SILICONE ADDITIVES TO INCREASE SOLIDS AND LOWER VOCS IN SOLVENTBORNE SYSTEMS

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Abstract

Alkyl silicones have been found to be very effective at surface modification of oils and esters. By using a small amount of these alkyl silicones, the surface tension of these oils and esters can be lowered to 20-22 dynes/cm which is almost the same as silicone oil. We will investigate using these silicones in high solids solvent-borne systems hypothesizing that these alkyl silicones can lower the surface tension and viscosity of the coating, and allow for higher solids and lower VOCs. The type and chain length of alkyl silicone as well as the degree of our proprietary treatment of the alkyl silicones will be investigated to see how they affect the performance of the coating.

Introduction

In order to comply with the volatile organic compounds (VOC) regulations in paint and coating industries in many states and countries, paint and coating manufacturers have gradually moved away from the conventional low solids, solvent-borne systems to several emerging technologies, which include high solids, UV coating, powder coating, water-borne and solvent-free system.[1-3]

The major barrier in achieving high solids is the rheological requirement of the coating. Applying a thin coat to a complex surface uniformly requires the coating have good flow and a suitable viscosity at a wide range of shear rates.[4-6] The viscosity of a coating depends very much on the molecular weight and molecular weight distribution of the resin used. One of the key approaches to increase solids of coating and paint has been focused on the redesign of resin structure, i.e. lower molecular weight, narrower molecular weight distribution and higher functionality, to achieve desirable rheological characteristics and film properties.[7,8]

Using lower molecular weight, higher functionality and more linear resin can produce lower viscosity but could create other problems in coating applications. For example, the coating prepared with low molecular weight resin could have high sag, low film toughness and high sensitivity to less than perfectly cleaned substrates. Another approach to achieve high solids is to use additives in the formulation.[9] It is well known that a small amount of additives i.e. silicone materials can be used in coating and paint to minimize foaming during application, to improve sag, flow, wetting of the coating and to enhance slip, mar resistance and stain resistance of the dried film.

Alkyl silicones have been widely used in personal care products to improve playtime and smooth feel.[10] Alkyl silicones have better solubility in oils and esters than pure silicone fluid. The solubility of alkyl silicone in oils and esters depends strongly on its chain length and type of alkyl group on the molecule as well as the degree of proprietary molecular weight modification of the silicone backbone. This modified alkyl silicone provides many unique properties, such as softness, lubricity, gloss and emmoliency in skin care applications. Some low molecular weight alkyl silicones provide excellent dry feel in personal care formulations and have been used as a suitable replacement for cyclopentasiloxane (D_5), the use of which may become limited in some applications due to the recent regulatory development. Based on its compatible nature with organic compounds, alkyl silicones have also been applied in coating formulations to improve solids, applicability and film properties.

Some silicones such as defoamers with a high percentage of silicone content are not compatible in water-borne and solvent-borne systems. These insoluble silicones will sometimes cause fisheye and crater effects on finish. Using alkyl silicone or silicone surfactant with silicone defoamer or surfactant in the coating formulation could resolve some of these issues. Alkyl silicone is not only compatible with most of water-borne and solvent borne coating, but also gives coating with better oxidation stability and less temperature-dependent rheology. Using the alkyl silicone with a right amount and type of alkyl group together with silicone defoamer could significantly eliminate fisheye and crater effects as well as enhance the defoaming effect of silicone defoamer.

It has recently been discovered that alkyl silicones can be used as an effective surface modifier for a diversity of oils and esters. The surface tension of these oils and esters can be significantly lowered which is particularly important for many applications. In this study, we will investigate the effect of using these alkyl silicones on several solvent-borne systems. The rheology and the film properties of these solvent borne paints will also be evaluated. The primary goal of this project is to demonstrate the effect of alkyl silicone on rheological properties of high solid coatings and their film properties. It is expected that lowering the surface tension and viscosity of the coating with these alkyl silicone will allow for higher solids and lower VOCs in the coating. The type and the chain length of alkyl as well as the degree proprietary treatment will be investigated to see how they affect the performance of the coating.

MQ resins have also been found to be an effective surface modifier and used successfully in defoaming and personal care applications. It is thought that MQ can also be useful in paint to reduce its viscosity. The benefit of having lower viscosity is to provide the formulator with greater feasibility in preparing even higher solids coating. This study also explores the effect of MQ resin on the rheological and film properties of high solids coating. Some MQ resins are screened against alkyl silicones as well in this study.

Experimental

All of the test panels are prepared by drawing down approximately 1 to 3 mL of paint on a 4" x 6.5" Leneta paper or 4” x 6” aluminum panel with a wire-wound rod, depending on the viscosity and the wet film thickness of the coating. The wet film is then dried in air for 2 days for oil based paints or in an oven at 110°C for 2 hours for acrylic melamine paint. Gloss is measured with BYK-Gardner 60° micro-glossmeter. Viscosity is measured using Brookfield Rheometer DV-III with an appropriate spindle at various shear rates. ChemInstruments Coefficient of Friction 500 is used to measure friction of coefficient with the setting: 15 cm/min test speed and 200 grams sled weight. Sutherland 2000 Ink Rub Tester is used to measure mar resistance with the settings: 50 - 500 rubs with a nylon scrubbing pad and 84 rpm stroke speed. The mar resistance is determined by the percentage change in gloss reading before and after rubbing. Flow is measured by running distance of 0.2 gram paint on a Leneta paper at 45° angle for 5 minutes. The following alkyl silicones and MQ resins (Table 1) were used in the experiment:

Table 1: Percentages of alkyl and silicone contents in various alkyl silicones

Alkyl Silicone/ MQ Resin	% Alkyl	% Silicone	Description
C-16 CR	63	37	Treated Siloxane with C-16 Pendant Groups
C-22 CR	53	47	Treated Siloxane with C-22 Pendant Groups
C-8 CR	90	10	Treated Siloxane with C-8 Pendant Groups
C-2 Si	75	25	Low Molecular Weight Siloxane with C-2 Pendant Groups
C-4 Si-a	64	36	Low Molecular Weight Siloxane with C-4 Pendant Groups
C-6 Si	55	45	Low Molecular Weight Siloxane with C-6 Pendant Groups
C-4 Si-b	67	33	Low Molecular Weight Siloxane with C-4 Pendant Groups
MQ Resin1	0	100	M1.25Q1 M_n = 2320
MQ Resin2	0	100	M2Q1 M_n = 2052

Alkyl Silicone as Surface Modifier for Oils

Alky silicones are found to be effective surface modifiers for oils. Figure 1 demonstrates that the surface tension of motor oil is significantly reduced with an addition of a small amount of modified alkyl silicones. A proprietary treated alky silicone with hexadecane pendant group (C-16 CR) is able to induce the silicone backbone acting on the surface of the oil effectively. The alkyl pendant group in the molecule, which is oleophilic portion of the alkyl silicone, is expected to dissolve well in the oil, whereas the siloxane portion has a tendency to migrate to the surface, lowering the surface tension. With only 0.5% alkyl silicone added to the oil, the surface tension decreases from 31 mN/m to 22 mN/m. The surface tension reduces to 24 mN/m at even 0.05% level. It is also interesting to observe that many stable bubbles are formed in the oil when the oil blended with 0.05% C-16 CR is shaken by hand gently a few times. The corresponding untreated alkyl silicone is found to be less effective. This indicates that the proprietary treatment plays a key role in reducing surface tension of the oil.

A low molecular weight alkyl silicone with ethyl pendant groups (C-2 Si) is also found to be an effective surface modifier for vegetable oils. Figure 2 indicates that the surface tension of various vegetable oils is reduced significantly with an addition of 2% alkyl silicone. C-2 siloxane in oils has been used as a replacement for D_5, which is widely used in personal care products[11]. Although they are not as effective as the treated alkyl silicone in reducing surface tension of oil, the fundamental principle of reducing surface tension is the same for both types of alkyl silicones. The organic portion of low molecular weight alkyl silicone is compatible with the oil and pushes the silicone portion to the oil surface. It is ascribed to the fact that the low molecular weight alkyl silicone is very mobile and makes the oil flow better and gives lower viscosity and lower surface tension than the control without alkyl silicone. In summary, both treated and low molecular weight alkyl silicones are found to be very effective surface modifiers to reduce surface tension of oils.

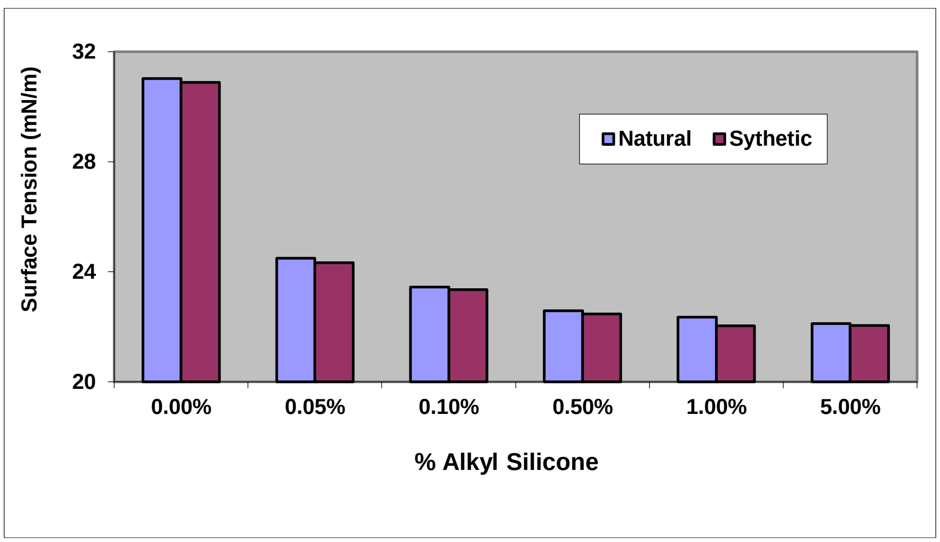

Figure 1. Surface tension of synthetic/natural motor oil modified with various level of C-16 proprietary treated alkyl silicone.

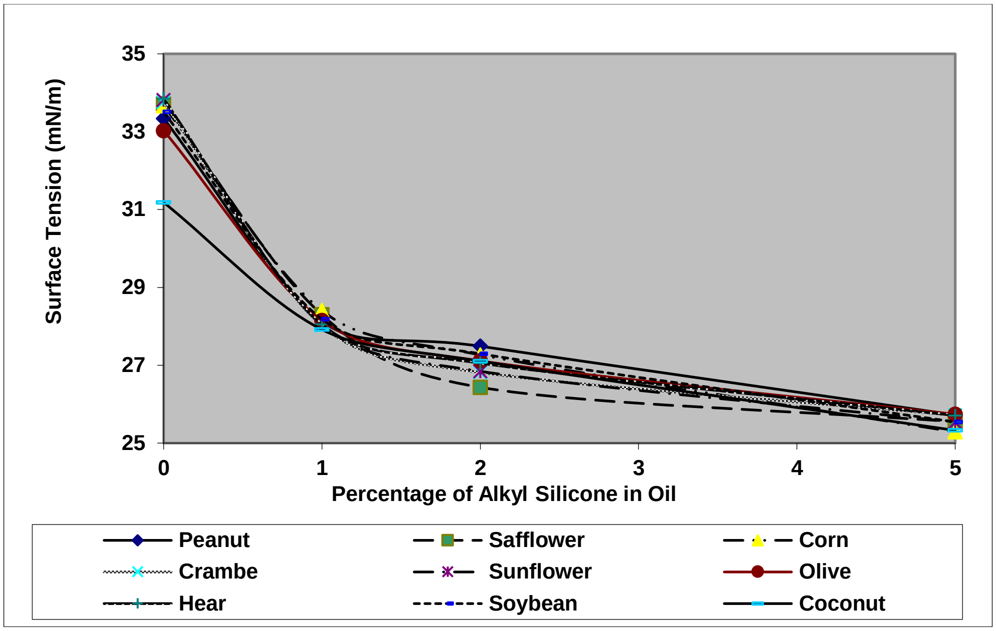

Figure 2. Surface tension of various vegetable oil modified versus % C-2 Si alkyl siloxane.

High Solids Gloss Black Enamel

High Solids Black Enamel having 315 g/L VOCs and 60% solids was used in the study. High solid enamel paints usually contain organic resin that is made from long chain alkyls, which are derived from vegetable oil. In some cases, a high percentage of oil-derived resin is used in the paint formulation. Due to the oil content in the paint, alkyl silicone could play an important role in modifying the paint rheology and its film properties. As discussed previously, the alkyl group on alkyl silicone is expected to be soluble in the oil-containing compound, forcing silicone groups to arrange on the surface. Because of this, the siloxane portion of the alkyl silicone becomes very active on the surface, resulting in lowering surface tension and viscosity, as well as enhancing flow.

Figures 3 and 4 indicate the results of viscosity and flow at various shear rates for the gloss black high solids Enamel treated with 0.5% alkyl silicone additive. Among all the test samples, C-2 Si generates the lowest viscosity. All of the samples prepared with alkyl silicone have better flow than the control. There is no significant difference in viscosity among the low molecular weight alkyl silicones but their viscosities are all lower than the modified alkyl silicones. This may indicate that low molecular weight alkyl silicone is more flowable than the modified longer chain one in the paint medium. There is no clear pattern observed with respect to alkyl chain length versus viscosity. Some other factors in molecular structure or interaction may have played some role in the viscosity measurement.

The film properties of enamel paint prepared with alkyl silicones are found to be significantly improved. Tables 2 & 3 and Figure 5 indicates that the coating prepared with treated alkyl silicone has lower surface tension, lower coefficient of friction and better mar resistance than the control and other alkyl silicone. As discussed previously, the modified silicone portion of the alkyl silicone can migrate to the coating surface more effectively during drying, resulting in lower friction and better mar resistance. On the other hand, the finish prepared with low molecular weight alkyl silicone contains less fisheyes than the control, whereas modified alkyl silicone has similar or slightly more fisheyes than the control. These defects are considered to be trivial and will not affect the aesthetic appearance of the coating, particularly, when using spraying equipment for the application.

MQ resins have also been used successfully in defoaming and personal care due to its effectiveness as surface modifier to reduce surface tension and viscosity of medium used. As indicated in the Figure 3, MQ resin also gives very low viscosity as compared to the control and other alkyl silicones. The MQ resin molecules are thought to arrange themselves in cubes with layered and planar structures and cover effectively on surfaces with a very thin layer of molecules.

The finish with MQ resin is slightly tacky due to the low molecular weight MQ resin used in the study, resulting in high friction and poor mar resistance. Tables 2 & 3 and Figure 5 indicate that the lowest viscosity is obtained from the sample prepared with MQ resin but it gives the highest surface friction and the lowest rating in mar resistance due to the presence of surface tack. It is expected that using higher molecular weight MQ resin could resolve the tack issue and to improve the slip and mar resistance.

Higher solid black enamel paint having 259 g/L VOCs and 65% solids was also prepared by adding more viscous resin in the formulation for this study. As indicated in Figure 6, all of the paint samples prepared with alkyl silicone give significantly lower viscosity than the control. The viscosity of the control increases rapidly with an addition of thick resin whereas the viscosity and flow of alkyl silicone samples increases just slightly under these conditions (Figures 6 & 8). The surface tension results for the higher solids black enamel paint are shown in Figures 7. C-8 CR and MQ resins shows the lowest surface tension, which has the same trend as in the less solids enamel. All the samples treated with alkyl silicones have lower friction, higher mar resistance than the control. The effect of alkyl silicones on improving the film properties for the higher solids is higher than the corresponding lower solids one (Table 4 and Figure 9).

In summary, the use of some alkyl silicone can lower viscosity, improve flow and allow for higher solids. The low molecular weight alkyl silicone gives lower viscosity of the paint than the modified alkyl silicone in the enamel paint whereas the latter gives better slip and mar resistance of dried film than the former. The effect of alkyl silicone on reducing viscosity becomes prominent. The benefit of using alkyl silicone to prepare paints with increasing solids becomes obvious.

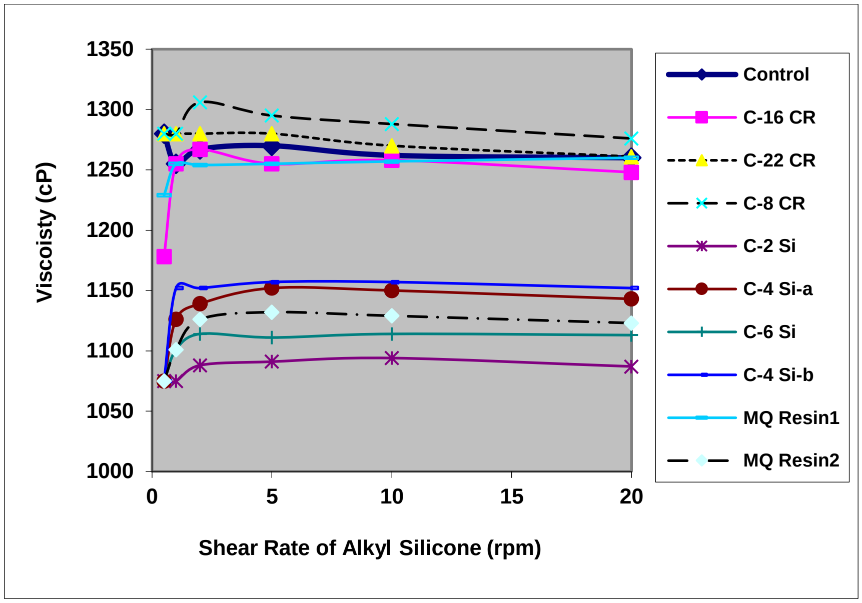

Figure 3. Viscosity of high solid gloss black enamel with 0.5% silicone additive.

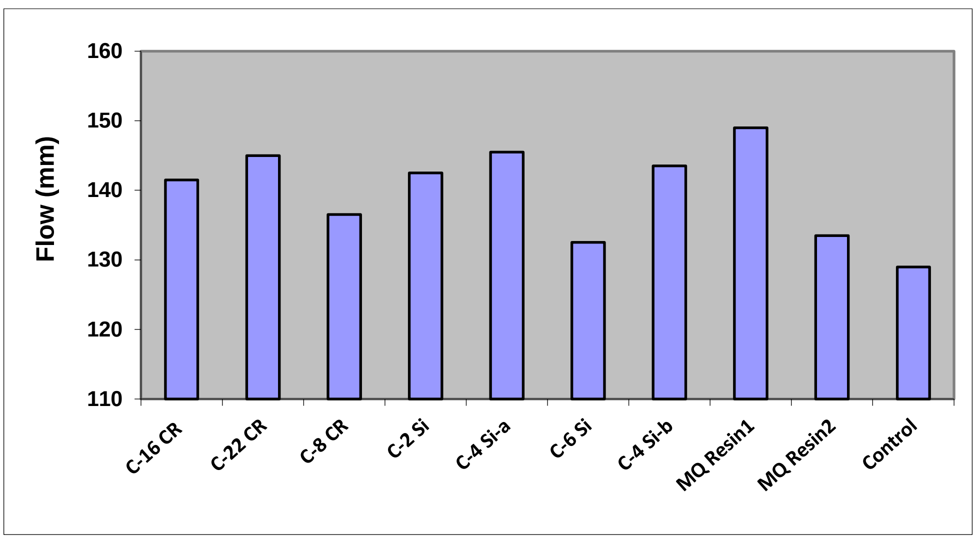

Figure 4. Five-minute running distance in mm using 0.2 g enamel at 45° angle for gloss black high solid enamel containing 0.5% silicone additive.

Table 2. Film Properties of Gloss Black Enamel with 0.5% Silicone Additive

HS Gloss Black Enamel with 0.5% Additive	Surface Tension (mN/m)	%Change in Surface Tension	Static CoF	%Change in Static CoF versus Control	Kinetic CoF	%Change in Kinetic CoF versus Control
Control	29.239	0.00%	1.270	0.00%	1.347	0.00%
C-16 CR	26.937	-7.87%	0.971	-23.51%	0.601	-55.37%
C-22 CR	27.545	-5.79%	1.007	-20.72%	0.612	-54.55%
C-8 CR	25.974	-11.17%	0.930	-26.74%	0.502	-62.72%
C-2 Si	28.347	-3.05%	1.067	-15.95%	0.932	-30.82%
C-4 Si-a	28.178	-3.63%	0.973	-23.40%	0.744	-44.78%
C-6 Si	27.971	-4.34%	1.018	-19.85%	0.797	-40.85%
C-4 Si-b	28.351	-3.04%	1.079	-15.05%	0.756	-43.89%
MQ Resin1	25.738	-11.97%	1.468	15.64%	1.537	14.11%
MQ Resin2	26.930	-7.90%	1.560	22.84%	1.662	23.43%

Table 3. %Change in Film Properties for Gloss Black High Solid Enamel with 5% Alkyl Silicone Additive

HS Gloss Black Enamel with 0.5% Additive	Gloss Before Mar Test	Gloss After Mar Test	% Change in Gloss after Mar Resistance Test	Finish
Control	83.3	62.5	-25.0%	Smooth with 10 small fisheyes
C-16 CR	82.1	71.7	-12.7%	Slightly rough with 40 small fish eyes
C-22 CR	81.2	71.2	-12.4%	Smoother than the control with 40 small fish eyes
C-8 CR	82.3	71.9	-12.6%	Smooth
C-2 Si	83.4	70.9	-15.0%	Very smooth
C-4 Si-a	82.1	71.5	-12.9%	Very smooth
C-6 Si	82.5	72.3	-12.4%	Very smooth
C-4 Si-b	81.7	72.3	-11.5%	Very smooth
MQ Resin1	82.7	51.9	-37.3%	Very smooth
MQ Resin2	82.4	66.6	-19.2%	Very smooth

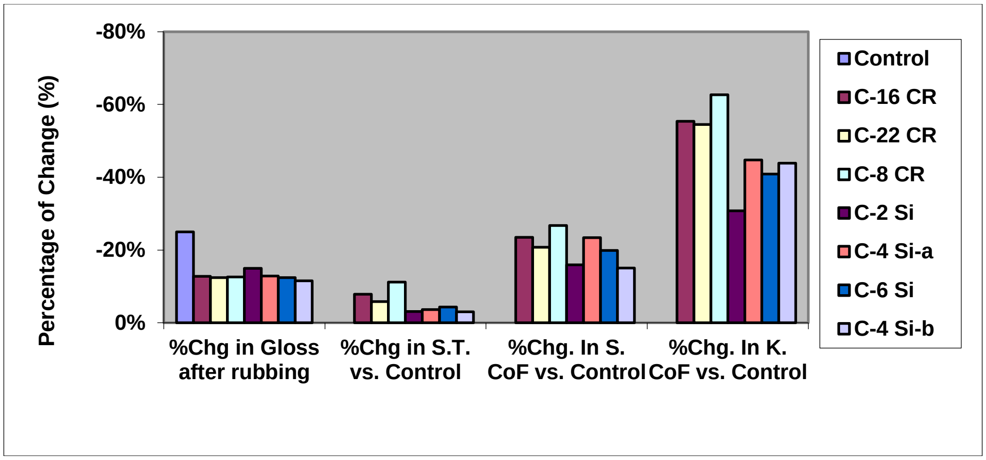

Figure 5. Percentage of change in film properties for high solids black enamel.

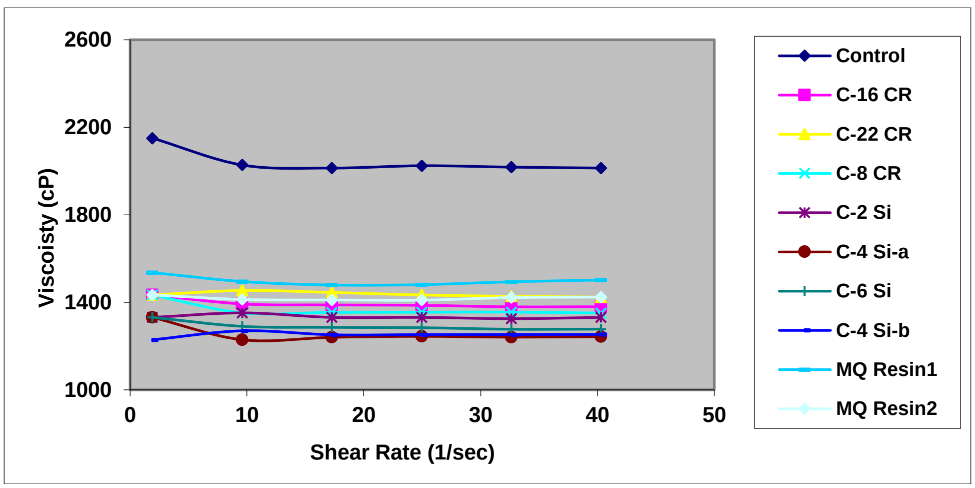

Figure 6. Viscosity of higher solids black enamel (65% solids) treated with 0.5% alkyl silicone.

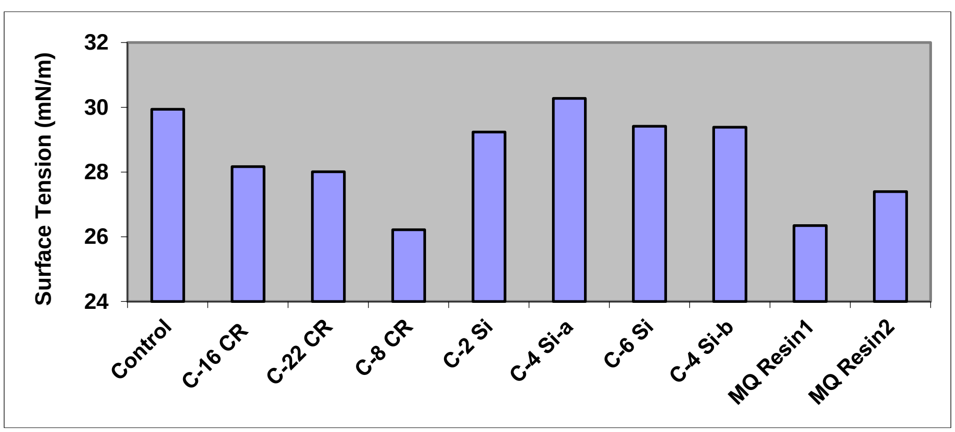

Figure 7. Surface tension of higher solids black enamel (65% solid) treated with 0.5% alkyl silicone.

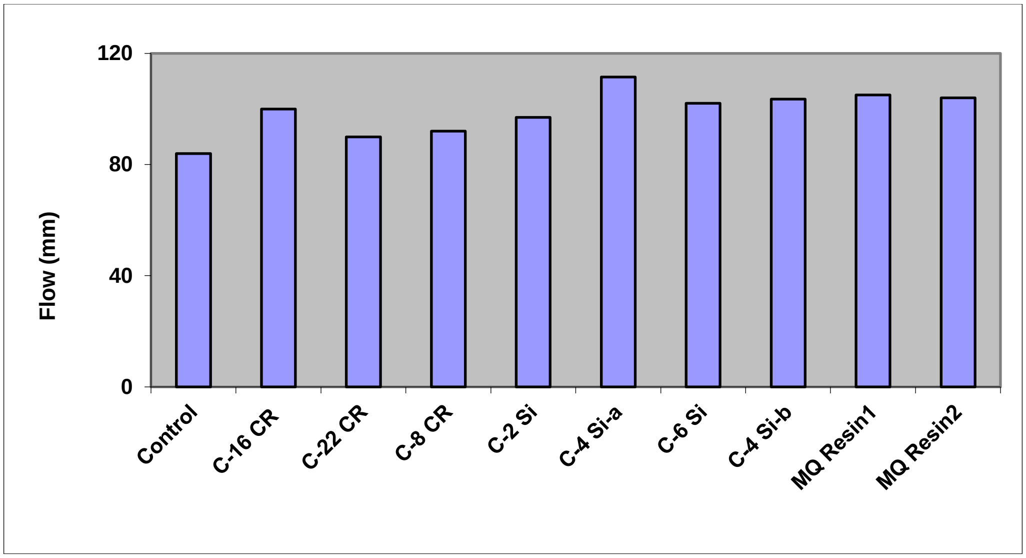

Figure 8. Flow of higher solids black enamel treated with 0.5% alkyl silicone

Table 4. Film Properties of Higher Solids Black Enamel Treated with 0.5% Alkyl Silicone

0.5% Alkyl Silicone in Higher Solids Black Enamel	%Change in Gloss after Rubbing	%Change in Surface Tension versus Control	%Change in Static CoF versus Control	%Change in Kinetic CoF versus Control	Finish
Control	-32.7%	0.00%	0.00%	0.00%	Smooth with 10 small craters
C-16 CR	-14.9%	-5.90%	-22.64%	-41.40%	Smooth with 2 small craters
C-22 CR	-14.8%	-6.43%	-17.15%	-38.79%	Smooth with 2 small craters
C-8 CR	-13.6%	-12.40%	-25.81%	-48.66%	Smooth with no crater
C-2 Si	-11.5%	-2.32%	-11.14%	-11.51%	Smooth with 4 small craters
C-4 Si-a	-9.2%	1.13%	-29.19%	-31.29%	Smooth with 4 small craters
C-6 Si	-10.9%	-1.73%	-25.77%	-34.82%	Smooth with 4 small craters
C-4 Si-b	-10.3%	-1.83%	-24.63%	-26.11%	Smooth with 4 small craters
MQ Resin1	-32.3%	-12.00%	24.35%	9.07%	Smooth with 20 small craters
MQ Resin2	-18.9%	-8.50%	15.69%	7.02%	Smooth with 4 small craters

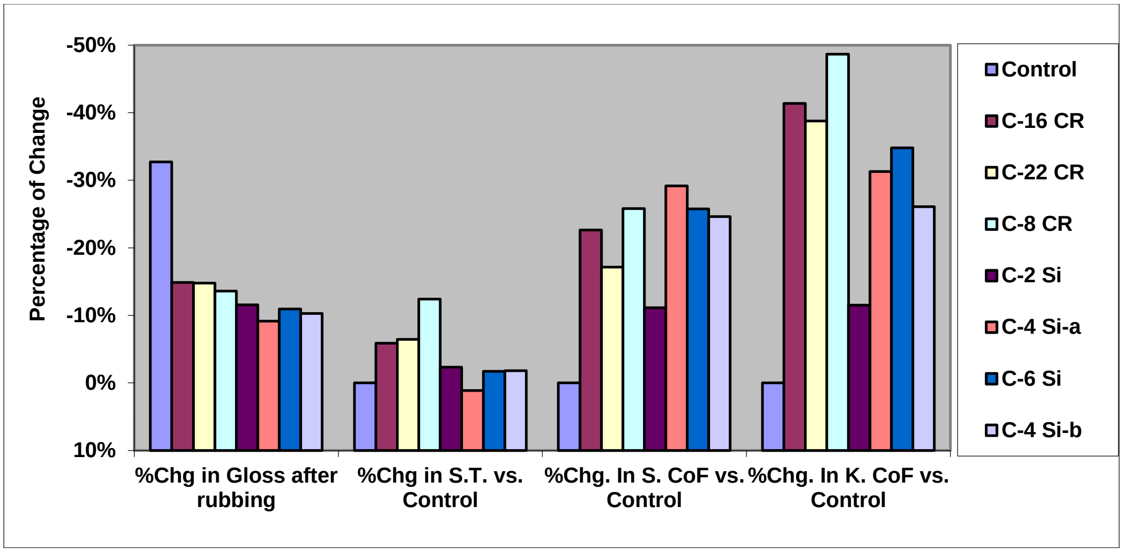

Figure 9. Percentage of change in film properties for higher solids black enamel.

High Solids Gloss White and Clear Topcoat with Unsaturated Nutshell Resin

In response to stricter VOCs regulation and demand for higher coating performance, resins derived from cashew nutshell liquid has been developed in many coating applications.[12] High Solid White Top Coat with nutshell resin having VOC 153 g/L and 89% solids is prepared using the following formulation (Table 5):

Table 5. The formula of high solids gloss white topcoat with unsaturated nutshell resin

Nutshell resin	42.30%
C-442 wetting agent	0.83%
Dispersant	0.53%
Xylene	5.29%
TiO_2	42.30%
6% Manganese solution	1.93%
12% Cobalt solution	0.58%
Accelerator	0.58%
Antiskin agent	0.58%
Xylene	5.10%
	100.00%

The differences in viscosity among all the test samples are insignificant, as demonstrated in Figure 10. C-22 CR gives the lowest viscosity at low shear rate whereas C-2 Si gives the lowest viscosity at high shear rate. Figure 11 indicates that all of the samples containing treated alkyl silicone give lower surface tension than the control. Treated alkyl silicone seems to be more compatible with the nutshell resin than low molecular weight alkyl silicone. The low molecular weight alkyl silicones have no observable effect on viscosity. In fact, C-2 Si and C-4 Si have higher viscosity than the control. They are not totally compatible with the nutshell resin. The film properties for the high solids white nutshell paint listed in Table 6 and Figure 12 indicate that alkyl silicones give significant improvements in slip and some improvements in mar resistance.

Higher solids white top coat with nutshell resin having VOC 86.8 g/L and 94% solids is also prepared using the same ingredients but with more resin and less solvent. The surface tension of the higher solids nutshell paint shows the same pattern as in the lower solids series. Treated alkyl silicone gives lower surface tension than the control and low molecular weight alkyl silicones (Figure 13). There is no significant difference in viscosity at low shear rate. But low molecular weight alkyl silicones give lower viscosity at higher shear rate than the control and treated alkyl silicones (Figures 14 & 15).

Overall, the effect of alkyl silicone on viscosity for nutshell paint is minimal. Nevertheless, the overall film properties of the higher solids white nutshell paint are improved significantly for the samples treated with alkyl silicone (Table 7 and Figure 16). The samples prepared with alkyl silicone are found to have better slip and mar resistance than the control. The extent of the improvements is similar to those for the lower solids series. Similar results are also obtained for higher solids **clear** nutshell top coat having 99.4 g/L VOCs and 90% solids (Table 8 and Figure 17).

MQ Resin1 gives the lowest viscosity at low shear rates among all the test samples. The surface tensions of the samples prepared with MQ resin are lower than the control and all modified alkyl silicones but higher than the low molecular weight alkyl silicones. The high solids finish with MQ resin is slightly tacky due to the low molecular weight MQ resin used in the study, resulting in high friction and poor mar resistance. The surface tackiness of nutshell resin is reduced significantly with higher solids nutshell paint. The surface fraction for the samples prepared with MQ resin is not as good as those prepared with alkyl silicones.

In summary, although no significant change in viscosity between the control and the alkyl silicone samples is observed, the coating prepared with modified alkyl silicones show excellent slip and low surface tension while low molecular weight alkyl silicones give good slip and good compatibility with this very high solids formulation. The high solids and higher solids coatings are very similar in performance.

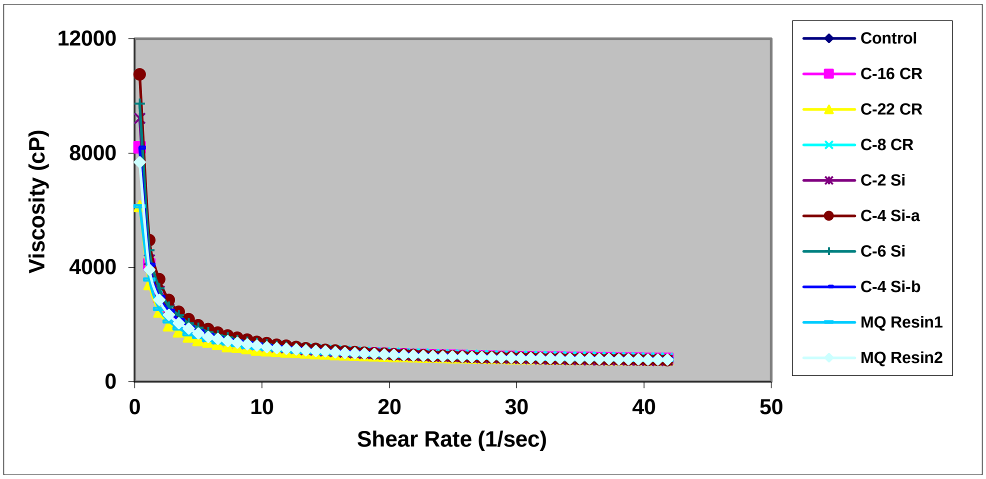

Figure 10. Viscosity of high solids white topcoat with nutshell resin.

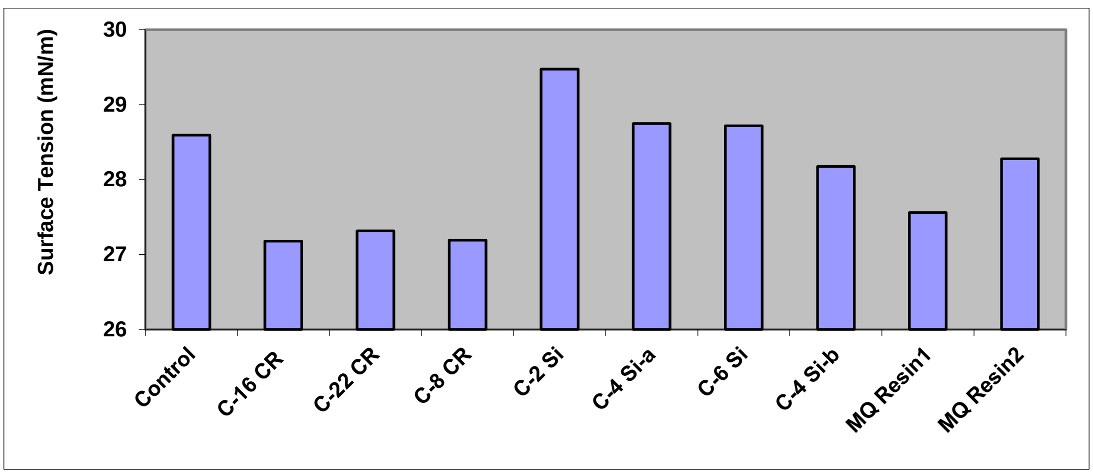

Figure 11. Surface tension of high solids white topcoat with nutshell resin.

Table 6. Film Properties of High Solids White Nutshell Paint

0.5% additive in High Solids Nutshell Paint	Surface Tension	Gloss Before	Gloss After	%Change in Gloss	Average Static COF	Average Kinetic COF	Finish
Control	28.594	85.4	68.5	-19.82%	0.820	0.745	smooth
C-16 CR	27.176	83.5	68.9	-17.56%	0.585	0.594	smooth
C-22 CR	27.314	83.8	69.8	-16.63%	0.664	0.623	smooth
C-8 CR	27.192	84.1	71.1	-15.50%	0.569	0.510	smooth
C-2 Si	29.473	83.2	70.8	-14.98%	0.494	0.442	smooth
C-4 Si-a	28.749	80.1	66.0	-17.53%	0.459	0.463	smooth
C-6 Si	28.718	77.4	68.2	-11.89%	0.412	0.381	smooth
C-4 Si-b	28.175	83.0	70.4	-15.17%	0.461	0.465	smooth

MQ Resin1	27.558	85.4	70.7	-17.22%	1.194	1.079	smooth with drawdown lines
MQ Resin2	28.277	84.9	69.0	-18.70%	1.130	1.008	smooth with drawdown lines

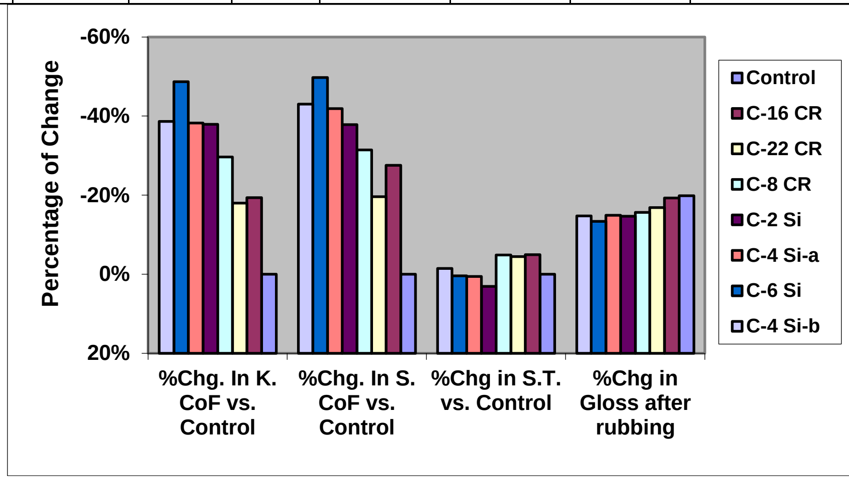

Figure 12. Percentage of change in film properties for high solids white nutshell paint.

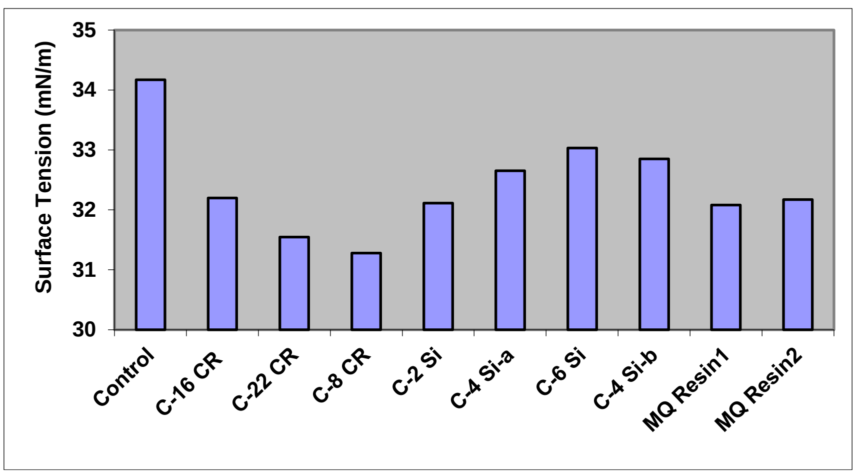

Figure 13. Surface tension of higher solid white top coat with nutshell resin.

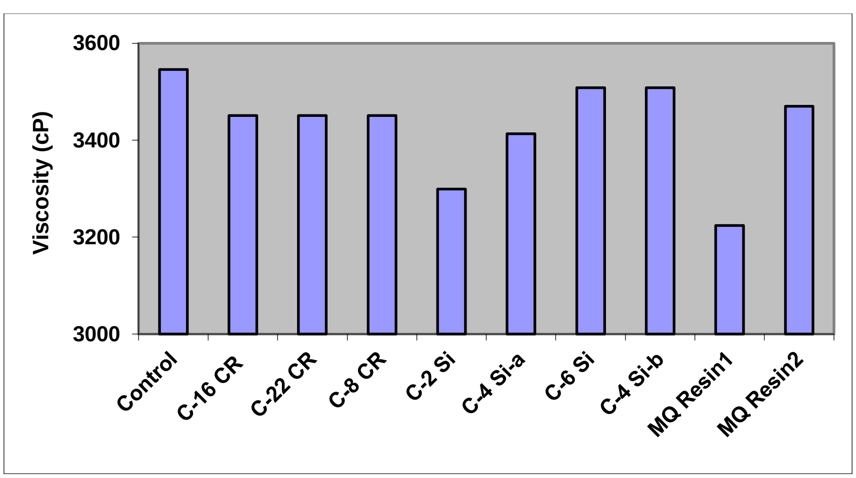

Figure 14. Viscosity of higher solids white nutshell top coat at low shear rate.

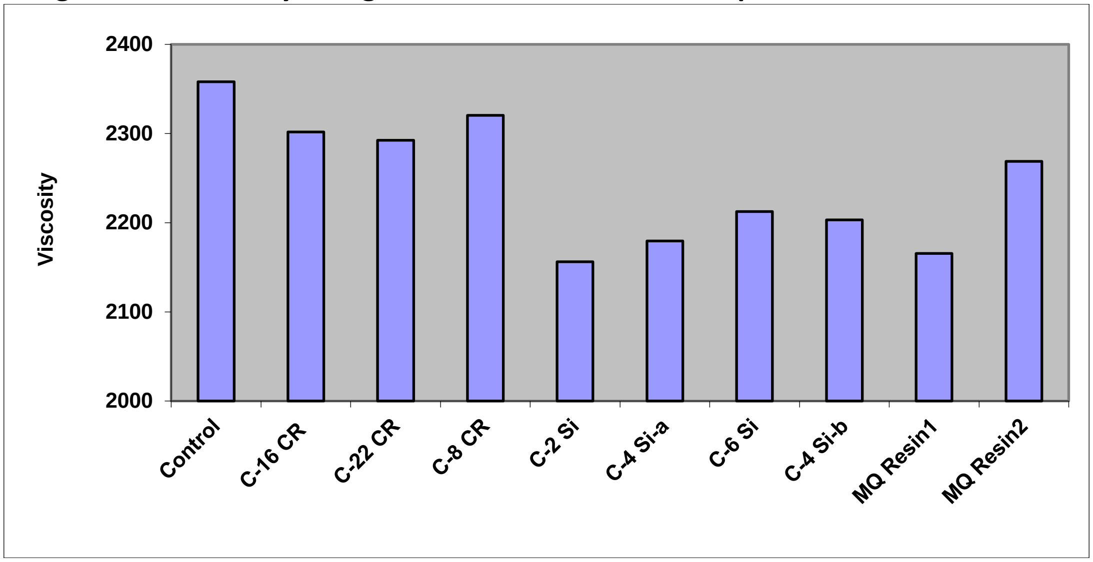

Figure 15. Viscosity of Higher Solids White Nutshell Top Coat at High Shear Rate

Table 7. Film Properties of Higher Solids White Nutshell Top Coat with 0.5% Silicone Additive

0.5% Silicone Additive in Top Coat	Static CoF	%Change in Static CoF	Kinetic CoF	%Change in Kinetic CoF	Finish
Control	1.238	0.00%	1.204	0.00%	Smooth with no fish eyes
C-16 CR	1.012	-18.26%	1.057	-12.21%	Smooth with no fish eyes
C-22 CR	0.956	-22.75%	0.979	-18.70%	Smooth with no fish eyes
C-8 CR	0.894	-27.80%	0.934	-22.39%	Smooth with no fish eyes
C-2 Si	0.619	-50.02%	0.639	-46.95%	Smooth with no fish eyes
C-4 Si-a	0.541	-56.32%	0.531	-55.92%	Smooth with no fish eyes
C-6 Si	0.499	-59.68%	0.467	-61.24%	Smooth with no fish eyes
C-4 Si-b	0.597	-51.76%	0.587	-51.23%	Smooth with no fish eyes
MQ Resin1	1.256	1.45%	0.931	-22.64%	Smooth but some small particles
MQ Resin2	1.338	8.12%	0.979	-18.65%	Some cratering

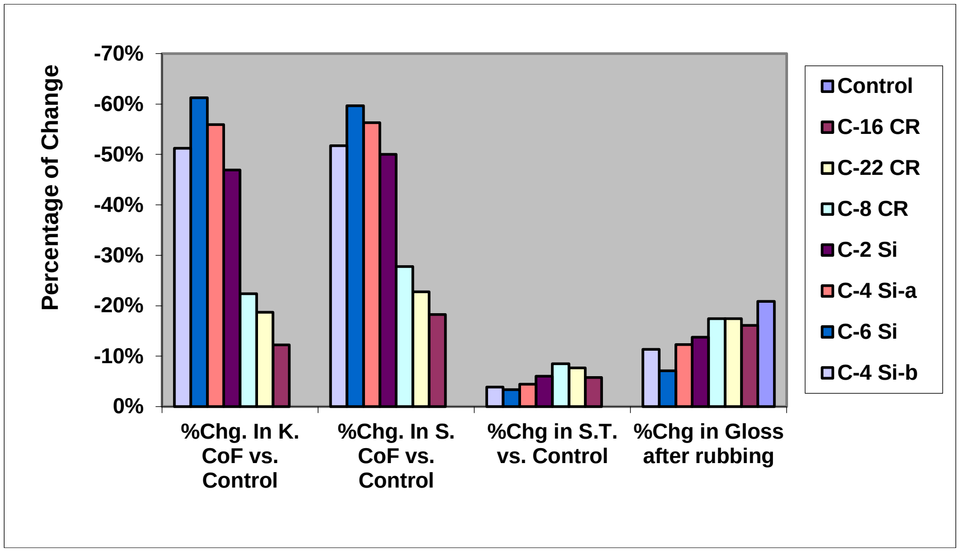

Figure 16. Percentage of change in film properties for higher solids white nutshell paint.

Table 8. Film properties versus Control (no additive) for Higher Solid Nutshell Resin Based Clear Topcoat with 0.5% silicone additive

0.5% Additive in HS Clear Topcoat	%Change in S.T. Versus Control	%Change in Gloss	%Change in Static CoF	%Change in Kinetic CoF	Finish
Control	0% (31.3 mN/m)	0% (91.3)	0% (1.093)	0% (1.035)	Smooth with 100 fish eyes
C-16 CR	-15.6%	0.0%	-42.6%	-49.1%	Rougher coating with 100 fish eyes
C-22 CR	-19.5%	-3.3%	-45.6%	-50.7%	Rougher coating with 50 fish eyes
C-8 CR	-23.2%	-1.9%	-57.6%	-68.3%	Smoother coating with 30 fish eyes
C-2 Si	-8.5%	-0.8%	-36.2%	-35.5%	Smooth but grainy with 20 fish eyes
C-4 Si-a	-8.5%	-1.6%	-43.5%	-37.0%	Smooth with 5 fish eyes
C-6 Si	-7.2%	-1.6%	-40.5%	-38.0%	Smooth with 25 grains and no fish eyes
C-4 Si-b	-8.4%	-1.3%	-41.8%	-36.9%	Smooth with less grains and no fish eyes
MQ Resin1	-17.7%	-0.5%	-19.4%	-7.9%	Smooth with very small grains and no fish eyes
MQ Resin2	-23.3%	-1.9%	4.2%	14.6%	Very smooth and glossy with very small grains

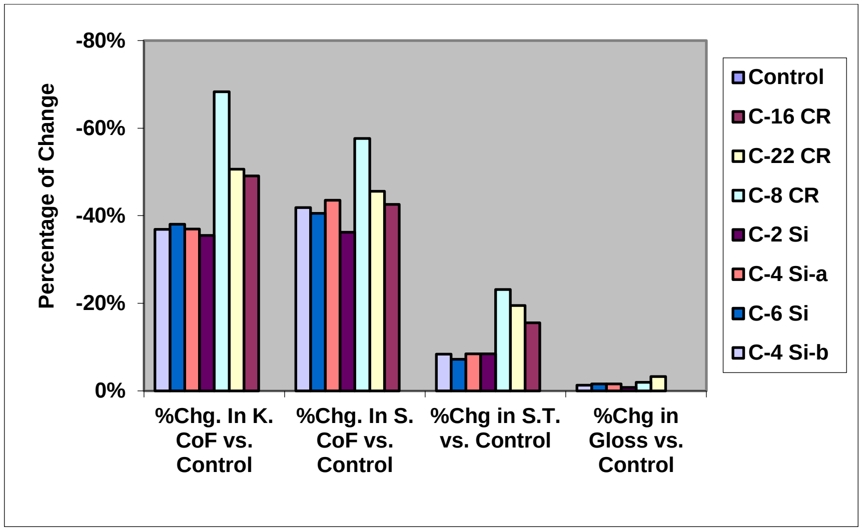

Figure 17. Percentage of Change in Film Properties for Higher Solids Clear Nutshell Paint.

High Solids Acrylic Melamine White Coat

Melamine formaldehyde resins have widely been used to crosslink many hydroxyl-functional resins for high solids coating applications[13]. High solids white top coat with acrylic melamine resin having 224 g/L VOCs and 83%Solids was prepared for electrostatic spray using the following formulation (Table 9):

Table 9. The formula of high solids acrylic melamine white coat

Acrylic resin	19.94%
Amyl acetate	2.01%
Dispersant	0.50%
TiO_2	32.41%
Acrylic resin	16.94%
Melamine resin	12.67%
n-Butanol	3.99%
Butyl acetate	4.99%
Acid catalyst	0.50%
Wetting agent	0.99%
Amyl acetate	5.06%
Total	100.00%

The acrylic melamine coating was cast on aluminum panel and cured at 110 °C for 2 hours. The viscosity of this formulation is relatively low which is suitable for electrostatic spray application. The effect of alkyl silicone on viscosity and flow for this system is trivial (Figures 19 and 20). As indicated in Figures 18 and Tables 10 & 11, the samples prepared with alkyl silicone show slight reduction in slip and surface tension but have insignificant effect on viscosity, flow, wetting and mar resistance. Alkyl silicone is less compatible with acrylic melamine system than with oil-based paint. The sample prepared with C-22 has low gloss. Also, most of the samples prepared with treated alkyl silicone contain some fisheyes.

Higher solids acrylic melamine top coat having 93 g/L VOCs and 92% Solids is also prepared using the same ingredients with more resin, filler and less solvent. The alkyl silicones have greater effect on this much higher viscosity than the lower solids one (Figure 21). All of the samples prepared with alkyl silicone show lower viscosity than the control. The surface tension for the sample prepared with alkyl silicone is also found to be lower (Figure 22). The differences in viscosity and surface tension between the alkyl silicone and the control are considered noteworthy. The film properties of higher solids acrylic melamine paint are similar to those of the lower solids series. This reduction of viscosity and surface tension will benefit in formulating high solids coating and paint.

MQ resins give the best flow and the lowest surface tension among all the samples in the high solid acrylic melamine top coat series. The surface tension and the viscosity of the higher solid one are also found to be significantly lower than the control. However, the film properties, i.e., slip and mar resistance are poor due to the surface tack for both high and higher solids series.

In summary, alkyl silicone shows some benefit for very high solid acrylic melamine paint but it has less effect on viscosity, surface tension and film properties than for oil-based paint.

Table 10. Film Properties of High Solids SB Acrylic Enamel White Electrostatic Spray with 0.5% silicone additive

0.5% Additive in HS SB Acrylic White Topcoat	%Change in Surface Tension	%Change in Gloss	%Change in Static CoF	%Change in Kinetic CoF
Control	0% (25.7 mN/m)	0% (82.5)	0% (0.678)	0% (0.662)
C-16 CR	-2.7%	-5.8%	-21.2%	-32.8%
C-22 CR	-3.3%	-28.6%	-25.0%	-37.0%
C-8 CR	-6.5%	-0.2%	-16.0%	-31.9%
C-2 Si	-0.9%	-6.1%	-19.9%	-23.2%
C-4 Si-a	-0.9%	-1.3%	-29.7%	-36.0%
C-6 Si	0.0%	-12.0%	-28.9%	-42.0%
C-4 Si-b	-0.6%	-0.8%	-32.8%	-40.6%
MQ Resin1	-11.2%	1.1%	128.8%	154.4%
MQ Resin2	-10.6%	4.2%	103.0%	139.4%

Table 11. Percentage of Change in Film Properties versus Control (No Additive) for High Solids Solventbased Acrylic White Enamel Topcoat with & without 0.5% Silicone Additive

Gloss White	Gloss Before	Gloss After	%Change in Gloss after Rubbing	Finish
Control	82.5	71.1	-13.86%	Smooth with 5 very small fish eyes
C-16 CR	77.7	65.3	-15.96%	~300 Fish eyes
C-22 CR	58.9	48.0	-18.51%	~1000 Fish eyes
C-8 CR	82.3	68.3	-17.00%	Rougher finish than control
C-2 Si	77.5	68.5	-11.57%	Similar to control
C-4 Si-a	81.4	67.8	-16.78%	Similar to control
C-6 Si	72.6	64.9	-10.52%	Similar to control
C-4 Si-b	81.8	69.3	-15.28%	Similar to control
MQ Resin1	83.4	66.9	-19.86%	50 Very small fish eyes
MQ Resin2	85.9	72.2	-16.02%	30 Fish eyes

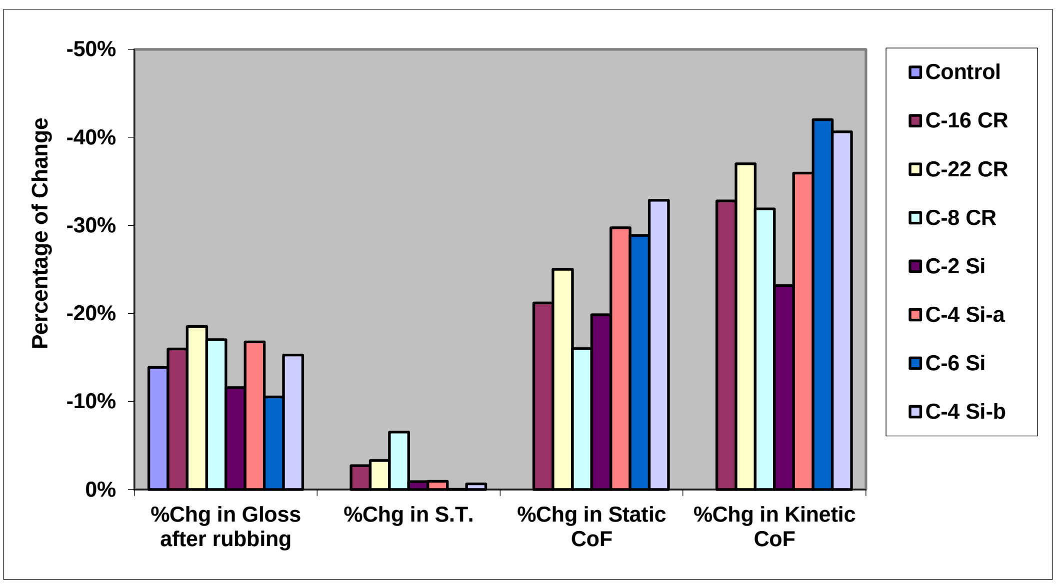

Figure 18. Percentage of change in film properties for high solids acrylic melamine white paint with 0.5% alkyl silicone.

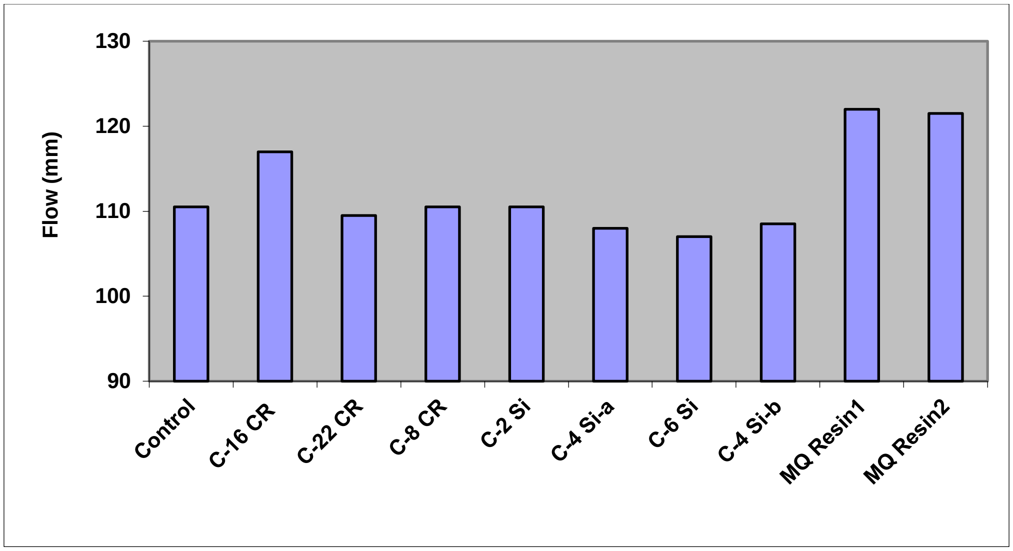

Figure 19. Flow of high solid white acrylic melamine top coat with 0.5% alkyl silicone.

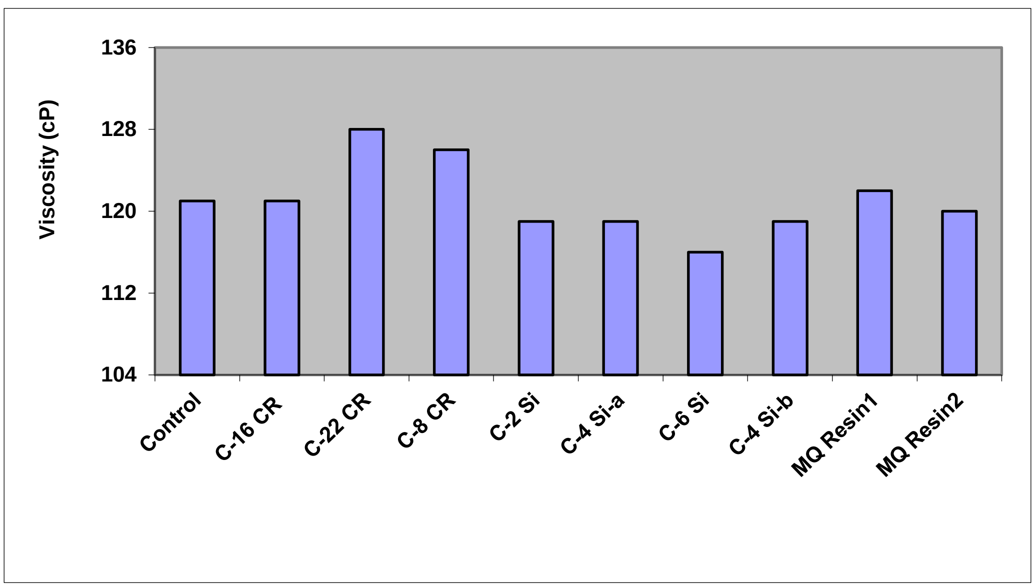

Figure 20. Viscosity of high solid white acrylic melamine top coat with 0.5% alkyl silicone.

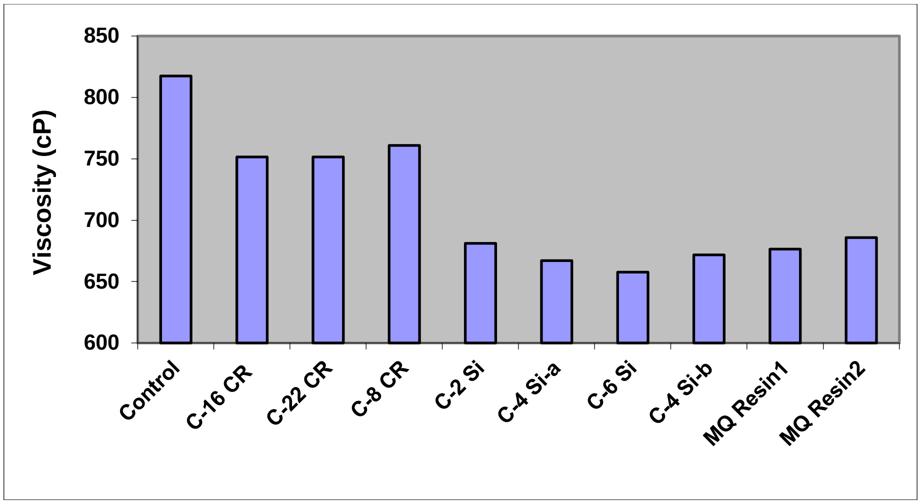

Figure 21. Viscosity of higher solids acrylic melamine top coat with 0.5% alkyl silicone.

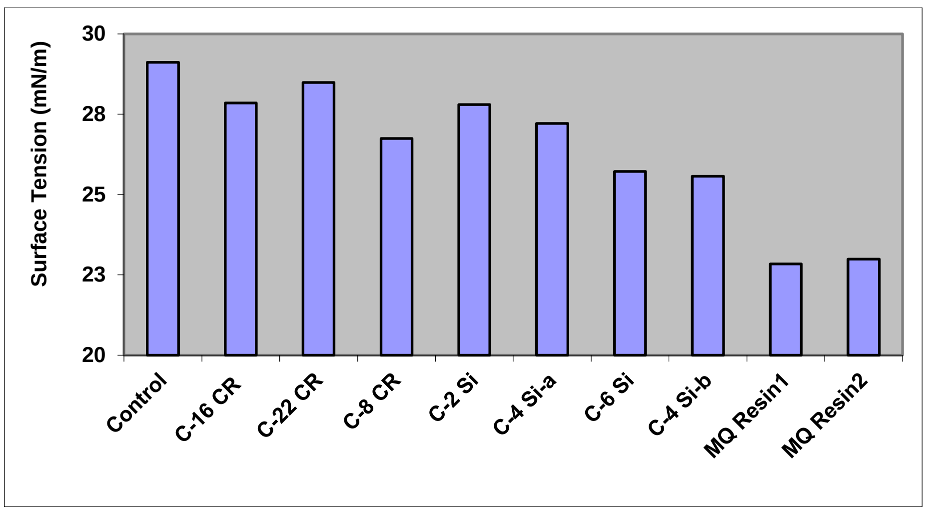

Figure 22. Surface tension of higher solids acrylic melamine top coat with 0.5% alkyl silicone.

Summary

Alkyl silicones are found to be very effective at reducing surface tension, improving flow and reducing defects in very high solids solvent-borne systems. Both modified and low molecular weight alkyl silicones are found to be very effective surface modifiers to reduce surface tension of oils. This study has demonstrated the positive effect of alkyl silicone on the rheological properties and their film performances for three different coating systems.

The relationships between the film properties and the chemical structures, i.e., the type and the chain length of alkyl as well as the degree of treatment are also investigated. For high solids black enamel, low molecular weight alkyl silicone gives lower viscosity than the treated alkyl silicone whereas the latter gives better slip and mar resistance of dried film than the former. The effect of alkyl silicone on reducing viscosity becomes prominent for very high solids paints.

In the case of the nutshell paint formulation, although no significant change in viscosity between the control and the alkyl silicone samples is observed, the coating prepared with modified alkyl silicones show excellent slip and low surface tension while low molecular weight alkyl silicones give good slip and good compatibility with these very high solids nutshell formulations.

Alkyl silicone shows some benefit for very high solid acrylic melamine paint but it has less effect on viscosity, surface tension and film properties than for oil-based paint. The benefit of using alkyl silicone becomes obvious in very high solids paints. This will provide formulator with greater feasibility in preparing even higher solid coatings and paints successfully.

MQ resins give low surface tension, low viscosity and good flow in many of these coating systems. In some cases, the surface tension and viscosity for the samples prepared with MQ resin are even lower than those with alkyl silicones. However, the major issue of using MQ resin in these systems is the surface tack which cause poor performance in slip and mar resistance. Using higher molecular weight MQ resin could resolve this problem.

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