THE USE OF Q RESINS AND OTHER MODERN SILICON CROSSLINKING MOIETIES TO CONFER WATER REPELLENCY, RELEASE AND PROTECTION PROPERTIES TO FABRIC, LEATHER, HARD SURFACES AND COATINGS

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Abstract

A series of reactive Q and T resins, $Si(OR)_4$ and $R'(SiOR)_3$ based units respectively, were formulated with reactive silicone polymers. The systems were evaluated in various fabric, leather, or hard surface treatments for water repellency, release, and anti-graffiti properties.

Introduction

Silicones, also known as siloxanes or polydimethylsiloxane (PDMS), are man-made polymers ultimately derived from silicon metal and chloromethane. Silicones have a surface energy of 20 mN/m, second only to perfluorinated alkanes. This low surface energy is the reason for many of its unique properties including low coefficient of friction (COF), high release, soft feel, and protection.

Silicones are both hydrophobic and lipophobic; not mixing well with either water or oils. As such, silicones are useful as hydrophobizing coatings or treatments and are probably the most overall effective way to do this. For lipophobic treatments, silicones can be effective but are generally not as efficient as fluoroalkanes, which are often the only product type to work effectively. Over the years, we have found some variations on silicones which can improve lipophobicity and can compete with fluoroalkanes in some situations. [1]

Typical approaches for making surfaces hydrophobic using silicones include applying silicone oils directly to the surface from solvent or water or creating a silicone coating with reactive silicone resins. Waterborne formulas are preferred for well-known environmental reasons, but the emulsifiers used are necessarily somewhat hydrophilic and can compromise hydrophobicity performance. Low hydrophilic-lipophilic balance (HLB) emulsifiers help, but don't completely resolve this weakness of waterborne formulations.

An especially useful approach is silicone film-forming emulsions that crosslink upon drying, leaving a silicone matrix. Again, one has to be careful when formulating the emulsifiers but in practice the crosslinking offsets much of the impact.

One can also incorporate specific chemical moieties to anchor the silicone to the surface into these approaches. Heteroatom-rich functionalities like hydroxyl, amine, or quaternary

ammonium compounds can anchor the polymer to the surface, providing organization of the hydrophobic polymer towards the environment and concomitant improved hydrophobicity.

Incorporation of long chain alkyl groups, generally eight carbons or higher, are known to improve hydrophobicity as well. In this case, the surface energy of these silicone organic hybrid systems is not as low and one sees diluted properties from the silicone. Reduced protection from stains, less tactile softness, and improved compatibility are typically noticed but hydrophobicity is often increased. In the real world, we must balance the most desirable properties with the less desirable ones as they may both be characteristics of the same structure.

One typically obtains contact angles of about 100° with these approaches. Attaining the vaunted superhydrophobic regions of contact angles 140° or better requires mesostructured systems. While silicones are often used to hydrophobize the nanoparticles in these complex systems, they cannot achieve this alone.

One cutting edge of silicone product research is using Q resins. The Q moiety is a silicon atom attached to four oxygen atoms, rather than methyl radicals. Using the Q resin approach maximizes crosslinking and associated properties, but can be tricky to control and predict. We accomplish this control by using reproducible preformed Q resins.

In driving this concept to real world systems, we also often incorporate T groups into these resins. The T moiety is a silicone atom attached to three oxygen atoms and one organic group. In both approaches, the OR groups react in a condensation fashion to form crosslinked silicon networks.

This QT resin approach has shown improvements in both hydrophobic and lipophobic treatments. In this paper, we will concentrate on different ways to treat surfaces with various silicone approaches to achieve hydrophobicity.

Experimental

A series of reactive Q and T resins, $Si(OR)_4$ and $R'(SiOR)_3$ based units respectively, are formulated with reactive silicone polymers. The systems were evaluated on various surfaces for applications in fabric and/or leather treatments and car care for water repellency, release, and film properties.

Contact angle is measured using the KRUSS GH11 MobileDrop. A syringe with deionized (DI) water is inserted into the syringe sleeve in the slit of the dosing head. The MobileDrop is placed onto the sample, pressing the dosing wheels down to lower the needle. The dosing wheel is rotated towards the palm of your hand for three click-points to generate a drop. The contact angle is recorded.

Dialkyl Quaternary Ammonium Functional Silicones

In this section, we see a series of dialkyl quaternary ammonium modified silicone polymers evaluated after being applied directly to the surface. Both the anchor and the long chain fatty group tactics to increase hydrophobicity are used.

The silicone dialkyl quat compounds were applied as a 0.1% solution in water and isopropyl alcohol (IPA) and allowed to dry. There are no hydrophilic emulsifiers to impact the results. The contact angle values of DI water on glass slides suggested that excellent hydrophobicity can be achieved by this approach.

The structures (Figure 1) are silicone polymers modified with an alkyl connector which has a quaternary ammonium group on the end. The quaternary ammonium site is also modified with long chain alkyl groups on the nitrogen. Sil(n) indicates the number of silicon atoms (x+y) in the silicone chain and ranges from 1 - 400. Alkyl(n) indicates the number of carbons in the alkyl chain (R) and range from 1 - 18. The terms pendant and linear refer to whether the organic (quat and alkyl) chains are attached to the silicone in the middle of the chain (pendant) or at the two ends (linear).
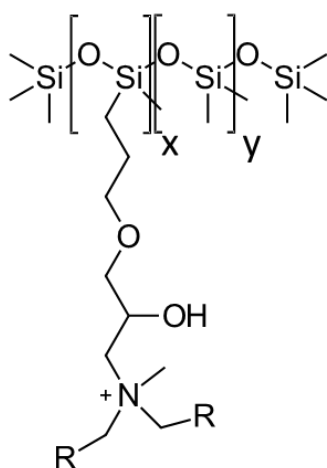
Figure 1. Pendant dialkyl quaternium silicone structure.

One can see in Table 1 that increasing silicone chain length improves the contact angle. For example, compare A, D, F and H to much larger J and L. The chain length of the alkyl is also proportional to the contact angle, e.g., comparing A to B to C; D to E; F to G. With this approach, high contact angles of 112° on glass slides were obtained.

Table 1. Quaternary Ammonium Silicones and Results

Reference	Sample	Sil (n)	Alkyl (n)	Architecture	(º)
Blank	Blank	na*	na	na	65
A	Sil(n) = 1; alkyl(n) = 8	1	8	Pendant	83
B	Sil(n) = 1; alkyl(n) = 12	1	12	Pendant	89
C	Sil(n) = 1; alkyl(n) = 18	1	18	Pendant	90
D	Sil(n) = 3; alkyl(n) = 1	3	1	Pendant	72
E	Sil(n) = 3; alkyl(n) = 18	3	18	Pendant	84
F	Sil(n) = 8; alkyl(n) = 1	8	1	Pendant	81
G	Sil(n) = 8; alkyl(n) = 18	8	18	Pendant	96
H	Sil(n) = 20; alkyl(n) = 1	20	1	Pendant	81
I	Sil(n) = 20; alkyl(n) = 18	20	18	Pendant	94
J	Sil(n) = 150; alkyl(n) = 1	150	1	Pendant	102
K	Sil(n) = 150; alkyl(n) = 15	150	15	Pendant	107
L	Sil(n) = 300; alkyl(n) = 1	300	1	Pendant	103
M	Sil(n) = 50; alkyl(n) = 18	50	18	Linear	111
N	Sil(n) = 100; alkyl(n) = 1	100	1	Linear	106
O	Sil(n) = 100; alkyl(n) = 18	100	18	Linear	112
P	Sil(n) = 400; alkyl(n) = 18	400	18	Linear	100

*na – not applicable

Film Forming Emulsions

In their simplest persona, film-forming silicone emulsions contain an emulsified reactive silicone, usually silanol functional in nature. Crosslinking is effected most commonly with a trialkoxy silane, but other crosslinkers such as triethoxy silane (TEOS) or Q resin will also function in this role. The fourth ligand on the trialkoxy silanes allows for some customization of properties by using an amine, long chain alkyl, or other functional ligand.

Water is a necessary component to keep the condensation reaction from occurring in the package. When spread onto a surface and allowed to dry, the multiple reactive polymers and crosslinker sites react forming an interpenetrating network (IPN). In many cases, catalysts are used to affect faster and/or lower temperature cures.
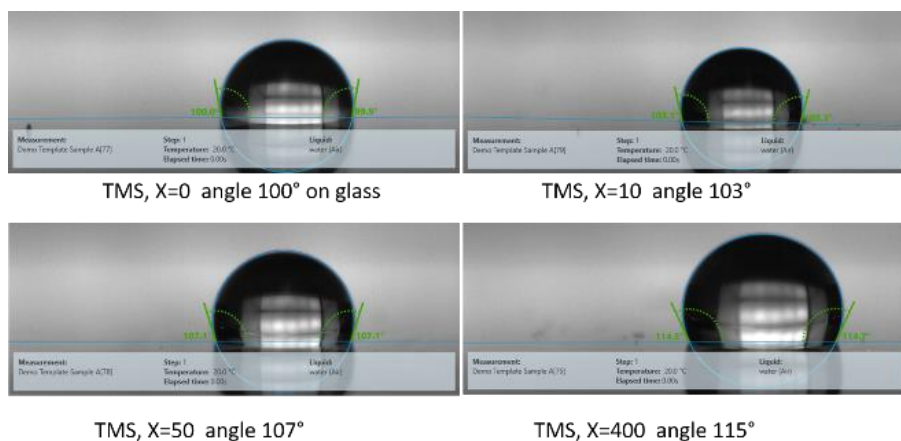
We published a study on these materials a few years ago.[2] Not wanting to spend too much space revisiting that study here, the summary is that adding 5% and 20% of these emulsions into waterborne coatings improved most of the expected properties such as stain resistance, mar resistance, COF reduction, and hardness but not the hydrophobicity. We concluded this was due to the emulsifiers whose partial hydrophilicity was antagonistic to the inherent hydrophobicity of the IPN silicone film. Including alkyl groups or amino groups on the crosslinker did modestly increase hydrophobicity as we saw with the dialkyl quaternary silicones.

We published another study in which the addition of silane-functional silicones into the mix improved the hydrophobicity (and other properties) of these film forming emulsions.[3] Typical contact angle measurements on glass surfaces are in the 80° range for this film forming approach and with silane-modified polymers added, this increased to about 90°.

Most interestingly, in the same reference, we showed that those silicone polymers with appended terminal trialkoxy silane moieties (T groups) add very good hydrophobicity when used directly rather than as additives in the film forming formulations. In this case, we achieved 115° DI water contact angle on glass. This approach remains one of the best we have today (Table 2 and Figure 2).

Table 2. Silane-modified Silicones and Results

Structure	Angle (°)
Sil(n) = 0	100
Sil(n) = 10	102
Sil(n) = 50	107
Sil(n) = 100	109
Sil(n) = 400	115
Sil(n) = 700	111

TMS, X=0 angle 100° on glass   TMS, X=10 angle 103°

TMS, X=50 angle 107°   TMS, X=400 angle 115°
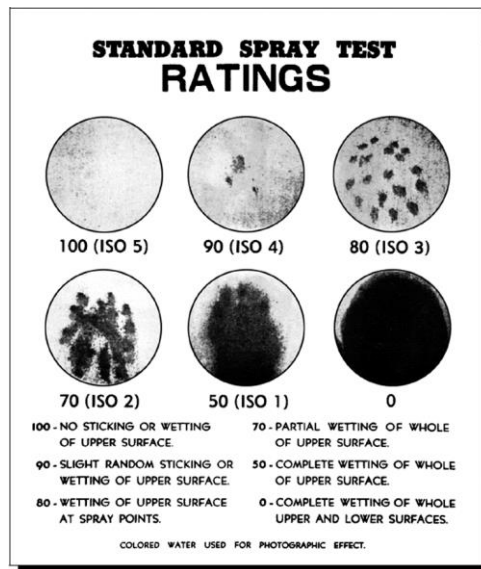
Figure 2. Contact angles.

The Use of Q And QT Resins in Solventbased Water Repellents

We synthesized a QT resin in our labs and blended it with silanol, trialkoxy silane, and catalyst, and then diluted it to 80% active content in solvent. These formulations are very similar to the film forming emulsions above with QT resins but are delivered in solvent. In this case, we can see the behavior without interference from emulsifiers.

This material was applied to four types of leather standards: brown, suede, grey, and black and compared to a commercially available over the counter product. The specific customer for this project needed a new material which performed comparably without a heat or extended ambient cure process.

The four substrate standards were cut into 3.5 square inch swatches and placed flat on the benchtop. They were sprayed with the prepared water repellent solutions and conditioned for three days at room temperature. The contact angle of DI water on these swatches was determined as described in experimental section.

We also conducted an AATCC 22 standard spray test. In this test, the swatches were sprayed with water and evaluated according to the standard chart (Figure 3). The materials were scored 0, 50, 75, 80, 90, or 100 with the score coming from the closest pattern match (100 indicates the best water repellency).

Figure 3. AATCC 22 Standard Chart.

In Table 3, we can see very good performance both across leather types and compared to the benchmark. The DI water contact angle values were up to 143° on the suede leather swatches. Our QT resin-based offering exceeded the contact angle of the benchmark on all but one leather type. The AATCC 22 spray test results (Table 3) scores were also similar to or better than the benchmark product.

**Table 3. Silane Modified Silicones and Results**

	Leather	Brown	Suede	Grey	Black
Contact angle	Benchmark	124	140	142	139
	80% QT resin/ silanol/ silane/ cat/ solvent	125	143	137	143
Spray test score	Benchmark	80	90	70	70
	80% QT resin/ silanol/ silane/ cat/ solvent	80	90	80	70

Heating for an hour at 68 °C did not significantly change the values. We tried lower actives, down to 55%, with little or no impact on performance. Accomplishing comparable performance with a different chemical approach allowed the customer to strengthen his supply chain without compromising the product.

The Use of Q and QT Resins in Waterborne Water Repellents

We wanted to evaluate waterborne versions of the QT resin containing repellents. To accomplish this while avoiding the emulsifier problem discussed elsewhere in this paper, we used sol-gels prepared from Q and alkyltrialkoxysilane (T) materials. The resultant sol-gel was a unique QT resin in ethanol/water.

Several similar sol-gel preparations were evaluated by immersing white cotton swatches in 3 mL of each sample, drying overnight, and then curing in an oven at 105 °C for 2 hours. Contact angles of DI water on the swatches were all close to each other and around 140°. The sol-gel products gave the cotton a soft feel as well. This sol-gel, designated as 87F, had a DI water contact angle of 145° and was used in the evaluations below (Figure 4).
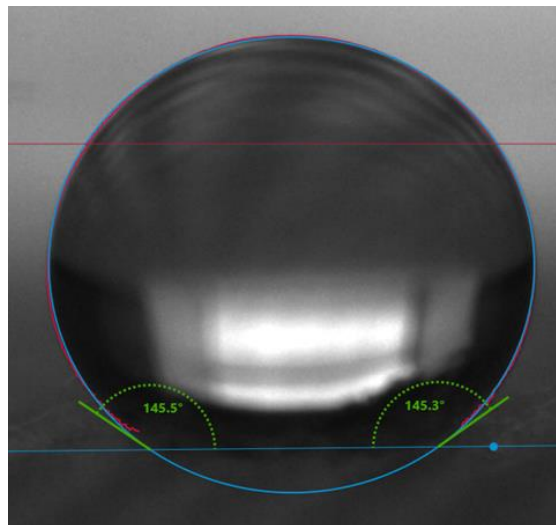
Figure 4. Water contact angle of sol-gel 87F on cotton.

To maximize performance, the QT resin sol-gel (87F) was mixed with a variety of other emulsions and crosslinkers. These included emulsions of silane functional silicones, aminosilicones, QT resins, and others. We diluted these to 10%, immersed cotton fabric swatches in them, dried the swatches in a 105 °C oven for 4 hours and rinsed with DI water. These were then evaluated using the AATCC 22 spray test against a commercial product as control.

The commercial product gave a score of 75. All the variations of QT resin sol-gels blended with <u>any emulsion</u> of silicone gave a 50 - 60 rating or worse. The four QT resin sol-gels that were blended with <u>non-emulsions</u> scored 70, close to but just below the control. These four included QT sol-gel blended with water alone (87F), aminosilicone (39D), a second aminosilicone (59A) and QT resin (55A).

Table 4. Sol-Gel Blend Results

Sample	Description	AATCC 22 Rating	AATCC 193 Rating
Control	Commercial product	75	3
87F	Sol-gel base	70	na*
55A	Sol-gel + QT resin	70	na
39D	Sol-gel + QT + aminosilicone 1	70	2.5
59A	Sol-gel + QT + aminosilicone 2	70	3.5
187	QT resin emulsion	70	na
28A	Silane modified silicone emulsion	50	na
16A	QT resin emulsion (187) + 28A	60	na
16B	16A + DTQ resin emulsion	60	na
16C	16A + Amino film forming emulsion 1	60	na
16G	16A + Sol-gel base (87F)	60	na
41B	16A + Amino film forming emulsion 1	0	na
41C	16G + More 28A	60	na
41D	16A + Amino film forming emulsion 2	0	na
41E	16A + Phenyl DTQ resin emulsion	0	na
41F	16A + Amino MQ resin emulsion	60	na
41H	16A + Q resin emulsion	60	na

*na – not applicable

Based both on the fact that any emulsion blend dropped the score relative to any non-emulsion blended sol-gel and the fact that this performance reduction is mostly small; it is believed that this is again the hydrophilicity of the emulsifiers that is adversely affecting the hydrophobicity. A secondary benefit here is that relative to the commercial product, the QT resin sol-gel treated materials felt much softer.

Samples 39D and 59A were further evaluated by AATCC 193 (a waterborne stain repellency evaluation). This test involves applying five standard aqueous dyed stains each with

progressively lower surface tension. A grade corresponding to the standard at which beading still occurs is given and ranges from 0 to 5 (best).   The standards are shown in Table 5, and the results are in Table 4.

Table 5. AATCC 193 Standards

AATCC 193 Standard Test Liquids			
AATCC Aqueous Solution Repellency Grade Number	Color	Composition (volume/volume)	Surface Tension (mN/m)
0	No color	None (fails 98% water)	
1	Blue	98:2 / Water: IPA	59
2	Pink	95:5 / Water: IPA	50
3	Orange	90:10 / Water: IPA	42
4	Yellow	80:20 / Water: IPA	33
5	Dark Blue	70:30 / Water: IPA	28

Sample 59A had the highest score at 3.5 meaning wetting starts to occur with the 20% IPA standard 4 solution. This exceeds the benchmark which completely absorbed standard 4. Figure 5 shows the side-by-side performances of sample 59A and the benchmark.
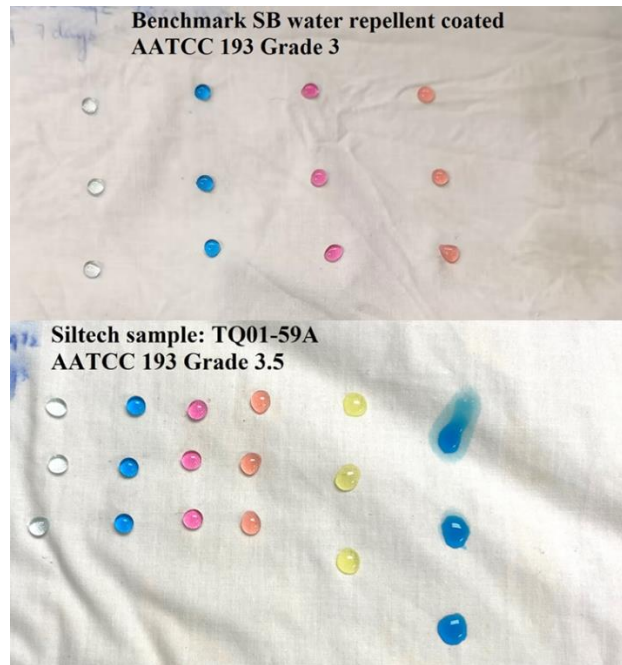
Figure 5. AATCC 193 results for sol-gel 59A.

Conclusions

Anchoring and inclusion of alkyl chains into a silicone formulation increases the hydrophobicity. Increasing the silicone chain length of the alkyl chain also increases the hydrophobicity. Contact angles of 112° DI water on glass can be achieved with this approach. The use of anchored silicones can achieve 115° DI water contact angle on glass.

Additional crosslinking of the silicone backbone with the use of QT resins provides a strong increase in the hydrophobicity. The silicone IPN often provides softness, slip, and additional protections typically seen with low COF coatings. Contact angle of 145° of DI water on leather can be achieved with this technology.

Waterborne systems are problematic because the emulsifiers needed to stabilize the oils in water also interfere with the hydrophobicity. To resolve this inherent weakness of traditional emulsion approaches to water-based systems, we have applied a unique sol-gel method.

We were able to match and even improve the water repellency of a solventbased benchmark using this sol-gel approach. Although on cotton rather than glass, this product exceeded the 140° contact angle often cited as the cutoff for super hydrophobicity without using nano-particles to stimulate mesostructure formation.

Continued exploration of this exciting new area in silicon chemistry is likely to result in many more interesting results in the future. We look forward to sharing those with the reader.

References

1)   T. Cheung and B. Ruckle, Novel OrganoSilicone Fluoro-Free Anti-Graffiti Agents, Proceedings of the 45th Annual International Waterborne, High-Solids and Powder Coatings Symposium, New Orleans, LA, **2018**.
2)   T. Cheung, B. Ruckle and S. Wilkowski, Reactive Siloxane Emulsions in Waterborne Coatings, Proceedings of the 45th Annual International Waterborne, High-Solids and Powder Coatings Symposium, New Orleans, LA, **2018**.
3)   B. Ruckle, T. Cheung and M. Gunther, The Evolution of Trialkoxysilane Monomers to Hybrid Silicones, Coatings Trends and Technologies (CTT), Chicago, IL, **2021**.