Bio-Organic Silicone Additives: Non-Petroleum Based Alternative Raw Materials.

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Abstract

There is a strong trend today to move away from petroleum-based chemical feedstocks in the name of sustainability[i]. In addition, security of supply and raw material sourcing flexibility have become critical global issues. Addressing both of these drivers, Siltech have evaluated bio-based hydrocarbon sourced portions of traditional organo-silicone coatings additives. Alternative supply chain pathways are available for both silicone polyethylene oxide and aliphatic hydrocarbon modified organo-silicones, two of the most frequently used types of organo-silicone ingredients in coatings additives.

These bio-organic silicone additives are synthesized from corn derived ethanol or from plant-based alpha olefins. In this paper, we compare several additives made from these bio-sourced feedstocks to the conventional petroleum-based products. Comparison data across two coatings systems shows that the origin of the organic portion of these is not decisive to performance.

Introduction

Silicones are man-made polymers penultimately derived from silicon metal and chloromethane. Silicon is the second most common element in the earth's crust behind oxygen. In the 1:2 ratio of silicon dioxide, the two elements comprise nearly 75% of the terrestrial elements[ii]. While most of the silicon on the planet is tied up as silicon dioxide in a multitude of geological forms, silicon is manufactured in large quantities for many industries including solar cells, electronics and silicones.

Chloromethane is currently derived from methanol which is in turn derived from natural gas. It is possible to make methanol in a non-petroleum green process, but that is not the predominate process today[iii].

Silicone additives for inks and coatings are actually hybrid polymers of silicone and organic portions which deliver the surface properties of the silicone merged with the solubility properties of the organic component. The two most common types of these hybrid organosilicone polymers are based on polyalkyleneoxide or hydrocarbon modified silicones. These are derived directly from hydride functional silicones and olefinic polyalkyleneoxides or hydrocarbons.

The hydrocarbons, in fact alpha olefins, are often fossil fuel derived; but there are biological sources for many of these materials. For example, Eugenol, an essential oil isolated from cloves[iv], is used commercially to manufacture some organomodified silicones today.

For reasons beyond the scope of this paper, silicone polyalkyleneoxides need to be synthesized from allyl functional polyalkyleneoxides. These polyalkyleneoxides can be ethyleneoxide, propylene oxide or both and are derived from allyl alcohol and ethylene oxide and/or propylene oxide. All of these are typically manufactured from fossil fuels.

Recently allyl functional polyethyleneoxides derived from plant-derived ethanol have come into the supply chain. In this paper, we made several of our standard coating additives from this raw material and compared those to the petroleum sourced analogues. We utilized a variety of comparisons such as foaming, surface tension, wetting, COF, and leveling.

Polypropyleneoxide derivatives, made from biological sources, are not available. Our silicone polyether bio-sourced options today are limited to EO chain derivatized materials. This is a limitation which in most cases, will be readily surmountable. The most important use of PO in these chains is to lower the crystallinity and $T_{(g)}$ of the materials. Pour points of PO containing silicone polyether derivatives are normally well below the temperature extremes seen in shipping, but the EO exclusively chained materials have pour points which can be reached during cold weather shipping. The effects of this are usually completely reversible upon warming.

Another key point of EO/PO silicone polyether additives is that they are GRAS listed by CAS number under an indirect food contact regulation[v] and so are often easier to gain food grade compliance. The underlying low toxicity and other considerations used in food grade determinations would apply to the all EO materials as well so they could be and in some cases have been granted food compliance by the FDA.

Experimental

The structures used in the study are shown in Figure 1 and Table 1. The pendant, often called comb type organosilicone structures (left side) are designated C1 to C5. The linear materials (right side) are designed L1 to L2. All are chosen to be dispersible to slightly soluble in water as these structures tend to have the highest surface activity and lowest tendency to stabilize foam. Many current coatings additives are designed this way.
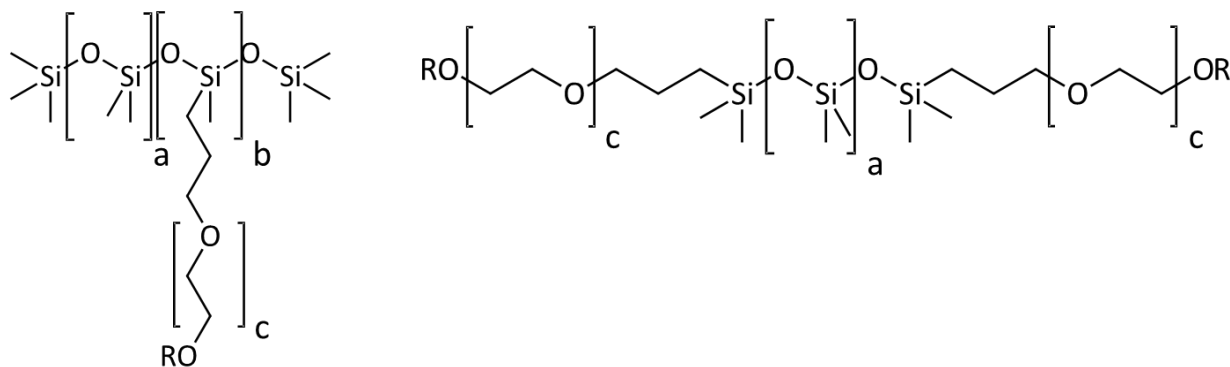

Figure 1: Structures

Table 1: Structural Details

Material	a	b	c	R	Water solubility
C1-P & C1-B	0	1	8	H	Dispersible
C2-P & C2-B	1	1	8	H	Soluble
C3-P & C3-B	12	2	8	H	Dispersible
C4-P & C4-B	22	2	10	Acetyl	Dispersible
C5-P & C5-B	8	4	8	H	Soluble
L1-P & L1-B	10	0	10	H	Soluble
L2-P & L1-B	25	0	10	H	Dispersible

Duplicate samples of these organomodified silicone derivatives were prepared with commercially practiced processes. One was prepared using standard petroleum derived organic feedstock and the other from the corresponding bio-sourced feedstock. Analysis of these corresponding feedstocks showed very similar but not analytically identical materials. In our experience these minor differences in the feedstocks would not be expected to cause significant differences in the products.

These are labeled with the suffix P for petroleum or B for bio-sourced. For example, material designated as C1 was prepared and evaluated in both C1-P and C1-B formats.

The seven silicone polyether derivatives, which were the focus of this work, were evaluated for a number of physical and surface properties using standard techniques. This was either done neat or as an aqueous solution.

These were post-added at 0.5% into two coatings systems. One was Quaker Color PR-1245, which is described as a 34% active medium-hard NMP free high performance aliphatic polyether polyurethane dispersion. The other was a customer supplied UV cured clearcoat based on an epoxy acrylate and reactive diluents. These coatings were drawn down on aluminum Q panels, cured or dried and evaluated for slip/COF, foam, appearance, and leveling.

For the Ross-Miles type foam test, a 1% stock solution in DI water was prepared. A 500 mL graduated cylinder was charged with 150 mL and sparged for 5 sec. The sparge was stopped and an initial foam height measurement was taken. Subsequent measurements were recorded at 1, 3, and 5 min intervals. The test was repeated 3x and averaged for the final recorded results.

Surface tension was measured using a KSV Sigma 70 Surface Tensiometer with a 0.1% stock solution in DI water. Settings were 20 mm/min (up and down), 5% dwell down, 4 sec stabilization and integration, 2mN/m detection range, and 40 mm/min reset speed. A 100 mL aliquot was charged and the Wilhelmy Plate was cleaned with a propane torch for 1 minute and then hung onto the micro-balance. Ten readings were taken and the averages recorded.

Coefficient of Friction was measured on a ChemInstruments COF-500 instrument with a 202 gm load cell and 15 cm/min settings. Averaged static and kinetic COF measurements were read directly from the instrument.

Drave's wetting was measured using a standard 5.0 ± 0.05 gm skein connected to a cylindrical anchor weight. The 1000 mL graduated cylinder is charged with 0.05% in DI water sample. Foam was allowed to dissipate and the skein was dropped into the solution. The time for the skein to sink was measured from touching the water to the weight's touching the bottom. This was repeated three times and the average recorded. If the weight/skein did not sink after 3 minutes, "NS" was recorded.

Results

Physical properties compare closely within the pairs of products. See Table 2. The bio-sourced series consistently has a slightly higher viscosity, indicating a higher $MW_{(Avg)}$ of the allyl polyalkyleneoxide.   Both the petroleum and the bio-sourced materials would be in the specification range of a commercially manufactured product.

Table 2: Physical properties

Sample	Viscosity, cPs	Appearance
C1-P	41	clear liquid
C1-B	51	clear liquid
C2-P	103	clear liquid
C2-B	170	clear liquid
C3-P	220	clear liquid
C3-B	252	clear liquid
C4-P	300	clear liquid
C4-B	343	clear liquid
C5-P	307	clear liquid
C5-B	313	clear liquid
L1-P	210	clear to hazy liquid
L1-B	292	clear to hazy liquid
L2-P	480	clear to hazy liquid
L2-B	567	clear to hazy liquid

Ross Miles foam height parallels the water solubility of a silicone polyether derivative and predicts foam generation and perhaps entrained air in waterborne coatings. The results are shown in Table 3 and Figure 2. In this testing, the materials looked very similar with a slightly lower foam height of the soluble materials and slightly higher foam from the dispersible species. This is a minor difference and is perhaps a symptom of the differing degrees of polymerization of the petroleum and bio-sourced allyl EO materials.

The standard deviation for this procedure is about ± 10 mL so nearly all of these are statistically the same.

Samples L2 and C4 were not evaluated for foam height due to their low solubilities.

Table 3: Aqueous foam heights

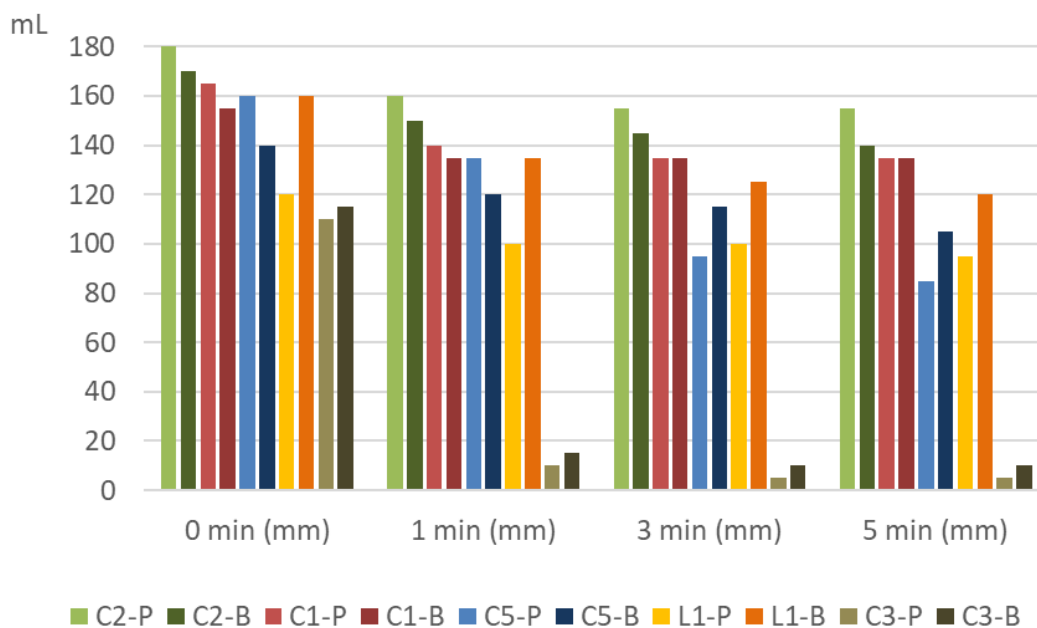| Sample	0 min (mL)	1 min (mL)	3 min (mL)	5 min (mL)	Comments	
C1-P	165	140	135	135	loose	hazy
C1-B	155	135	135	135	loose	hazy
C2-P	180	160	155	155	tight	clear
C2-B	170	150	145	140	tight	clear
C3-P	110	10	5	5	none	hazy
C3-B	115	15	10	10	none	hazy
C5-P	160	135	95	85	loose	clear
C5-B	140	120	115	105	loose	clear
L1-P	120	100	100	95	loose	clear
L1-B	160	135	125	120	loose	clear

Figure 2: Aqueous foam heights

Surface tension measurements are usually very sensitive to structural variations in silicone surfactants. In this series, minor differences are seen in the water soluble pairs of petroleum and bio-sourced polymers. The C3 and L2 pairs, which are only dispersible, show a larger difference. The C4 pair was not measured due to poor dispersibility in pure water. Results are shown in Table 4 and Figure 3.

Table 4: Aqueous surface tension and Draves wetting

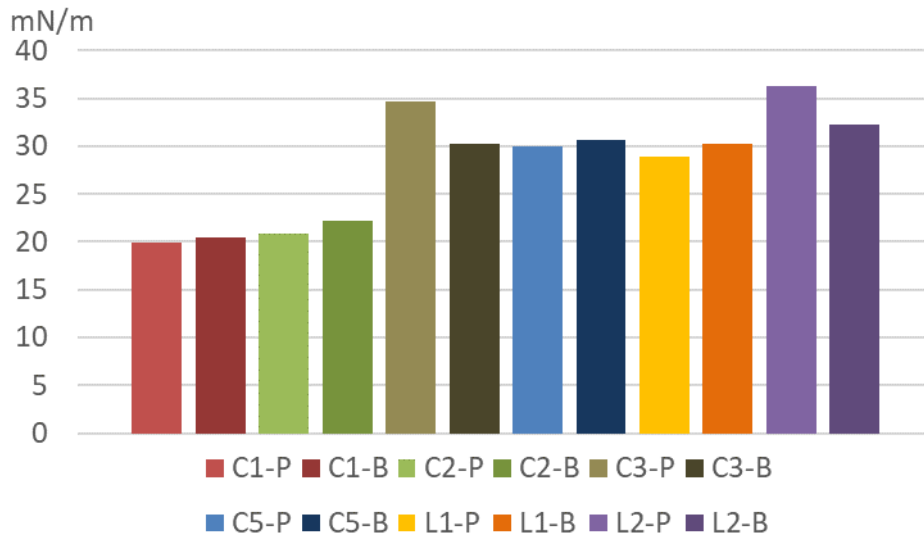| Sample	ST mN/m	Draves (s)	Sample	ST mN/m	Draves (s)
C1-P	20.0	14.5	**C1-B**	20.4	19.0
C2-P	20.8	35.2	**C2-B**	22.2	47.1
C3-P	34.7	>180	**C3-B**	30.3	na
C5-P	29.9	na	**C5-B**	30.7	na
L1-P	29.0	na	**L1-B**	30.2	na
L2-P	36.3	na	**L2-B**	32.2	na

Figure 3: Aqueous surface tension

The Draves wetting test is a good indicator for wetting out a higher surface energy material. Referring back to Table 4, the two low surface tension paired materials, C1 and C2, wet the skein allowing for a complete measurement. The higher ST materials typically do not wet the skein and that is what is seen here. C1-P and C1-B are reasonably close but significantly different. C2-P and C2-B show a very significant difference in wetting the surface.

Comparison of the additives in the 1K PUD showed good flow and leveling, appearance, foaminess and solubility in all samples except the C4-P and C4-B which were not very soluble and caused defects. The appearance of these were similar to each other. Static and kinetic COF was measured and is shown in Table 5 and Figure 4. COF values were very close for the corresponding petroleum and bio-sourced materials.

Table 5: COF in coatings systems.

|	0.5% in 1K PUD		0.5% in UV clearcoat	
Sample	Static	Kinetic	Static	Kinetic
none	0.572	0.500	0.550	0.500
C1-P	0.720	0.601	0.588	0.508
C1-B	0.755	0.607	0.539	0.515
C2-P	0.700	0.533	0.639	0.629
C2-B	0.703	0.531	0.637	0.639
C3-P	0.473	0.332	0.310	0.297
C3-B	0.468	0.328	0.320	0.297
C5-P	0.662	0.547	0.468	0.425
C5-B	0.651	0.542	0.473	0.429
L1-P	0.499	0.322	0.314	0.306
L1-B	0.501	0.318	0.288	0.237
L2-P	0.397	0.259	0.288	0.209
L2-B	0.424	0.263	0.244	0.208
C4-P	na	na	0.292	0.266
C4-B	na	na	0.275	0.266
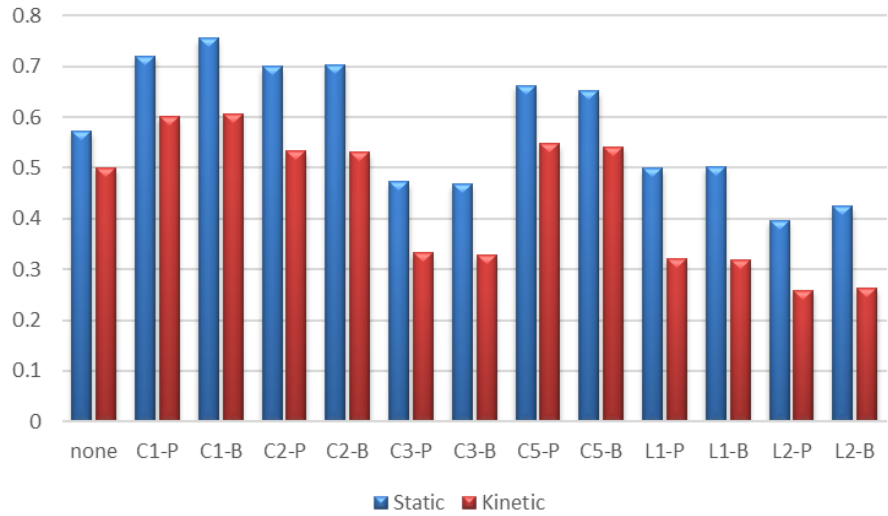
Figure 4: 0.5% COF in 1K PUD

Finally, a customer supplied formulated UV cured clearcoat was post-treated with 0.5% of these additives. The coatings were drawn down and cured.

In this formulation, all of the products were soluble and defect free with similar foam generation within each pair. Unlike in the waterborne examples presented so far, the C4-P and C4-B

materials, which are designed for UV systems rather than waterborne, are soluble in this system. The COF results are shown in Table 5 and Figure 5.
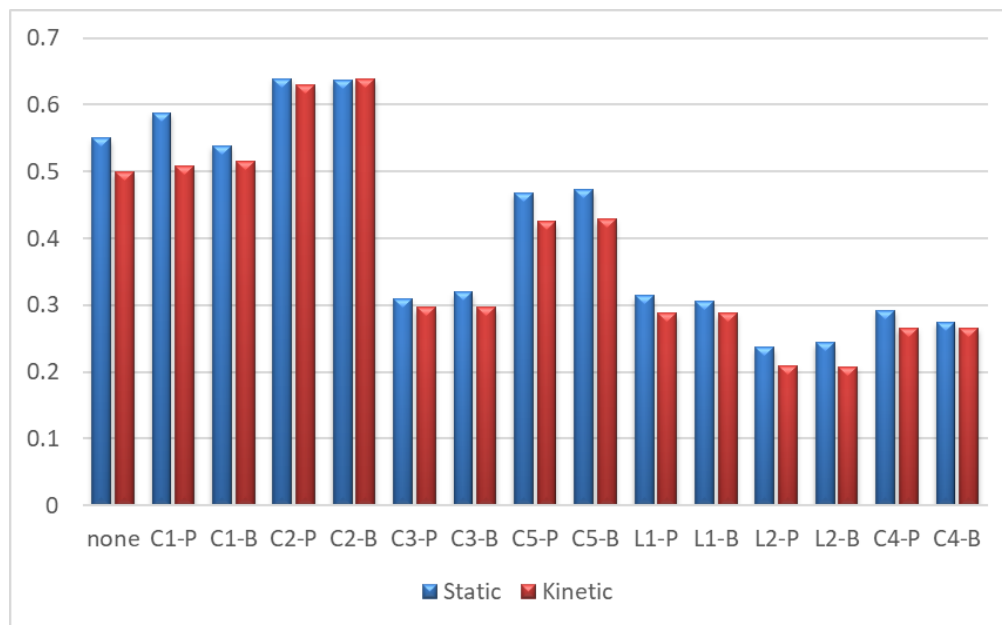

Figure 5: 0.5% COF in UV cured coating

Conclusions

Comparison of seven petroleum and bio-sourced silicone polyether derivatives with analytical tests showed some minor differences. That is expected as we choose to do these experiments with different lots of silicone as well as the different polyether sources. The idea was to evaluate if all would be within normal variations of these polymers.

None of these differences were large and we do not believe they are likely to be significant. Certainly, minor formulation adjustments would be expected to resolve any performance differences.

When compared in the two real-world formulations, the polymers from different sources behaved identically to each other.

We believe that these bio-sourced organomodified materials can be interchanged with little concern.

Although this paper is intended as a non-commercial; it is certain that many will wonder how these bio-sourced materials would affect cost and supply. To the former, early indications of pricing predict a manageable premium over the petroleum-based materials.

To the second point, this validated bio-sourced pathway certainly gives us one more sourcing option.

[i] A recent social media survey, sponsored by Siltech, showed 65% of the respondents thought this was critical or very important to their product choices

[ii] https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust

[iii] https://www.methanol.org/renewable/ and many other references available

[iv] Khalil,A.A. *et.al.*; "Essential oil eugenol: sources, extraction techniques and nutraceutical perspectives", RSC Advances, Issue 52, **2017**

[v] C.F.R 176.210 which governs the components of defoamer formulations used in pulp and paper which is used to make food containers lists CAS# 71965-38-3 as generally regarded as safe.