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.

Bob Ruckle; Tom-Seung Cheung; & Yanjun Luo

Siltech Corporation
Toronto, ON Canada
Robert@siltech.com, Tom2@siltech.com
+1 (416) 424 4567

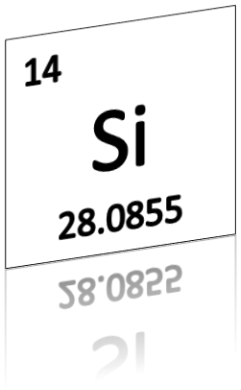
Agenda

- Quick Silicone Background
- State of the Current Art
- New Approaches
- Conclusions

Hypothesis

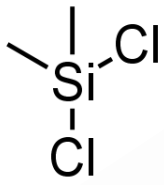
Highly cross linked silicon systems based on Q and T moieties will provide improved water repellency and protection.

The Road from Silicon to Silicone



1) **Methanol**: A naturally occurring biochemical very common in nature. Generally made from Natural Gas.
2) **HCl**: a naturally occurring mineral acid

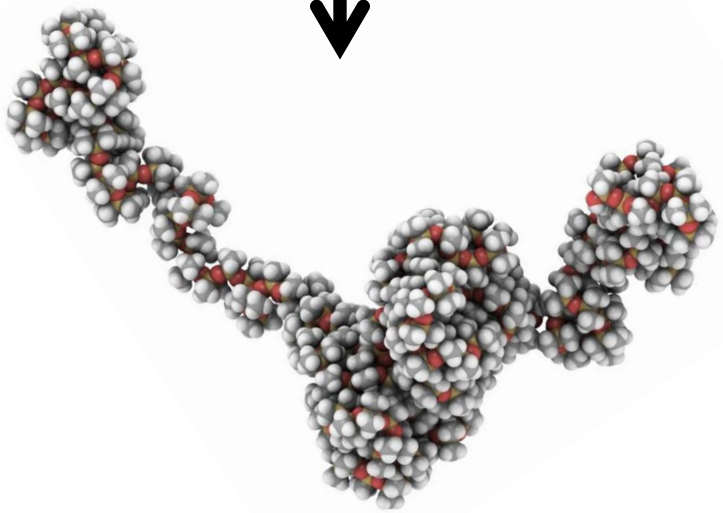
Catalysts:
From the Earth



A variety of **chlorosilanes**: man-made, highly reactive intermediates. These are only used by chemical companies.

Water:
Natural

Elemental **Silicon**:
Abundant in the earth's crust predominately as oxide minerals; silica, sand, quartz, or gemstones.



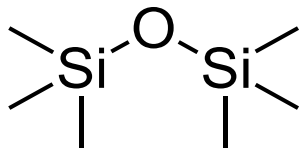
Why Use Silicone Additives: PDMS Properties

- Free Radical Stability (O_2, O_3, Sunlight)
- Insulative (Electrical and Thermal)
- High Thermal Stability: 250°C
- Low Surface Tension: 20 mN/m
- Excellent Spreading & Wetting
- Minimal Interfacial Tension
- Low Coefficient of Friction
- Low $T_{g:}$ 153°K: -120°C
- Low Odor & Toxicity
- Water Repellent
- Gas Permeable
- **Incompatible**

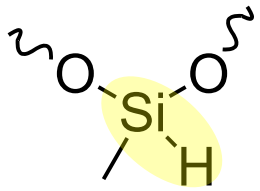
Affects other properties to differing degrees

To remedy incompatibility: react with an organic moiety

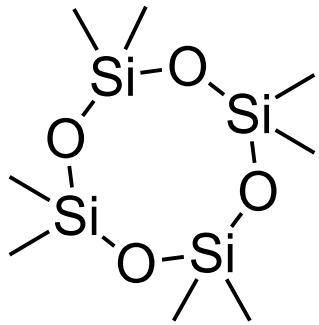
Silicone Hybrid Chemistry



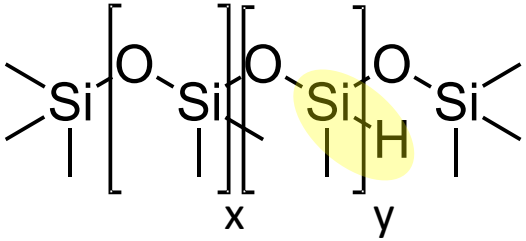
End Capper (MM)



Reactive Site (D*)

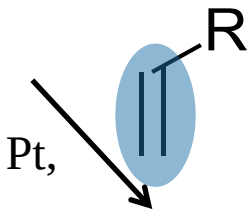


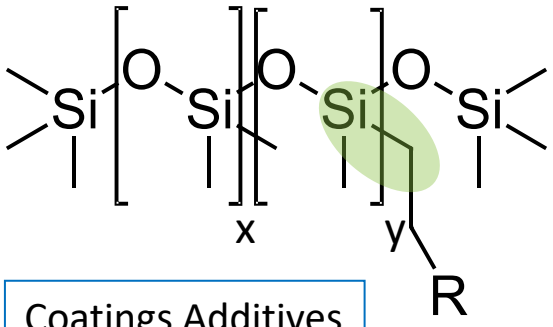
Chain Extender (D_4)



Silanic H type

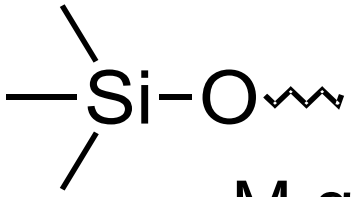
Bio source



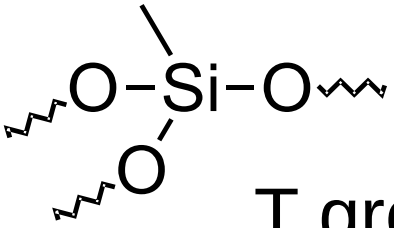


Coatings Additives

Silicon Nomenclature

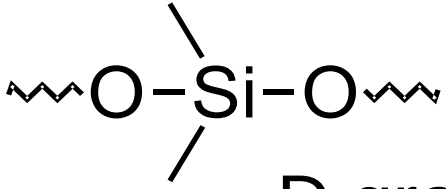


M group

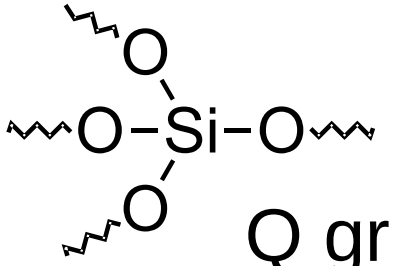


T group

Trialkoxy silanes are T groups



D group



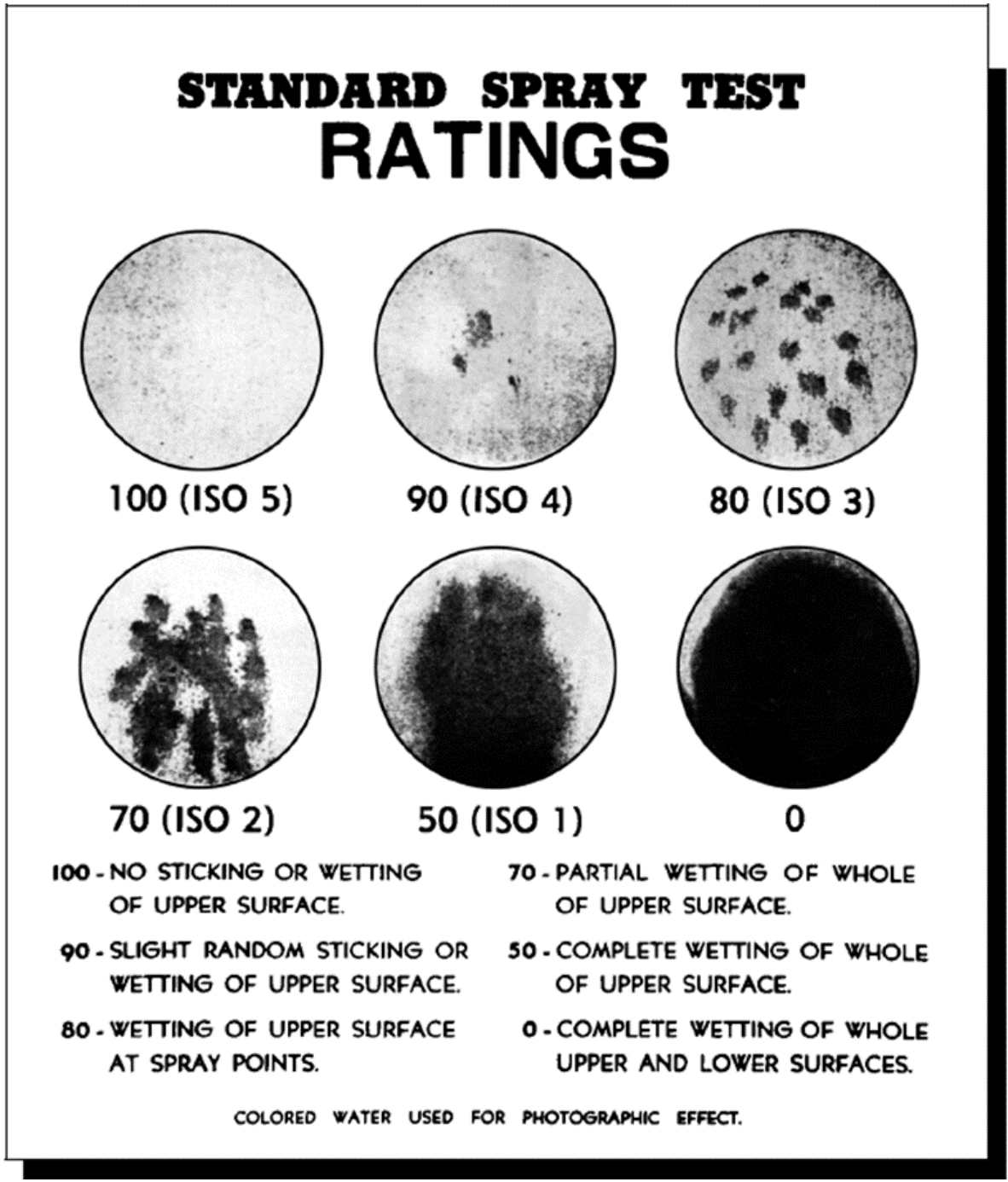
Q group

MD_xM is the standard formula for silicone

Experimental

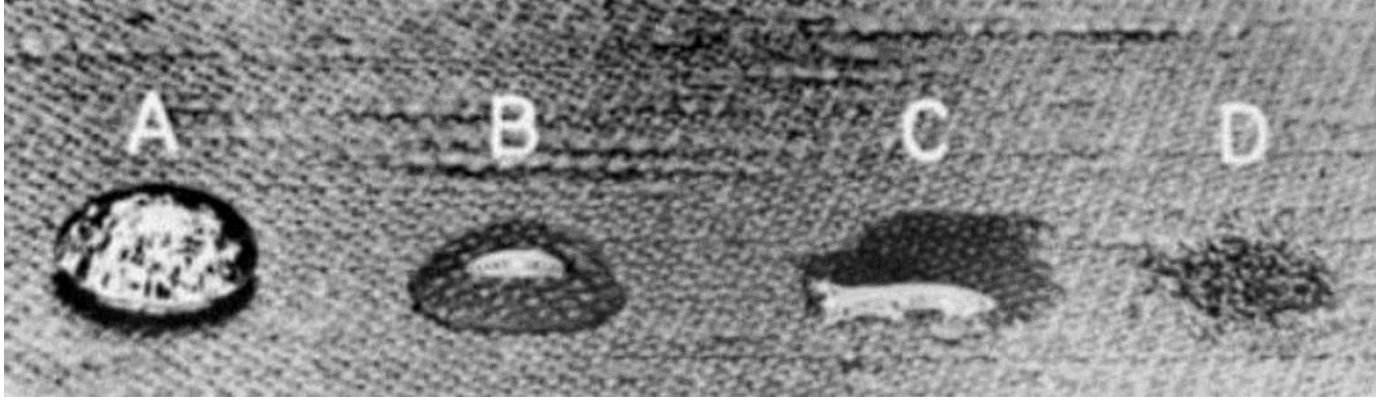
- A series of reactive Q and T resin based formulations are evaluated for contact angle and water repellency.
- Contact angle is measured using the KRUSS MobileDrop GH11 Measuring system.
- Sliding angle is determined by the smallest inclination angle of a sample that causes a 50 µL water droplet to start sliding.
- AATCC 22 and AATCC 193 methods are used to evaluated repellency on fabrics

AATCC 22 Standard Spray Test



Fabrics Used

AATCC 193



A: pass
B: borderline rounded droplet
C: fail wicking
D: fail wetted

AATCC 193 Standard Test Liquids			
AATCC Aqueous Solution Repellency Grade (0-5 best)	Color	Water/IPA (vol/vol)	Surface Tension (mN/m)
0	None	100:0	72
1	Blue	98:2	59
2	Pink	95:5	50
3	Orange	90:10	42
4	Yellow	80:20	33
5	Dark Blue	70:30	28

Example Untreated Cotton

Existing Water Repellents Approaches (without C-F bonds)

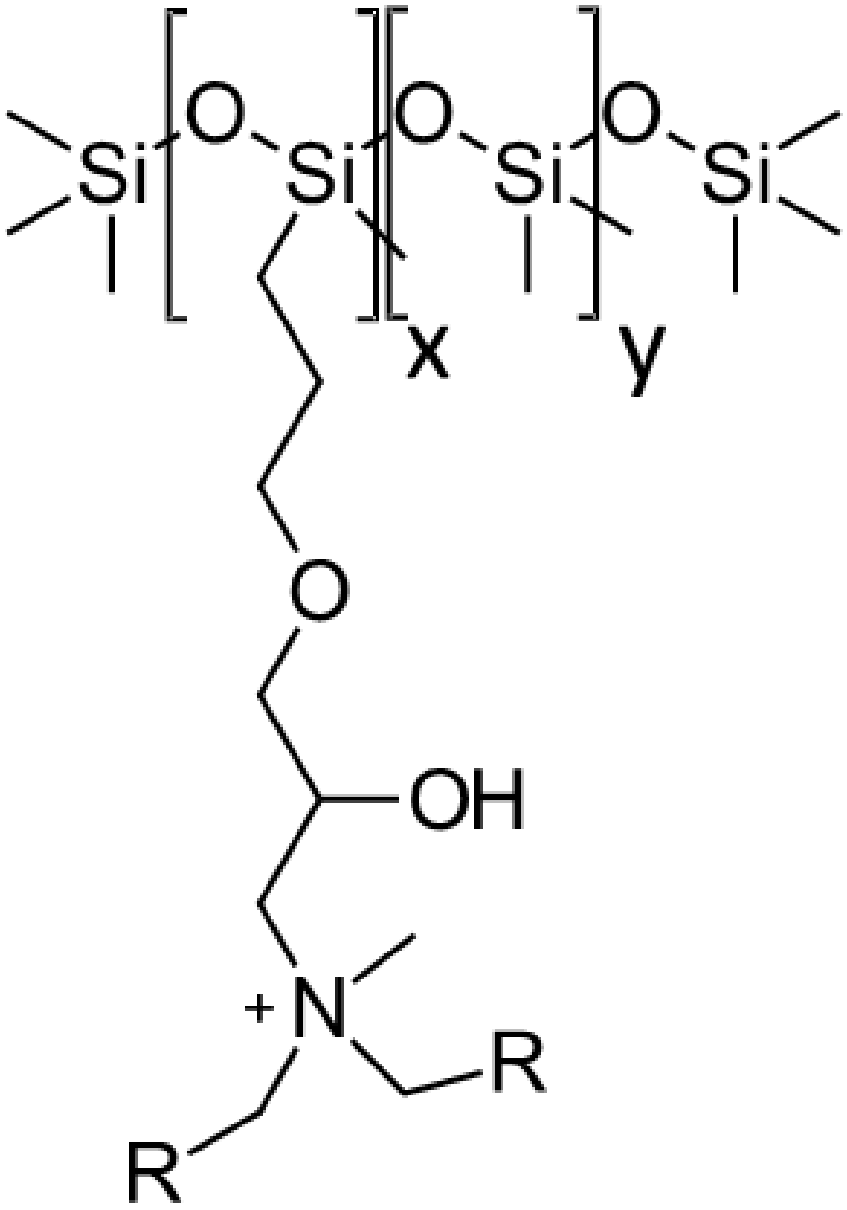
- DiAlkyl Quat

  D resin types with dialkyl quaternary ammonium chain

- Cured Film Forming Emulsions

  D and T resins with emulsifiers

Pendant Dialkyl Quaternium Silicone Structure



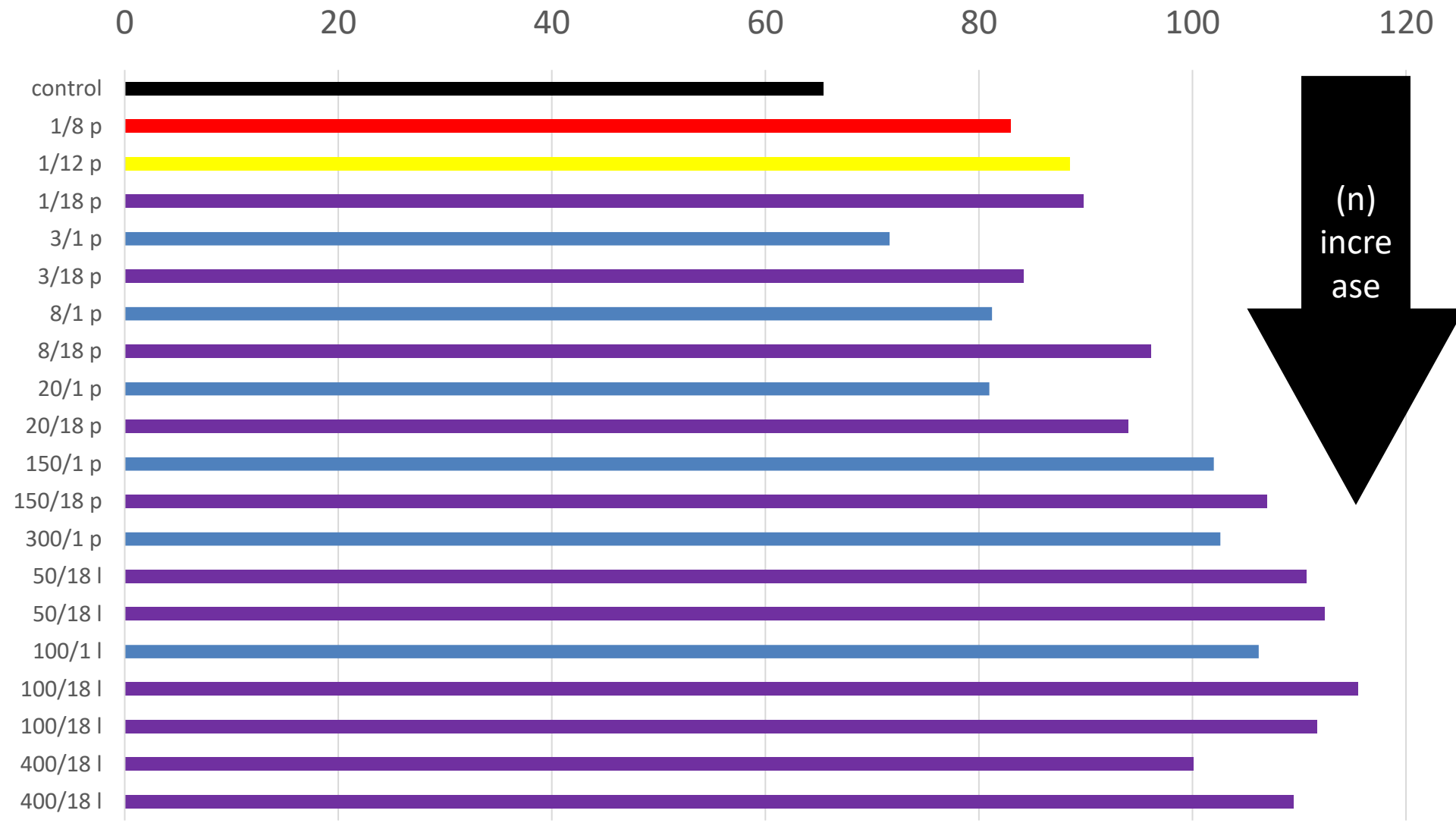
Sil(n): x+y
Alkyl(n): R
Are both variables.
x/y ratio
Pendant/linear
Are minor variables at best

Glass Contact Angle

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

115°

Glass Contact Angle: DiAlkyl Silicone Quats

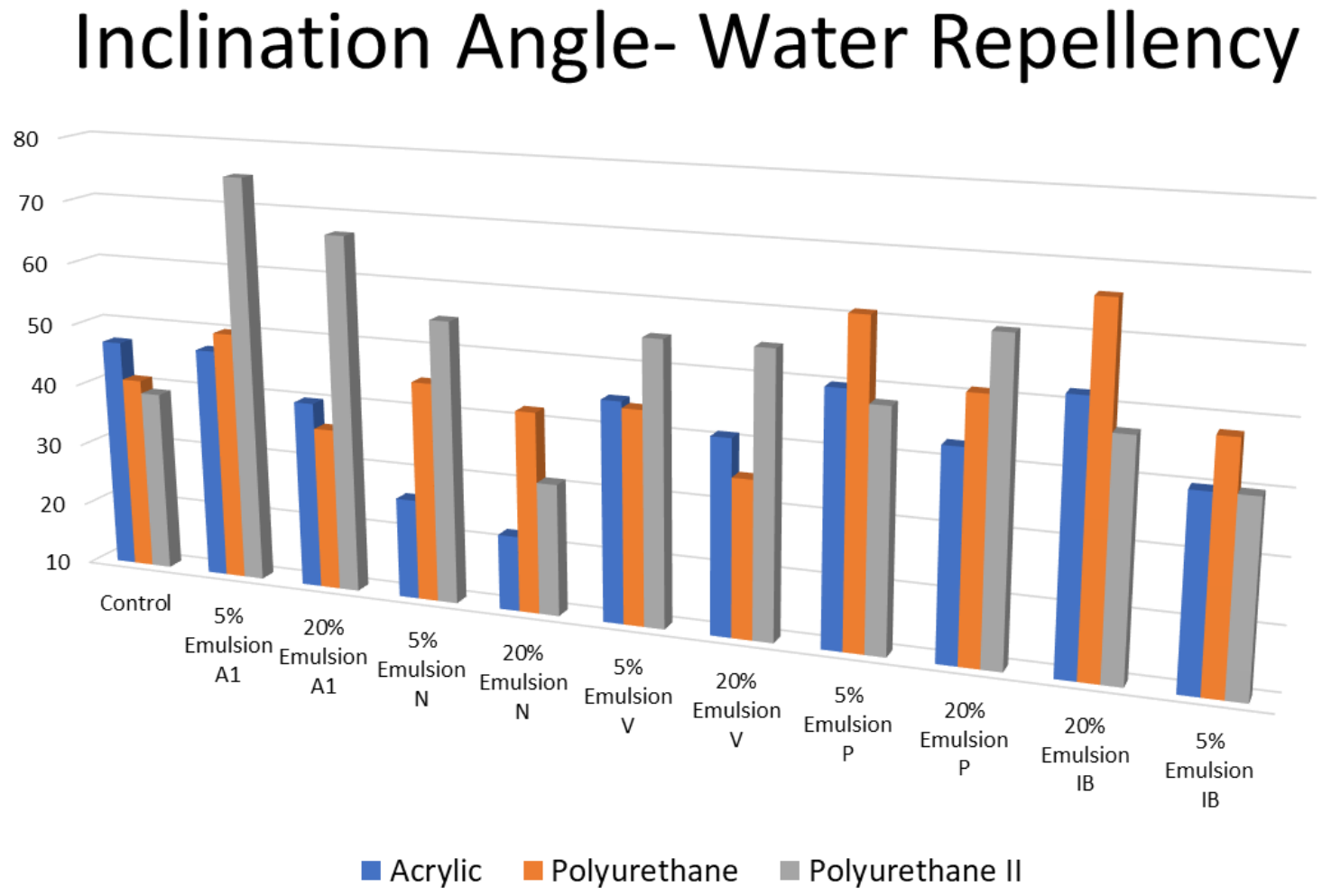


DT Resin Emulsions

- Emulsified MD_xM silicones
- Alkoxy T groups
- React when dried to form a crosslinked film.

Film Forming Emulsions
(from 2018 presentation)

~ 80°



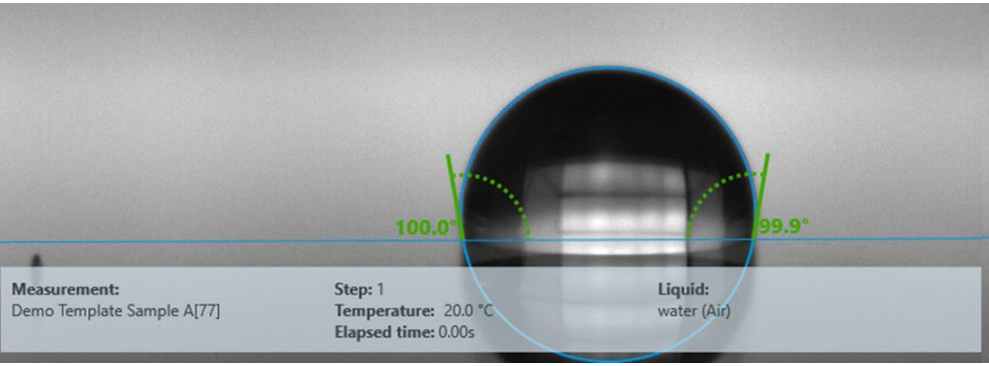
Result WB DT Emulsions

Our belief is that the emulsifiers in these materials is providing wetting which offsets the inherent hydrophobic nature of the X-linked silicone network.

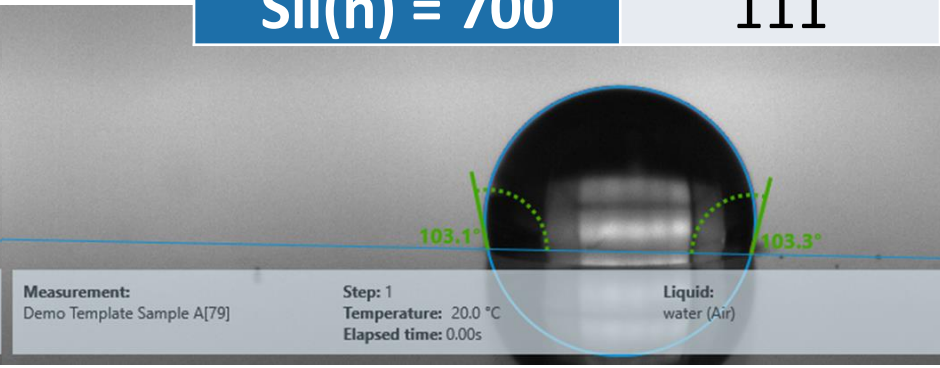
115°

TD_xT Silicones Used Alone

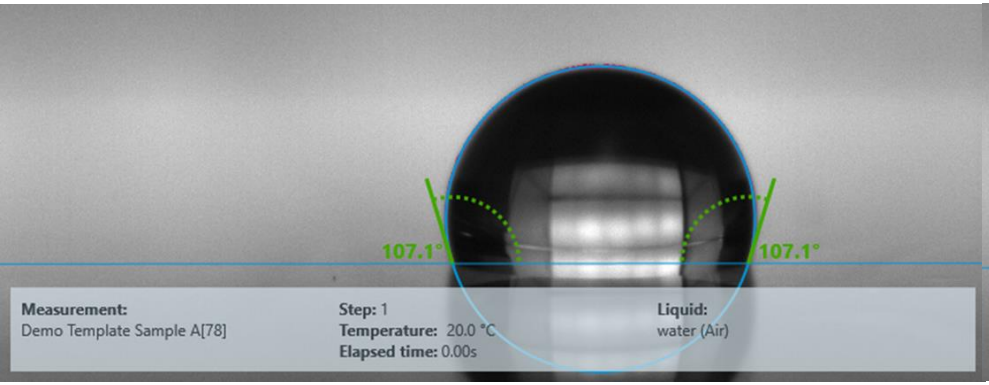
Structure	Angle (°)
Sil(n) = 0	100
Sil(n) = 10	103
Sil(n) = 50	107
Sil(n) = 100	109
Sil(n) = 400	115
Sil(n) = 700	111



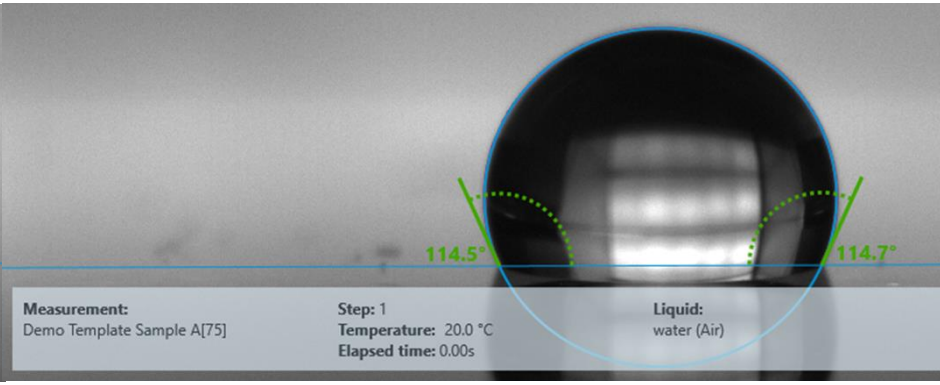
X=0 angle 100° on glass



X=10 angle 103°



X=50 angle 107°



X=400 angle 115°

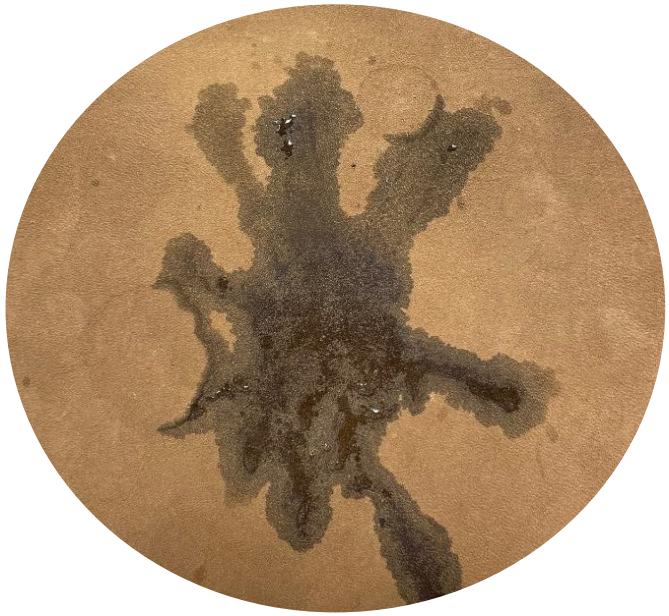
142° (on leather)

SB QT Resins vs. Commercial Benchmark

3 day R.T. cure + 1 hour @ 68 degree C		Test specimens			
		Brown Leather	Suede Leather	Grey Fabric	Black Fabric
Benchmark	WCA	117.7°	142.2°	136.9°	144.6°
	Water droplet	rolls / leaves streaks	Wicks ~45s	rolls off	rolls off
YL7-53B	WCA	124.7°	141.6°	136.9°	141.0°
	Water droplet	rolls / leaves streaks	rolls off	rolls off	rolls off

AATCC 22 Spray Test on Brown Leather

Benchmark water repellent **Rating: 80 (ISO 3)**	**Siltech YL7-53B** **Rating: 80 (ISO 3)**
	

Benchmark water repellent Rating: 70 (ISO 3)	Siltech YL7-53B Rating: 80 (ISO 3)
	

Suede

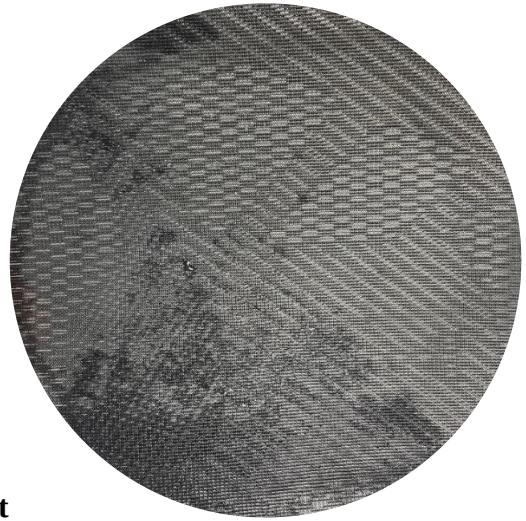
Benchmark water repellent Rating: 70 (ISO 3)	Siltech YL7-53B Rating: 70 (ISO 3)
	

Brown

Benchmark water repellent

Rating: 90 (ISO 4)

front



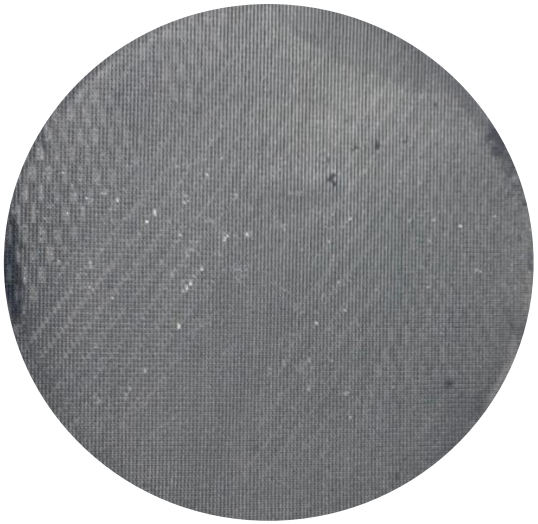
back

Grey

Siltech YL7-53B

Rating: 90 (ISO 4)

front



back

QT Resins in Solvent

	Leather	Brown	Suede	Grey	Black
Contact angle	Benchmark	118°	142°	137°	145°
	80% QT resin/ silanol/ silane/ cat/ solvent	125°	143°	137°	141°
Spray test score	Benchmark	80	70	90	70
	80% QT resin/ silanol/ silane/ cat/ solvent	80	80	90	70

108°

Glass Contact Angle QT Resins in Solvent

Sample	WCA	sliding angle
Blank	84°	22°
Benchmark	109°	6.5°
YL7-143B	108°	27°

SB QT Resins are better

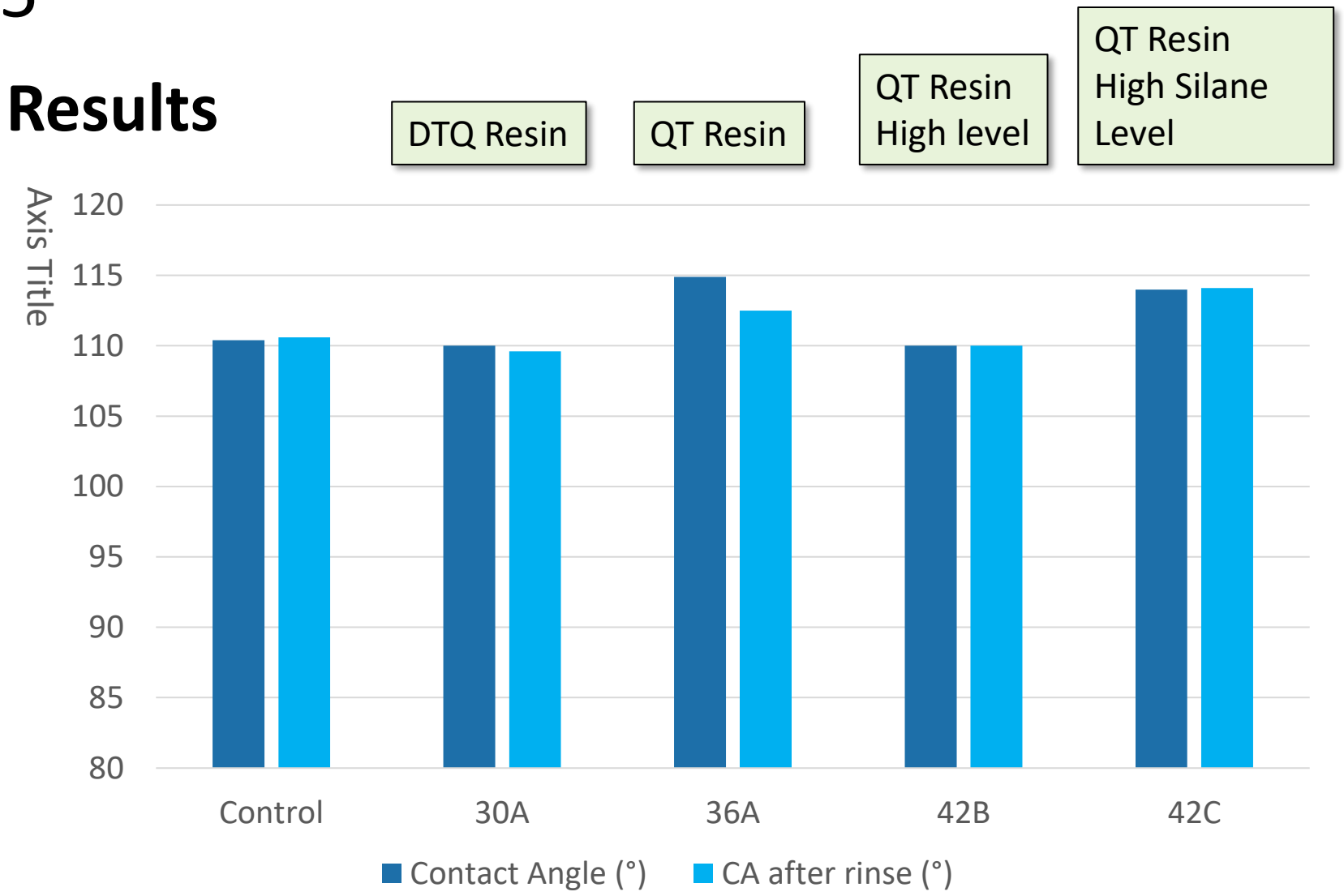
- The SB QT resins used are very similar to the film forming emulsions reported in 2018 but without emulsifier
- Performance is improved and comparable to commercial benchmark

QT Resin Emulsions w/ Polysilazine

Sample	Formulation	CA (°)	CA after rinse (°)	SA (°)	SA after rinse (°)	Durability
Commercial DIY "Ceramic" Car Care Product		111	111	41	40	5
30A	1% Polysilazine/ 0.5 % Aminosilicone 1/ 1% DTQ Resin/ 1% SILANE	110	109	35	34	4
36A	5% Polysilazine/0.5% Aminosilicone 2 / 1% QT resin / 1% SILANE/ 1% PDMS/ 1% Alkyl Silicone	115	113	44	38	4
42B	5% Polysilazine/ 0.5% Aminosilicone 2 / 11% % QT resin / 1% SILANE/ 1% Alkyl Silicone	110	110	25	25	5
42C	5% Polysilazine / 0.5% Aminosilicone 2 / 1% QT resin / 6% SILANE / 1% PDMS/ 1% Alkyl Silicone	114	114	35	33	5

105°

Results



Durability is determined by contact angle lost after rinsing under a 25℃ flow of water for 1 minute.

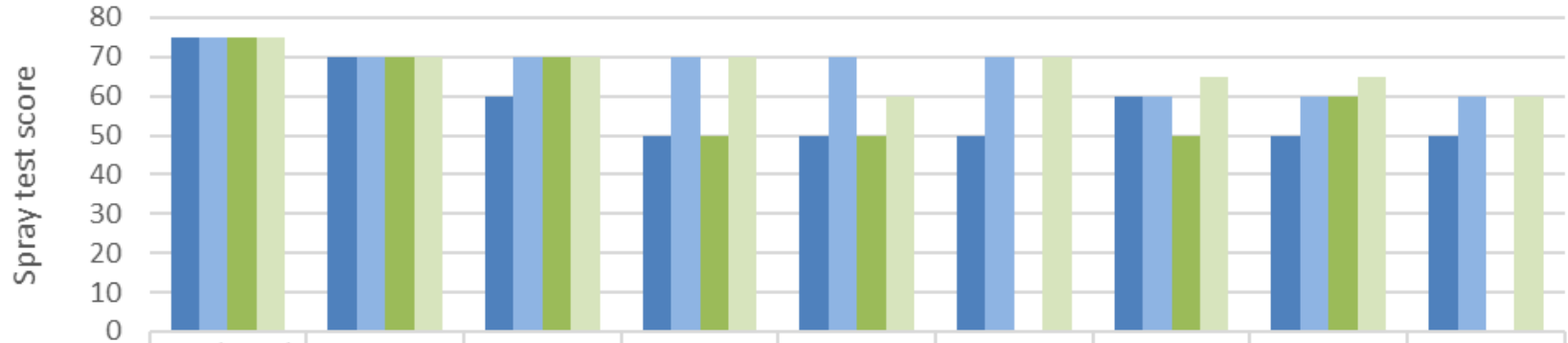
QT Sol-Gel Experimental

- Prepare premixed samples based on various Siltech emulsions, best sol-gel sample (in ethanol), water, and glycol ethers.
- Prepare 10% dilution of these samples and coat on untreated cotton fabric
- Dry the cotton fabrics by using the following methods.
  - Heat 105°C oven for 4 hours or
  - Dried at RT for 7 days
- Measure contact angle, AATCC 22 spray test, and softness before and after rinsing with water.
- For samples that shows good AATCC 22 spray test result, perform AATCC 193 aqueous liquid repellency test.

Sol-Gels of QT Resins (WB but no Emulsifier)

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

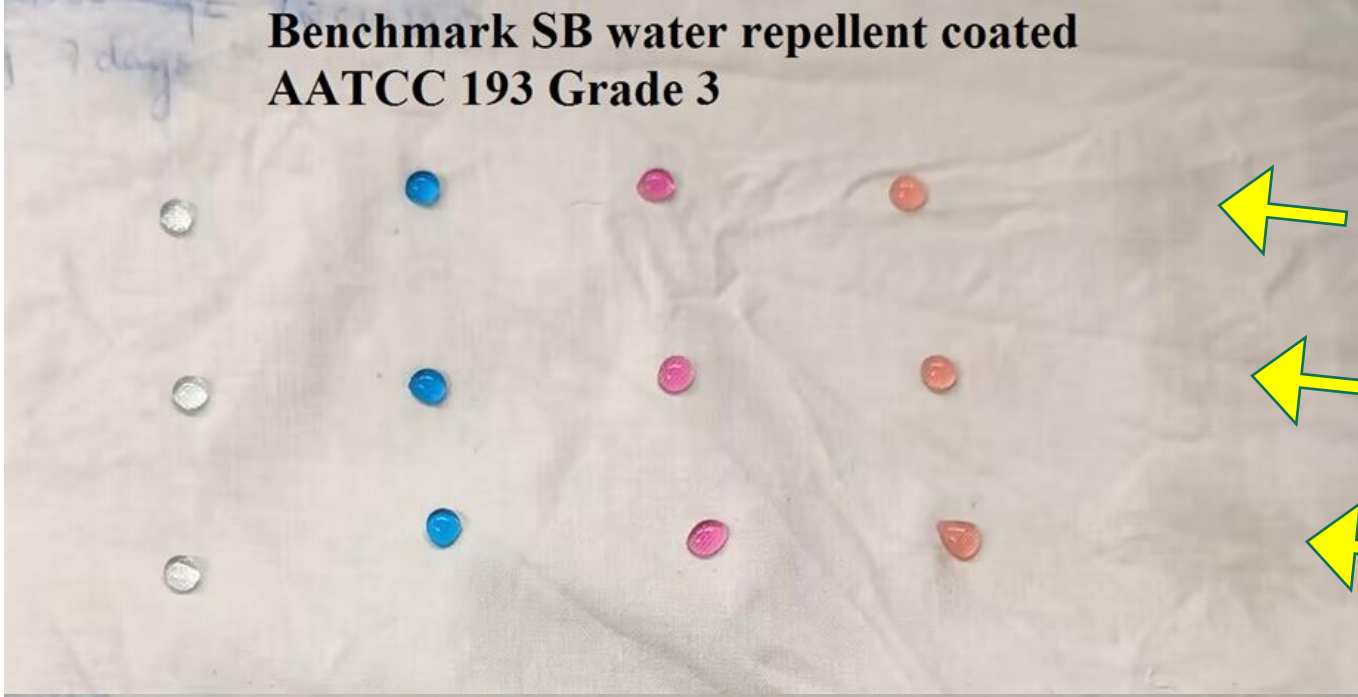
AATCC 22 spray test result for heat cured and R.T. cured sample before and after rinse

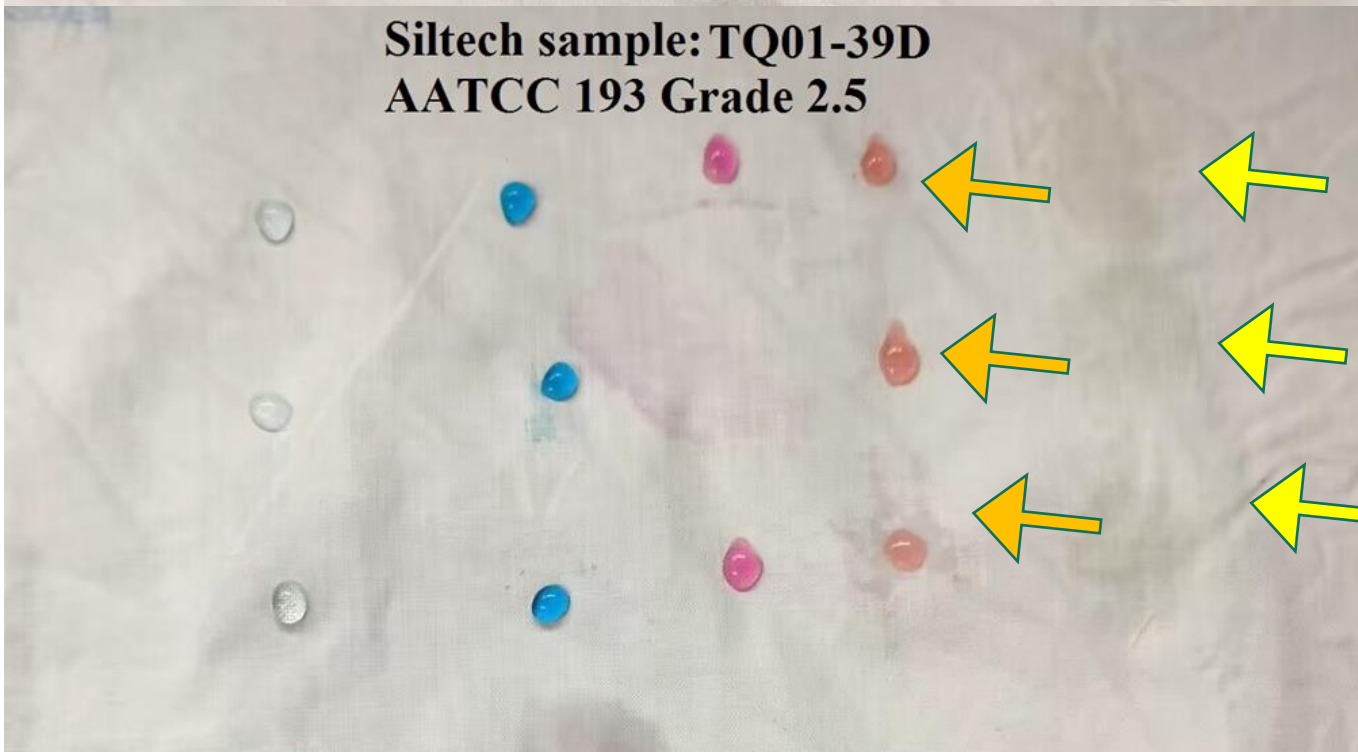


	Benchmark solvent-based silicone water repellent	TQ01-39D	TQ01-59A	TQ01-55A	TC15-87F	BQ-19-187	TQ01-16A	TQ01-16G	TQ 01-41C
heat cure-before rinse	75	70	60	50	50	50	60	50	50
heat cure-after rinse	75	70	70	70	70	70	60	60	60
R.T. cure-before rinse	75	70	70	50	50	0	50	60	0
R.T. cure-after rinse	75	70	70	70	60	70	65	65	60

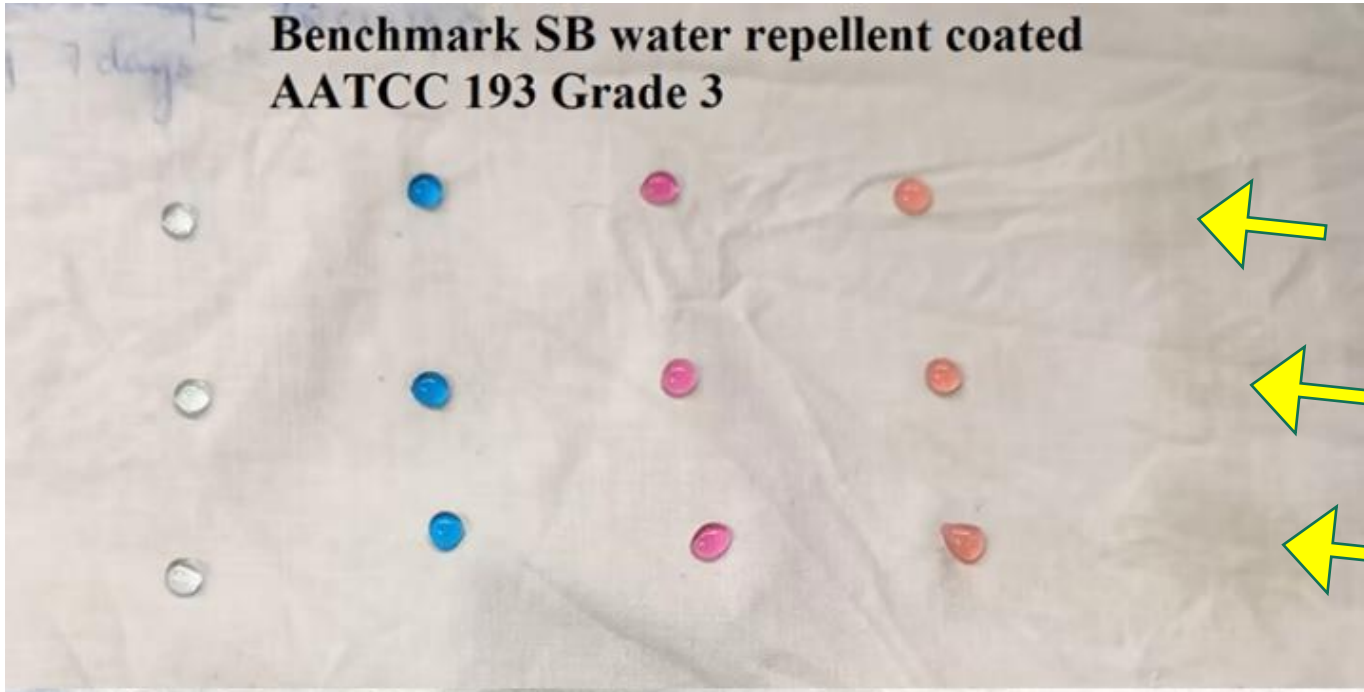
- Heat Curing not critical
- Rinsing can show difference (esp. with emulsions)
- 39D and 59A are the best (mixed with aminosilicones)
- Probably better than 87F and 55A (sol-gel alone)

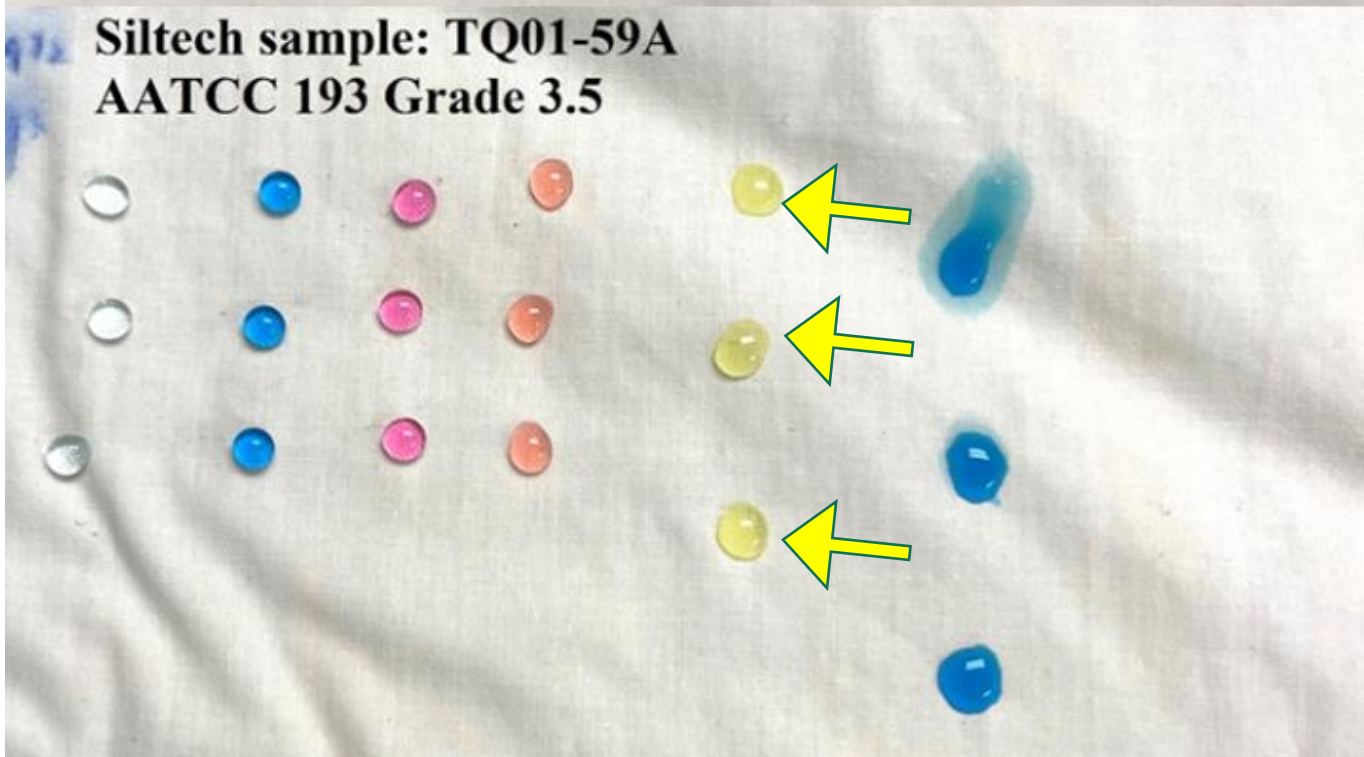
39D: Sol-gel / QT resin / aminosilicone #1





59A: Sol-gel / QT resin / aminosilicone #2

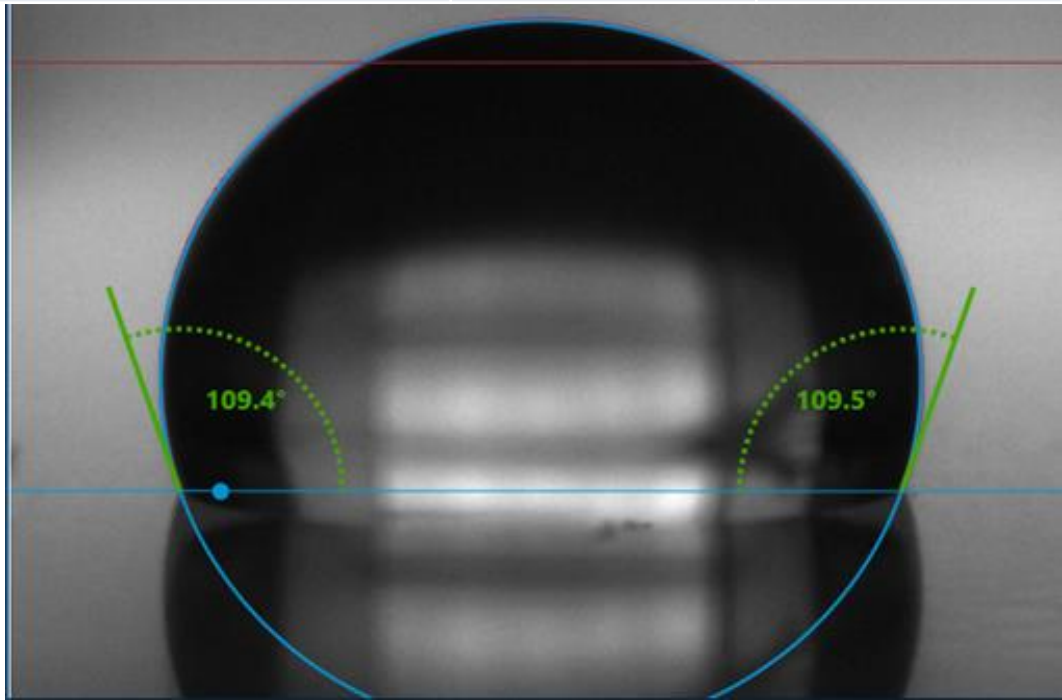




114°

Sol-Gel QT Resins: Glass Contact Angle

system	Sample	WCA	sliding angle
	Blank	84.2°	22°
solvent-based silicone	Benchmark	108.7°	6.5°
water-based	55A	109.4°	20°
water-based	87F	87.2°	26°
water-based	59A	105.3°	30°
water-based	39D	114.3°	42.5°



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.

Water/Glass Contact Angles of 115° are achieved with this approach.

This approach can be pricey, hard to formulate and has an alkyl “hand” but repellency and durability are maxed out.

Conclusions

SB QT resins improve performance over the DT emulsions (state of the art in 2018).

The additional crosslinking of the silicone backbone from the QT resins provides a strong increase in the hydrophobicity. Water/Fabric CA of 145° and Water/Glass CA of 108° is achieved.

As an added benefit, the silicone IPN provides softness, slip, and additional protections typically seen with low COF coatings.

Conclusions

TDxT systems discussed in 2018 gave Water/Glass CA of 115° and remain a great approach.

Waterborne systems are problematic: emulsifiers interfere with the hydrophobicity. To resolve this weakness, we have applied a unique sol-gel method.

This improved the water repellency of a SB benchmark. Water/Cotton Contact Angles of 143° and Water/Glass CA of 114° were achieved.

Thank You