A New Tin-Free Silicone Gum Dispersion for use as a High Slip Agent for Coatings and Leather

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Abstract

The market, especially the European market, has developed a tin-sensitivity. In this paper we report the development of a tin-free aqueous silicone gum dispersion from early tin-based compositions. This class of additive has historically been very difficult to manufacture especially without the tin condensation catalysts. These new compositions will be compared in several formulations against each other and the industry standard for their ability to reduce COF, provide slip and mar resistance while maintaining coating properties.

Introduction

These high molecular weight silicone dispersions are used in many coatings and leather treatment formulations to provide slip and mar and stain resistance. The standard process, which includes catalysis with tin, is under strong regulatory pressure especially in the EU due to toxicity concerns of the residual tin compounds.

Variations in formulation and processing the high molecular weight silicone oil and silicone gum dispersions are evaluated against the commercially available product with the goal of achieving comparable or improved slip, dispersibility and stability.

Experimental

The experimental additives were screened at 0.5% or 1.25% in a variety of waterborne and solvent borne formulations. The details of these formulations are shown in the formulations section at the end of the paper. In examples 35 A, 45 A and 45 B, the formulations labeled SB and WB HG enamels are proprietary formulations.

Two control experiments were conducted in each case. The first is a comparable use level of the commercially available competitive product labeled COMP and the second is no additive labeled CONTROL.

Variations in the silicone dispersions are shown as 40 A-F which are variations on one tin-catalyzed base formulation which uses a high MW silicone. Formulations 40 G-J are variations on a second base formulation which differs in the inclusion of higher MW silicone.

Finally, the best results are obtained with 35 A and 45 A-B which are dispersions of a silicone gum with minor changes in the three formulations.

Test Panel Preparation

For the solvent based acrylic clear coating, acrylic latex paint and 2K waterborne polyurethane clear coating, all tested panels are prepared by drawing down approximate 1 ml coating liquid on a 4" X 6.5" Leneta paper with wire-wound rod #30. The wet films are allowed to dry at ambient conditions for at least four days, except where otherwise noted.

For 1K waterborne polyurethane coating, wire-wound 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 Test

Mar resistance is measured using a Sutherland 2000 Ink Rub Tester. We used the 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 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.

In the case of samples 35 A, 45 A and 45 B, shown in Table 5, 300 rubs were used to increase the stress of the test.

Coefficient of Friction

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 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.

Results

With the initial formulation (Table 1), we find the performance of our first sample, labeled 40 A, to be as good or better than COMP in terms of gloss retention and COF reduction. However compatibility in WB formulations is not nearly as good as evidenced by the surface appearance. Further work focused on improving the dispersibility with particle size and stabilizer packages.

Table 1. Sample 40 A

	SB Acrylic			WB Acrylic			WB/PU-1K			WB/PU-2K		
	40A	COMP	CONTROL	40A	COMP	CONTROL	40A	COMP	CONTROL	40A	COMP	CONTROL
Static COF	0.650	0.691	1.389	3.135	3.218	3.637	0.631	0.695	0.922	0.801	0.723	1.372
Kinetic COF	0.437	0.320	1.262	0.931	0.977	1.480	0.328	0.372	0.648	0.638	0.401	1.925
Gloss Before	72.9	76.2	84.9	46.2	42.2	47.1	14.4	14.5	15.0	22.8	39.4	90.8
Gloss After	65.6	64.4	18.4	43.1	39.2	10.6	13.9	14.0	14.3	21.5	35.9	69.7
% Change	-10.1%	-15.4%	-78.4%	-6.7%	-7.0%	-77.5%	-3.6%	-3.2%	-4.7%	-5.7%	-8.8%	-23.2%
Surface Appearance	Mild wave	Wave pattern	Smooth	Many craters	Many craters	Smooth	5 craters	Smooth	Smooth	Orange peel Many craters	Orange peel	Some craters

In the first variations, shown in Table 2, we see a similar result where physical properties are acceptable for 40 A and 40 C, but compatibility is not acceptable in any of the three variants. In fact the deviations from 40 A to 40 B to 40 C result in worse performance.

Table 2. Samples 40 A-C

	40 A-C	Static COF	Kinetic COF	Gloss Before	Gloss After	% Gloss Change	Surface Appearance
WB/PU-2K	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 craters
	40A	0.347	0.265	86.9	78.7	-9.5%	Few 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	40B	0.389	0.314	37.5	31.8	-15.2%	Orange peel
	40C	0.265	0.184	66.0	56.2	-14.8%	Orange peel
	40A	0.255	0.194	55.9	47.8	-14.5%	Orange peel
	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
WB/PU-1K	40B	0.526	0.363	20.2	19.1	-5.4%	Smooth
	40C	0.450	0.261	20.2	18.8	-6.8%	Smooth
	40A	0.408	0.271	20.6	19.2	-6.6%	Smooth
	COMP	0.450	0.308	19.5	18.1	-7.3%	Smooth
	CONTROL	0.538	0.391	19.5	18.0	-7.5%	Smooth
1K SB/PU	40B	0.747	0.510	16.3	15.1	-7.4%	Smooth
	40C	0.817	0.421	19.8	19.7	-0.6%	Smooth
	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 Acrylic	40B	0.696	0.644	5.0	5.1	1.0%	Droplets
	40C	0.741	0.645	4.5	5.3	16.2%	Droplets
	40A	0.812	0.659	5.2	5.6	9.0%	Droplets
	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	40B	0.658	0.413	34.9	20.0	-42.8%	Smooth
	40C	0.713	0.300	33.4	21.3	-36.0%	Smooth
	40A	0.506	0.320	30.0	17.2	-42.7%	Smooth
	COMP	0.576	0.390	34.6	23.4	-32.5%	Smooth
	CONTROL	1.020	0.883	31.2	4.4	-85.8%	Smooth

In this next set of variations, seen in Table 3, 40 D, 40 E and 40 F show at least comparable and often better performance compared to the competitive offering. These samples are also much closer in compatibility in most formulations. However, significant differences in appearance are still seen in the 2K PU formulations.

Table 3. Samples 40 D-F

	40 D-F	**Static COF**	**Kinetic COF**	**Gloss Before**	**Gloss After**	**% Change**	**Mar Resist**	**Stain Resist**	**Surface Appearance**
WB Acrylic	40D	0.253	0.168	15.9	11.6	-27.4%	1.9	6.5	Droplets
	40E	0.263	0.167	14.5	10.5	-27.6%	1.9	5.5	Droplets
	40F	0.273	0.173	13.8	10.2	-25.8%	2.5	7.5	Droplets
	COMP	0.533	0.292	15.1	11.1	-26.4%	2.3	5	Smooth
	CONTROL	0.543	0.357	14.4	10.3	-28.8%	1.4	1.5	Smooth
WB 1K PU	40D	0.298	0.167	19.7	17.6	-10.8%	8.0	6.5	Droplets
	40E	0.304	0.148	22.5	19.6	-12.7%	7.3	5.5	Droplets
	40F	0.260	0.152	21.8	19.5	-10.2%	8.2	7.5	Droplets
	COMP	0.381	0.205	19.6	17.3	-11.8%	7.6	5	Smooth
	CONTROL	0.641	0.435	20.9	17.8	-14.7%	6.6	1.5	Smooth
SB Acrylic	40D	0.335	0.184	29.8	21.7	-27.1%	2.0	6.5	Smooth
	40E	0.319	0.186	29.7	24.2	-18.7%	5.1	7	Smooth
	40F	0.340	0.180	30.9	24.7	-20.0%	4.6	5.5	Smooth
	COMP	0.431	0.194	29.0	23.8	-17.9%	5.4	7.5	Smooth
	CONTROL	0.673	0.763	31.0	20.9	-32.8%	0.0	1.5	Smooth
SB 1K PU	40D	0.532	0.248	14.8	10.7	-27.5%	1.9	5.5	Smooth
	40E	0.610	0.258	13.7	10.5	-23.6%	3.3	5.5	Smooth
	40F	0.666	0.253	14.0	11.5	-17.6%	5.5	6.5	Smooth
	COMP	0.677	0.335	15.3	12.4	-18.8%	5.1	6.5	Smooth
	CONTROL	1.014	0.845	14.3	10.2	-28.4%	1.6	1.5	Smooth

In this series of 40 G-J, Table 4, we again see the now familiar pattern. Physical properties are very similar and these variants are very close in compatibility.

Table 4. Samples 40 G-J

	40 G-J	Static COF	Kinetic COF	Gloss Before	% Change	Mar Resist.	Surface Appearance
WB Acrylic	CONTROL	0.922	0.590	14.3	-15.1%	2.8	Smooth
	40G	0.854	0.322	14.3	-14.5%	3.2	Smooth
	40H	0.899	0.314	15.1	-15.0%	2.8	Smooth
	40I	0.889	0.326	14.9	-13.8%	3.5	Smooth
	40J	0.784	0.304	14.8	-14.6%	3.1	Smooth
	COMP	0.900	0.383	14.5	-13.2%	3.9	Smooth
SB Acrylic	CONTROL	0.994	0.752	20.3	-19.6%	0	Smooth
	40G	0.791	0.313	21.5	-12.1%	4.6	Smooth
	40H	0.669	0.282	18.4	-13.8%	3.6	Smooth
	40I	0.641	0.279	18.6	-10.2%	5.7	Smooth
	40J	0.714	0.294	19.3	-10.6%	5.5	Smooth
	COMP	0.592	0.242	18.3	-10.8%	5.4	Minor Lines

1K WB PU	CONTROL	0.948	0.678	20.8	-9.1%	6.4	Smooth
	40G	0.686	0.304	19.0	-8.8%	6.6	Minor Lines
	40H	0.650	0.293	18.5	-7.8%	7.2	Smooth
	40I	0.729	0.324	20.0	-6.8%	7.8	Minor Lines
	40J	0.649	0.283	19.2	-7.7%	7.3	Smooth
	COMP	0.765	0.312	17.1	-8.7%	6.7	Craters
1K SB PU	CONTROL	1.427	0.653	13.7	-9.3%	6.3	Smooth
	40G	1.396	0.371	13.2	-4.9%	9	Mild Wave
	40H	1.355	0.364	13.6	-4.9%	9	Smooth
	40I	1.228	0.362	14.3	-8.7%	6.7	Smooth
	40J	1.063	0.355	13.5	-4.2%	9.4	Smooth
	COMP	1.266	0.393	14.9	-9.1%	6.5	Smooth
2K WB PU	CONTROL	2.669	2.894	90.3	-13.3%	3.9	Few Craters
	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	1.353	88.1	-8.6%	6.7	Few Craters, Mild Wave
	40J	1.209	1.202	86.4	-8.7%	6.7	Few Craters, Mild Wave
	COMP	1.332	0.784	79.6	-6.1%	8.3	Few Craters, Mild Wave
2K SB PU	CONTROL	2.853	2.751	96.5	-10.2%	5.7	Few Craters
	40G	1.361	1.343	94.8	-10.1%	5.8	Craters
	40H	1.437	1.278	93.2	-11.2%	5.2	Craters
	40I	1.302	1.181	86.9	-14.5%	3.1	Craters
	40J	1.203	1.021	90.4	-12.8%	4.2	Craters
	COMP	0.926	0.840	90.3	-9.0%	6.5	Wave

In the final series, seen in Table 5, Samples 35 A, 45 A and 45 B are shown. These use an ultra-high molecular weight silicone gum and no tin catalyst with unique dispersing packages. The two samples denoted 45 A and 45 B show especially good compatibility as indicated by leveling and lack of defects even over the competitive material in the SB test. Kinetic COF is as low as the samples labeled COMP.

Table 5. Samples 35 A and 45 A-B

	35 A, 45 A,B	Static COF	Kinetic COF	Mar Resist	Appearance
SB HG Black Enamel	CONTROL	0.960	0.438	4	Poor leveling. No fish eyes.
	COMP	1.733	0.449	7.5	Fair leveling. No fish eyes.
	35 A	1.198	0.355	7	Good leveling. No fish eyes.
	45 A	1.323	0.368	7	Good leveling. No fish eyes.
	45 B	1.520	0.337	7	Good leveling. No fish eyes.
WB HG Black Enamel	CONTROL	1.862	0.890	3	Good leveling. No fish eyes.
	COMP	1.733	0.445	7	Good leveling. No fish eyes.
	35 A	1.994	0.450	7.5	Good leveling. No fish eyes.
	45 A	1.731	0.468	7.5	Good leveling. No fish eyes.
	45 B	1.748	0.461	7.5	Good leveling. No fish eyes.
1K WB PU	Control	1.353	1.684	4	Good leveling. No fish eyes.
	COMP	0.385	0.300	7	Good leveling. No fish eyes.
	45 B	0.463	0.282	7	Good leveling. No fish eyes.
	45 A	0.526	0.300	7	Good leveling. No fish eyes.

Conclusion

As we progressed from the earliest structural variation we found it was straightforward to match the COF reduction and performance properties of the commercial silicone gum dispersions. Even compatibility in SB formulations was good in the early samples.

The trick was to improve waterborne compatibility, which we eventually accomplished primarily by altering the dispersion packages. In doing so, we found comparable or in some formulations superior performance to the target product.

Formulations

WB 1K PU	Supplier	%
Solucote 1011	Soluol	80%
Water	N/A	12%
Emulsion 32535	Michem	5%
Emulsion 43040	Michem	3%
Silsurf A208	Siltech	1%

SB 1K PU	Supplier	%
Solucote 8980	Soluol	58.34%
Toluene	N/A	23.12%
Isopropanol	N/A	5.37%
MEK	BDH	13.16%

WB 2K PU	Supplier	%
Part A		
Bayhydrol A145	Bayer	47.1%
Borchigel PW25	Lanxess	0.2%
Surfynol 104 DPM	Air Products	1.1%
De-ionized Water		20.1%
Part B		
Bayhydur 302	Bayer	20.2%
Bayhydur XPLS2150/1	Bayer	7.2%
Exxate 600	Univar	4.1%

SB 2K PU	Supplier	%
Part A		
Desmophen A870 BA	Bayer	46.9 %
Desmophen 670A-80	Bayer	31.4 %
Dabco T-12	Air Products	0.1 %
n-BA	Univar	5.5 %
PMA	Univar	7.3 %
EEP	Univar	8.8 %
Total weight of Part I		100.0 %
Part B		
Desmodur N-3390 BA/SN	Bayer	100.00 %
Mixing Ratio (A/B)		73.3/ 26.6

SB Acrylic	Supplier	%
Elvacite 2013	Lucite	11.2%
Elvacite 2552	Lucite	11.0%
Cellulose Acetate Butyrate	Eastman	7.3%
MIBK	N/A	21.3%
IPA	N/A	1.9%
MEK	N/A	24.7%
BA	N/A	15.1%
Toluene	N/A	7.3%
Silsurf Di 1010	Siltech	0.1%

WB Acrylic	Supplier	%
White Latex Paint	ICI	100%