6.9	Few Craters
	40H	1.293	1.420	86.5	-7.5%	7.4	Few Craters
	40I	1.390	1.390 1.353 88.1 -8.6% 6.7	6.7	Few Craters,		
PU		1.390	1.333	00.1	-0.0%	0.7	Mild Wave
2K WB	40J	1.209	1.202	86.4	-8.7%	6.7	Few Craters,
X	403	1.209	1.202	00.4	-0.7%	0.7	Mild Wave
~		1 222	0.704	70.6	G 10/	0.2	Few Craters,
	COMP	1.332	0.784	79.6	-6.1%	8.3	Mild Wave
	CONTROL	2.669	2.894	90.3	-13.3%	3.9	Few Craters



SB PU 2K

	Sample	Static COF	Kinetic COF	Gloss Before	% Gloss Delta	Mar Resist.	Surface Appearance
	40G	1.361	1.343	94.8	-10.1%	5.8	Craters
P	40H	1.437	1.278	93.2	-11.2%	5.2	Craters
	40I	1.302	1.181	86.9	-14.5%	3.1	Craters
SB	40J	1.203	1.021	90.4	-12.8%	4.2	Craters
2K	COMP	0.926	0.840	90.3	-9.0%	6.5	Wave
	CONTROL	2.853	2.751	96.5	-10.2%	5.7	Few Craters



35A, 45 A,B

- 40G-J weaker performance
- 40C,D, E are the best options

Final Variations:

- No Tin, silicone gum, mixed dispersant
- 35A minimal dispersant
- 45 A,B contain more dispersant
- 45A doesn't have preservative, 45B does.



SB HG Enamel

		Sample	Static COF	Kinetic COF	Mar Resist	Appearance
		35 A	1.198	0.355	7	Good leveling. No fish eyes.
Black	<u>a</u>	45 A	1.323	0.368	7	Good leveling. No fish eyes.
1	name	45 B	1.520	0.337	7	Good leveling. No fish eyes.
SB HG	Ш	COMP	1.733	0.449	7.5	Fair leveling. No fish eyes.
		CONTROL	1.960	0.438	4	Poor leveling. No fish eyes.



WB HG Enamel

	Sample	Static COF	Kinetic COF	Mar Resist	Appearance
	35 A	1.994	0.450	7.5	Good leveling. No fish eyes.
Black	45 A	1.731	0.468	7.5	Good leveling. No fish eyes.
1 4 - 3	45 B	1.748	0.461	7.5	Good leveling. No fish eyes.
WB	COMP	1.733	0.445	7	Good leveling. No fish eyes.
	CONTROL	1.862	0.890	3	Good leveling. No fish eyes.



WB PU 1K

	Sample	Static COF	Kinetic COF	Mar Resist	Appearance
	45 B	0.463	0.282	7	Good leveling. No fish eyes.
B PU	45 A	0.526	0.300	7	Good leveling. No fish eyes.
1K WB	COMP	0.385	0.300	7	Good leveling. No fish eyes.
_=	CONTROL	1.353	1.684	4	Good leveling. No fish eyes.



Conclusion

- We found it was straightforward to match the performance properties.
- The rub was to improve waterborne compatibility, which we accomplished by altering the dispersion packages.
- We found superior performance to the COMP product without Tin or solvents.



