Replacing PFAS with Modern Silicon Cross-linking Moieties to Confer Water and Oil Repellency, Release and Protection Properties.

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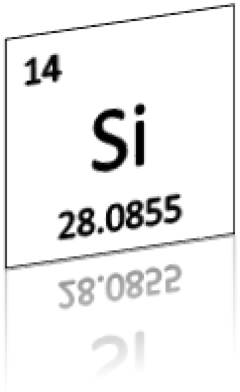
A series of reactive Q and T resins, $Si(OR)_4$ and $R'(SiOR)_3$ based units respectively, are formulated with reactive silicone polymers. The systems are evaluated in various fabric, leather, or hard surface treatments for water and oil repellency, release and anti-graffiti properties on various surfaces.

Agenda

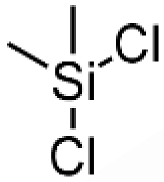
- Quick Silicone Background
- Replacing PFAS
- ST and COF
- Hydrophobicity
- Oleophobicity
- Chemical Resistance
- Conclusions

The Road from Silicon to Silicone



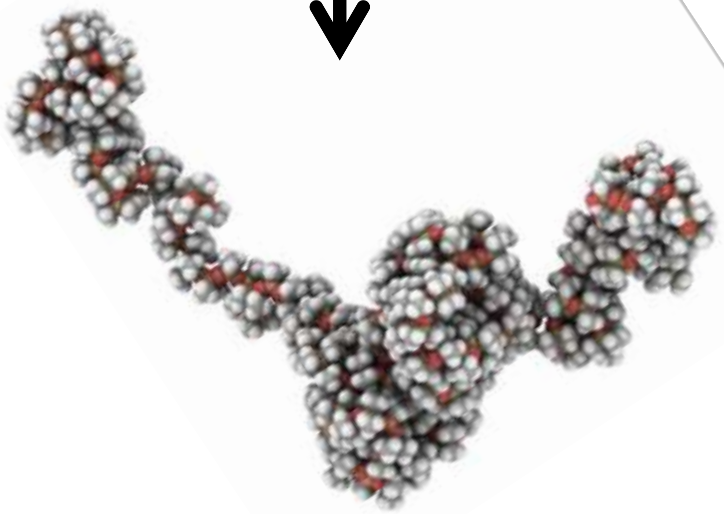
1) **Methanol**: A naturally occurring biochemical very common in nature. Generally made from Natural Gas.
2) **HCl**: a naturally occurring mineral acid

Catalysts:
From the Earth



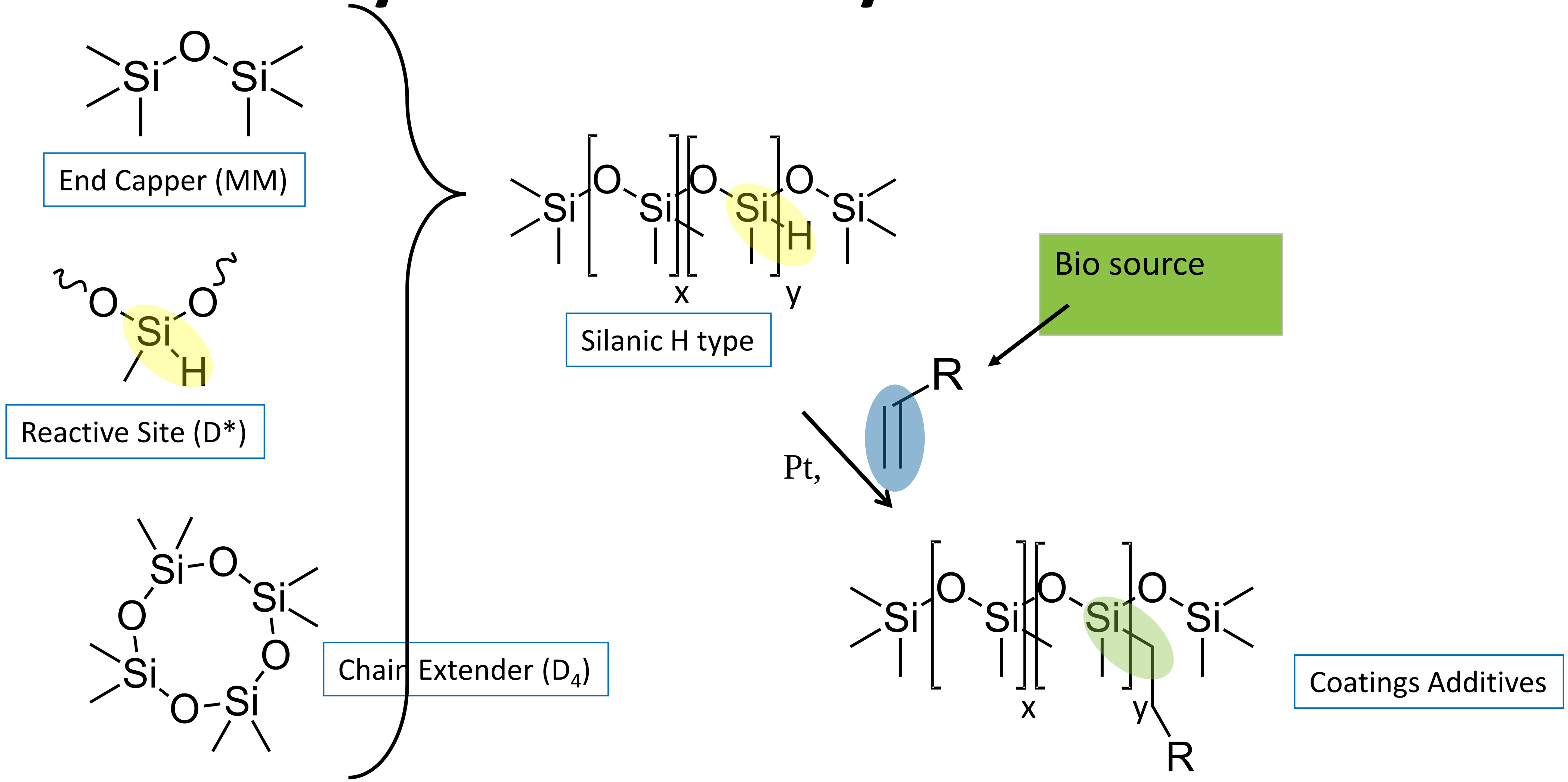
A variety of **chlorosilanes**: man-made, highly reactive intermediates. These are only used by chemical companies.

Water:
Natural

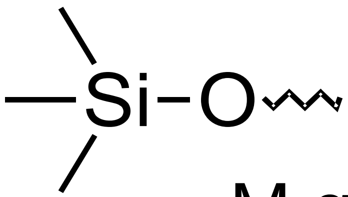


Elemental **Silicon**:
Abundant in the earth's crust predominately as oxide minerals; silica, sand, quartz, or gemstones.

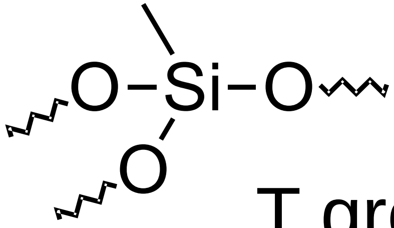
Silicone Hybrid Chemistry



Silicon Nomenclature

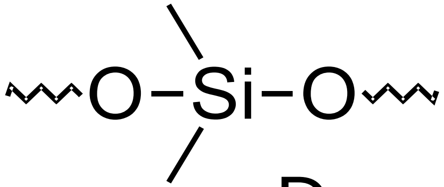


M group

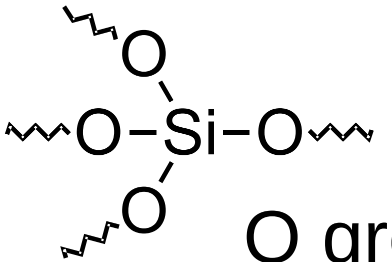


T group

Trialkoxy silanes are T groups



D group



Q group

MD_xM is the standard formula for silicone

PFAS

- EPA and ECHA are acting to heavily regulate compounds with ~$(CF_2)_n$ where $n \geq 2$ (EPA) or $n \geq 1$ (EU).
- Many End Users are Attempting to Formulate These Out.

The Things PFAS Do Well.

- Lower Surface Tension/ Energy
- COF Reduction
- Water Repellency
- Oil Repellency
- Chemical Resistance
- Low Use Level

How Do PDMS Types Compare?

PFAS / PDMS

PFAS unique properties

ST 14-20 mN/m

Water and Oil Repellency

Chemical Stability.

PDMS based materials:

ST 20-30 mN/m

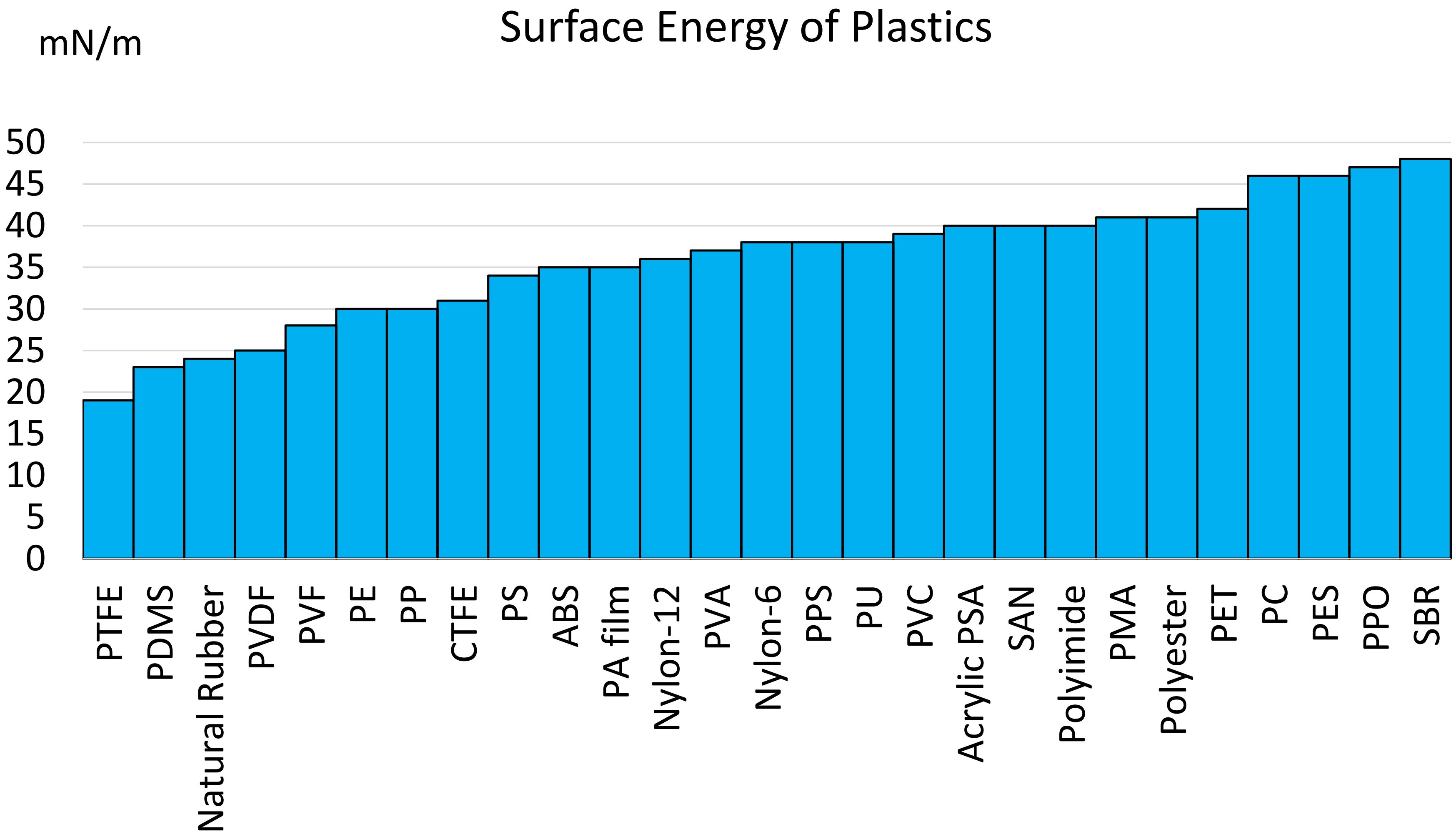
Water Repellency

Can we develop Oil Repellency?

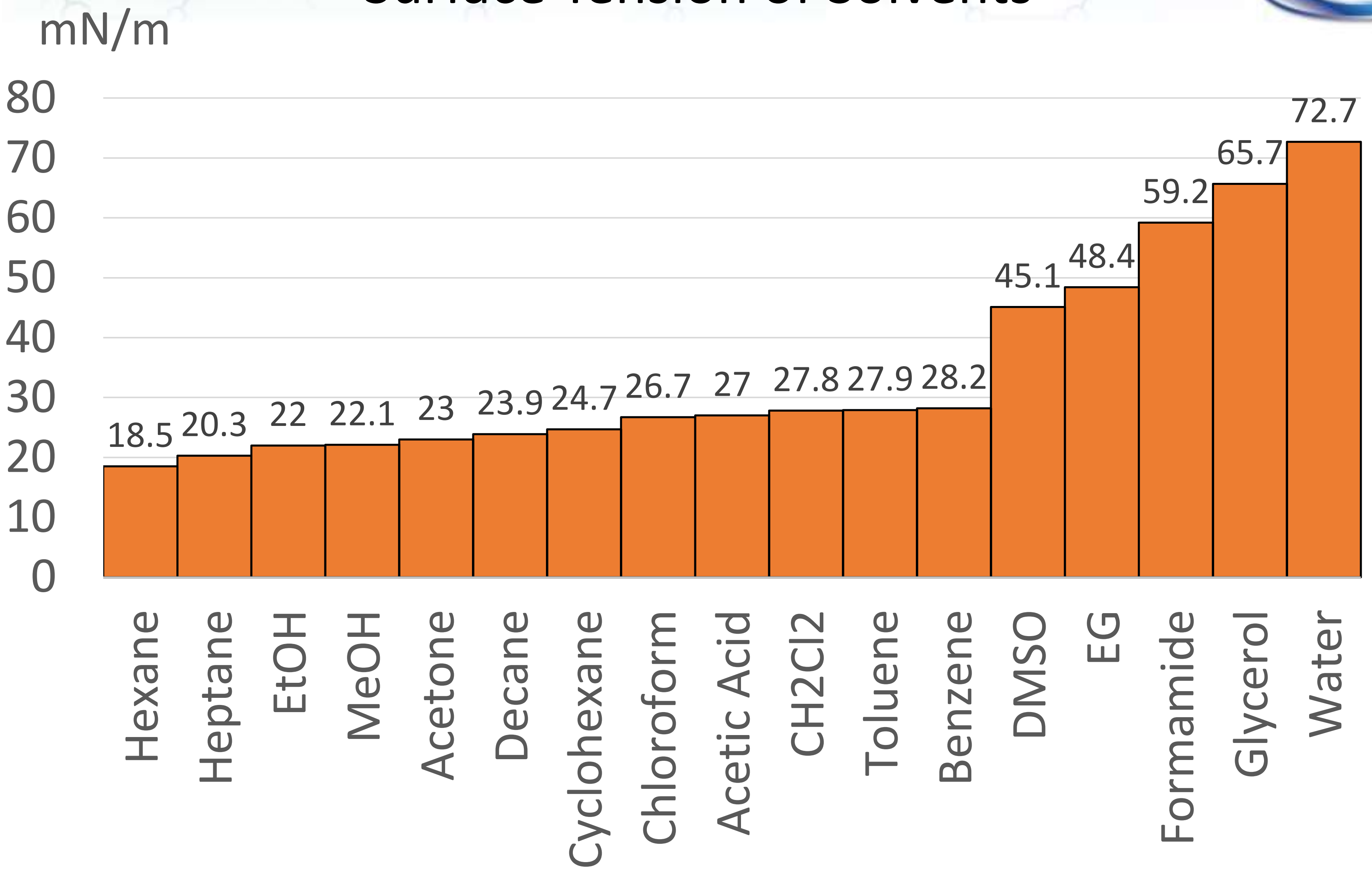
Surface Energy/ Surface Tension

- PDMS derivatives can achieve ST in the low 20 mN/m range
- The best PFAS based materials can achieve lower ST, down to 14 mN/m
- There is nothing between 14 and 20 to be wetted
- Use levels differ by a factor of about 10. Which is offset by higher dollar cost.

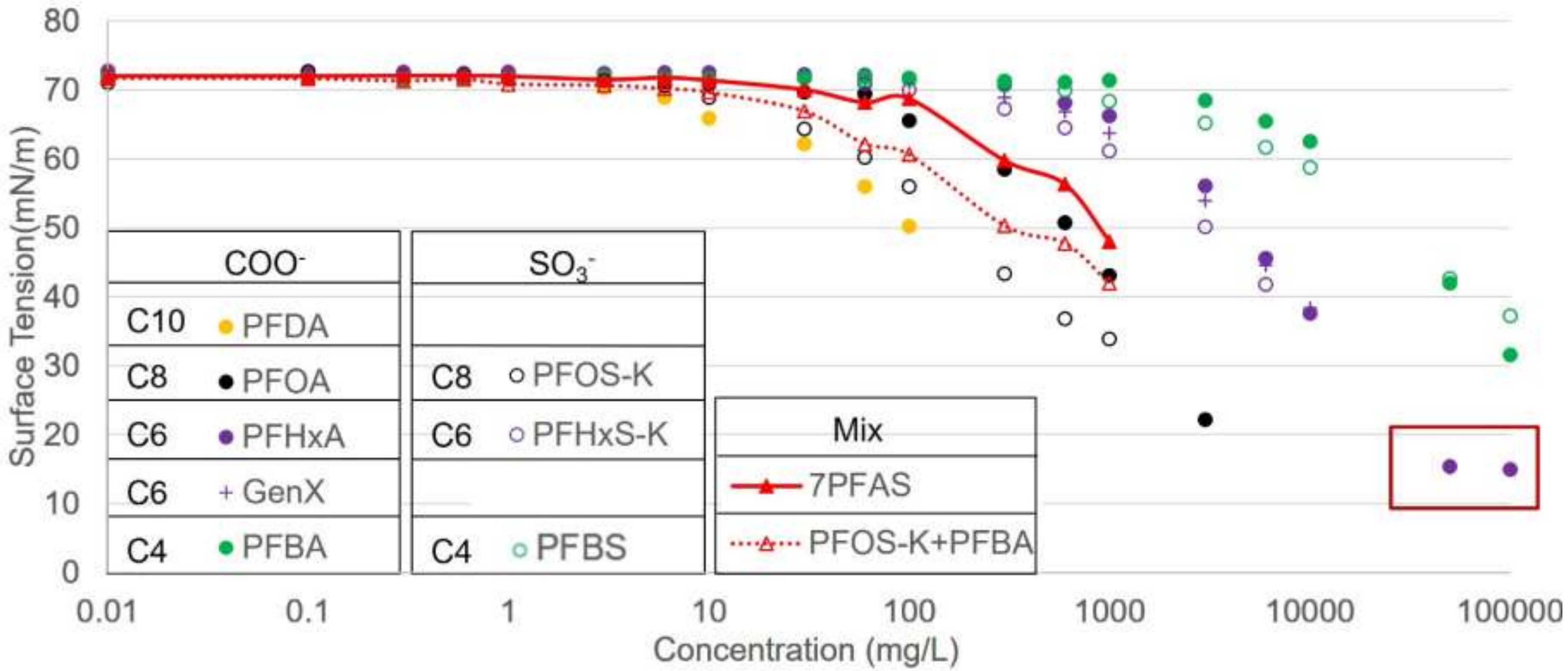
What Is Needed?



Surface Tension of Solvents

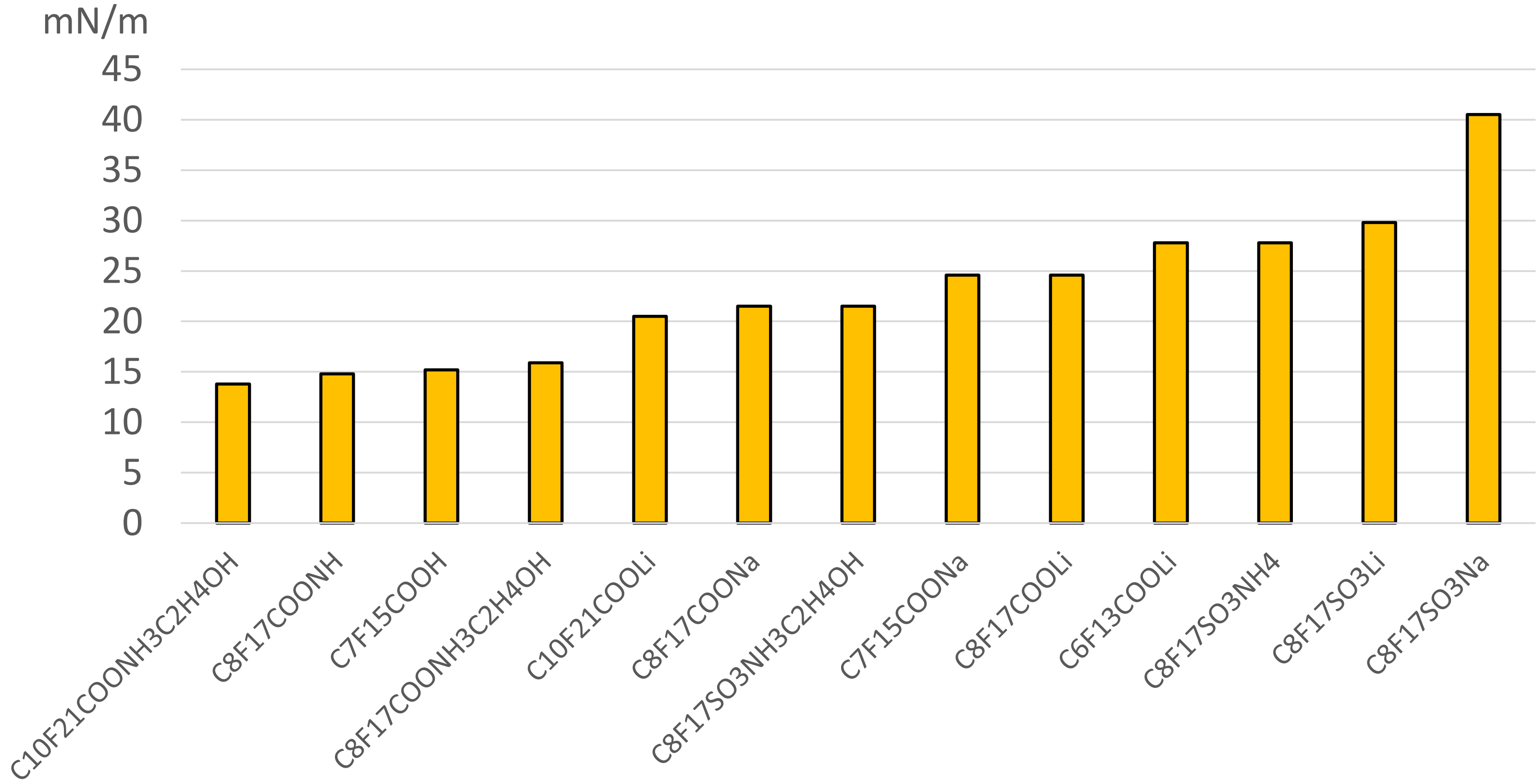


ST of some PFAS in Water



https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=CESER&dirEntryId=354206

ST of PFAS Surfactants in Water



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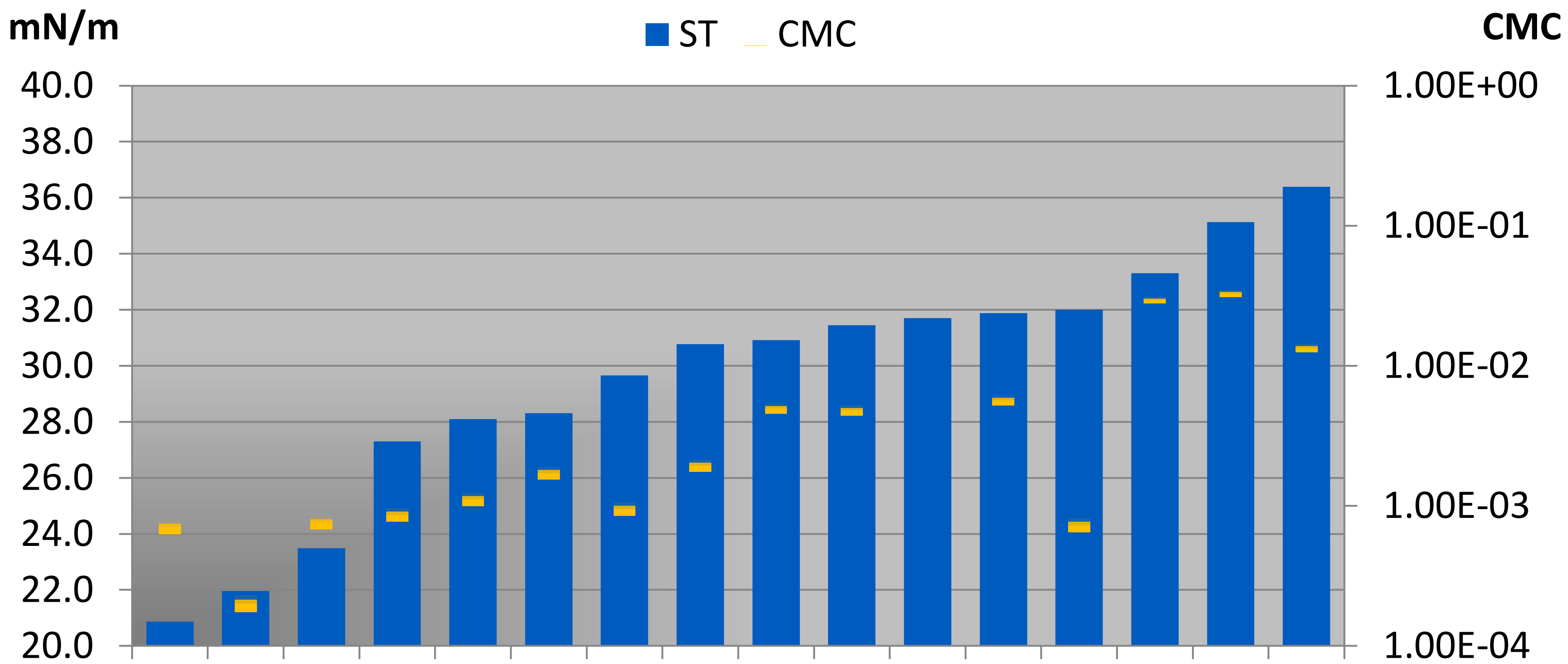
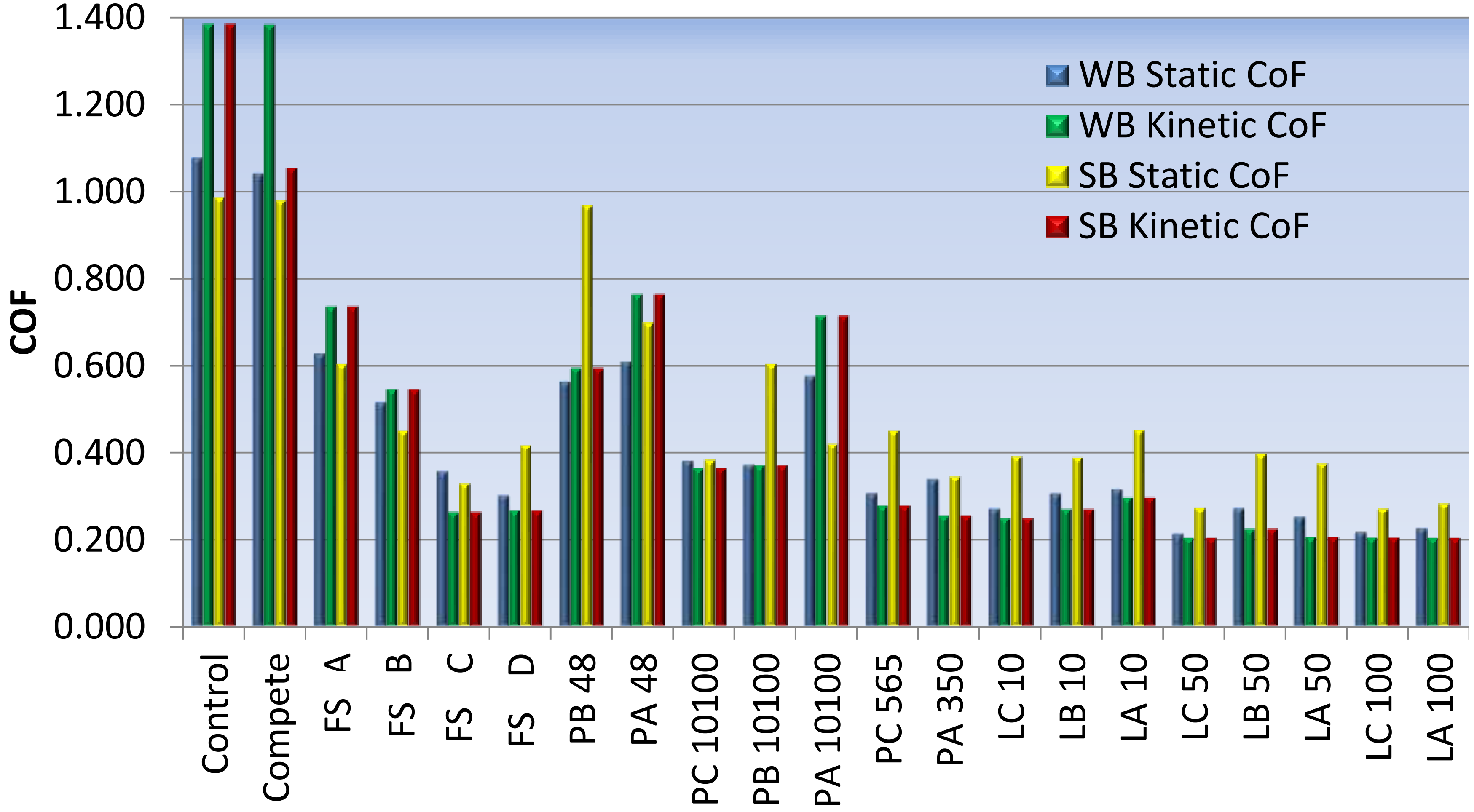
Silicone Surfactant ST in Water



COF Reduction

- PDMS derivatives designed for COF reduction will reduce COF of a cured film to 0.180 - 0.200 consistently.
- The best of these outperform our Fluorosilicones at COF reduction

COF Of PU Coatings With 2% Additives



Water Repellency

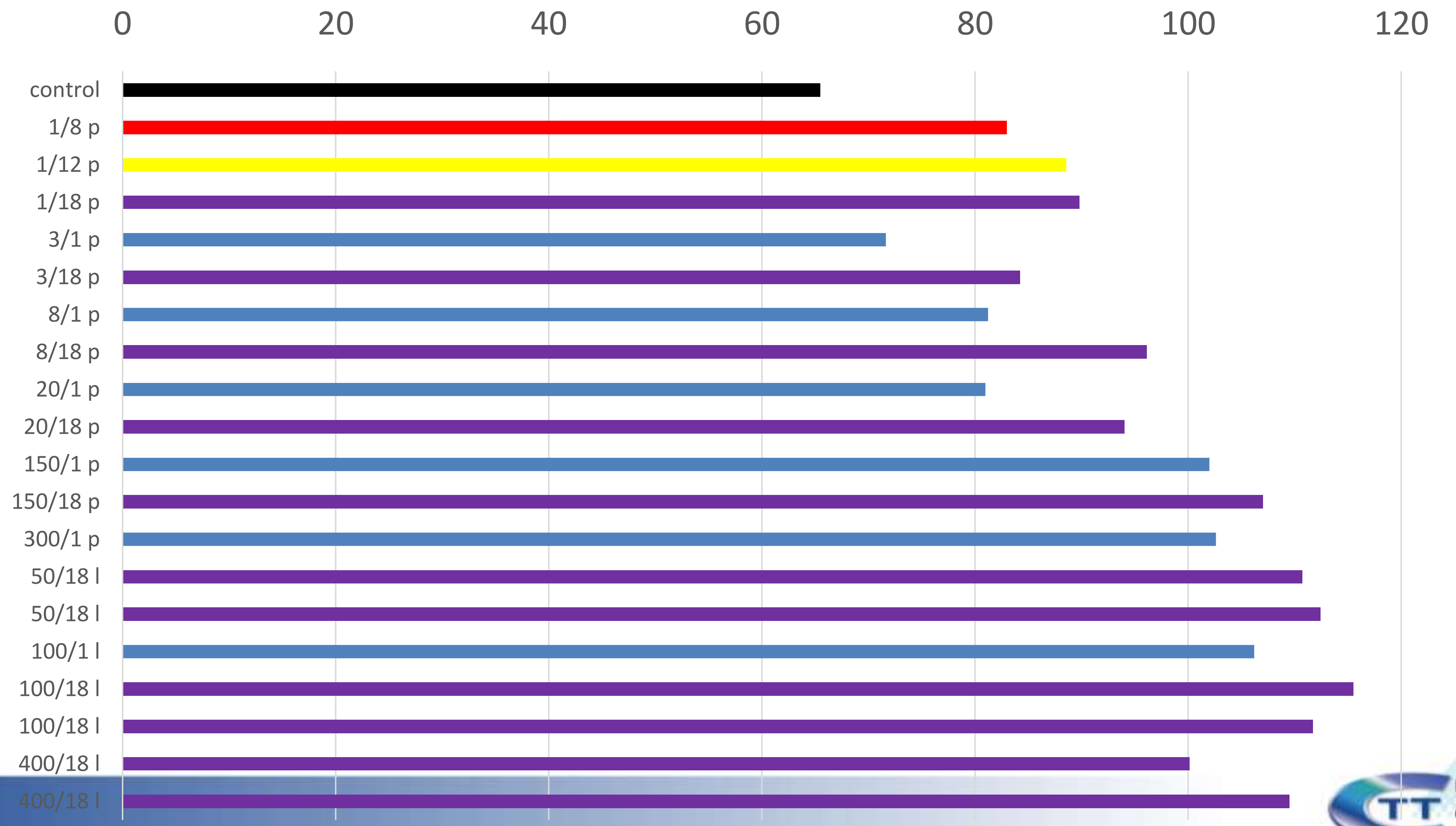
- We have recently published work that shows we have multiple approaches to achieve 115° aqueous contact angle on glass.
  - Dialkyl Quats
  - DT Emulsions
  - T-Dx-T
  - DTQ Resins

Silicone Dialkyl Quats.
Glass Contact Angle

Reference	Sil (n)	Alkyl (n)	Architecture	(o)
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	116
P	400	18	Linear	100

Glass Contact Angle: DiAlkyl Silicone Quats

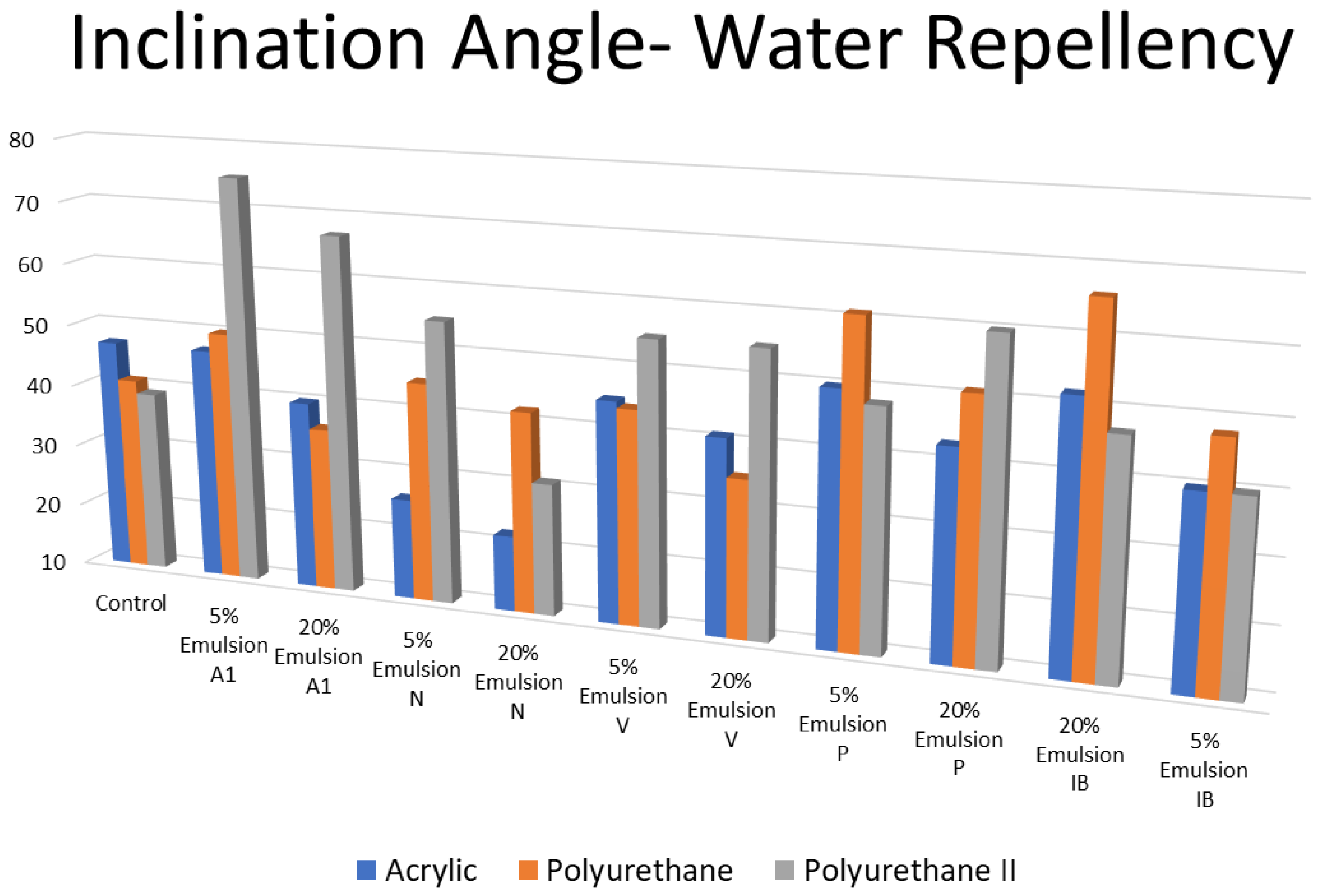
116°



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

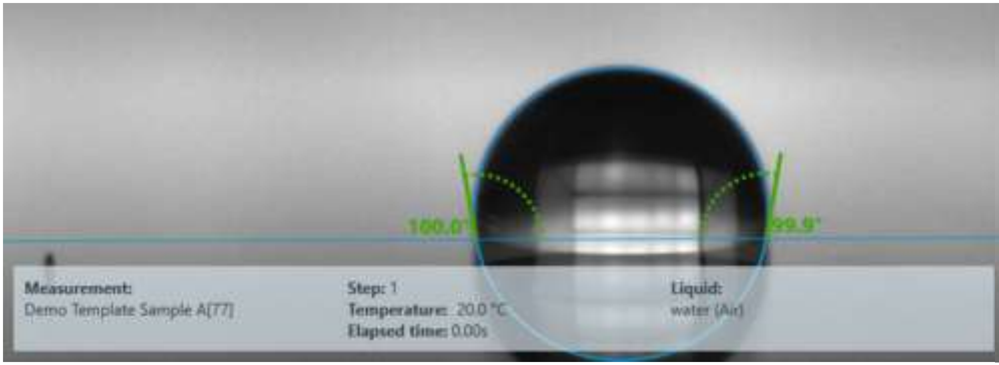
Our belief is that the emulsifiers in these offset the inherent hydrophobic nature of the X-linked silicone network.

SB similar systems give 115°.

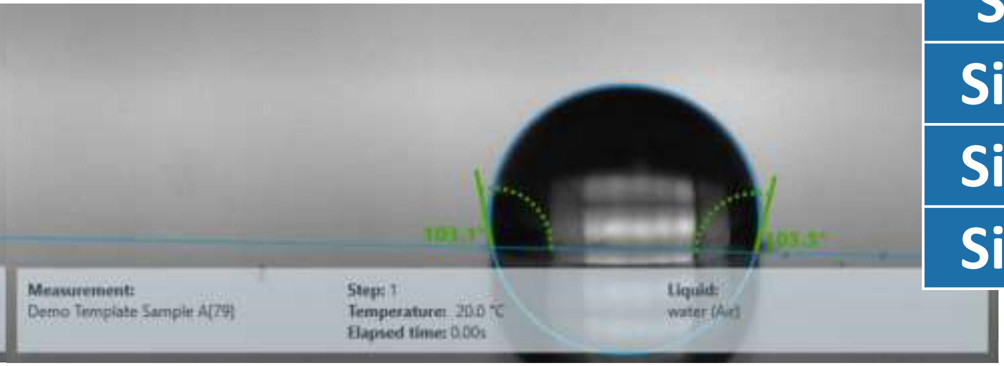
In real world examples these are commonly used and are highly cost effective and elegant in their simplicity.

TD_xT Silicones Used Alone

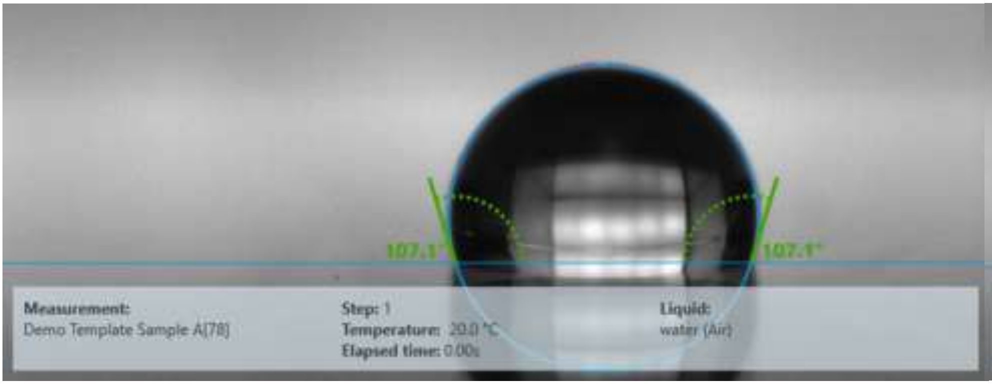
Structure	Angle (°)
Sil(n) = 0	100
Sil(n) = 10	103
Sil(n) = 50	107
Sil(n) = 100	109
Sil(n) = 400	115
Sil(n) = 700	111



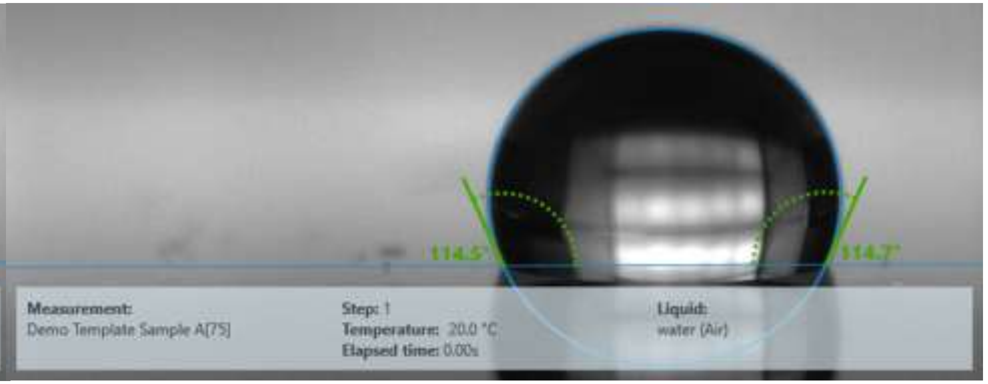
X=0 angle 100° on glass



X=10 angle 103°



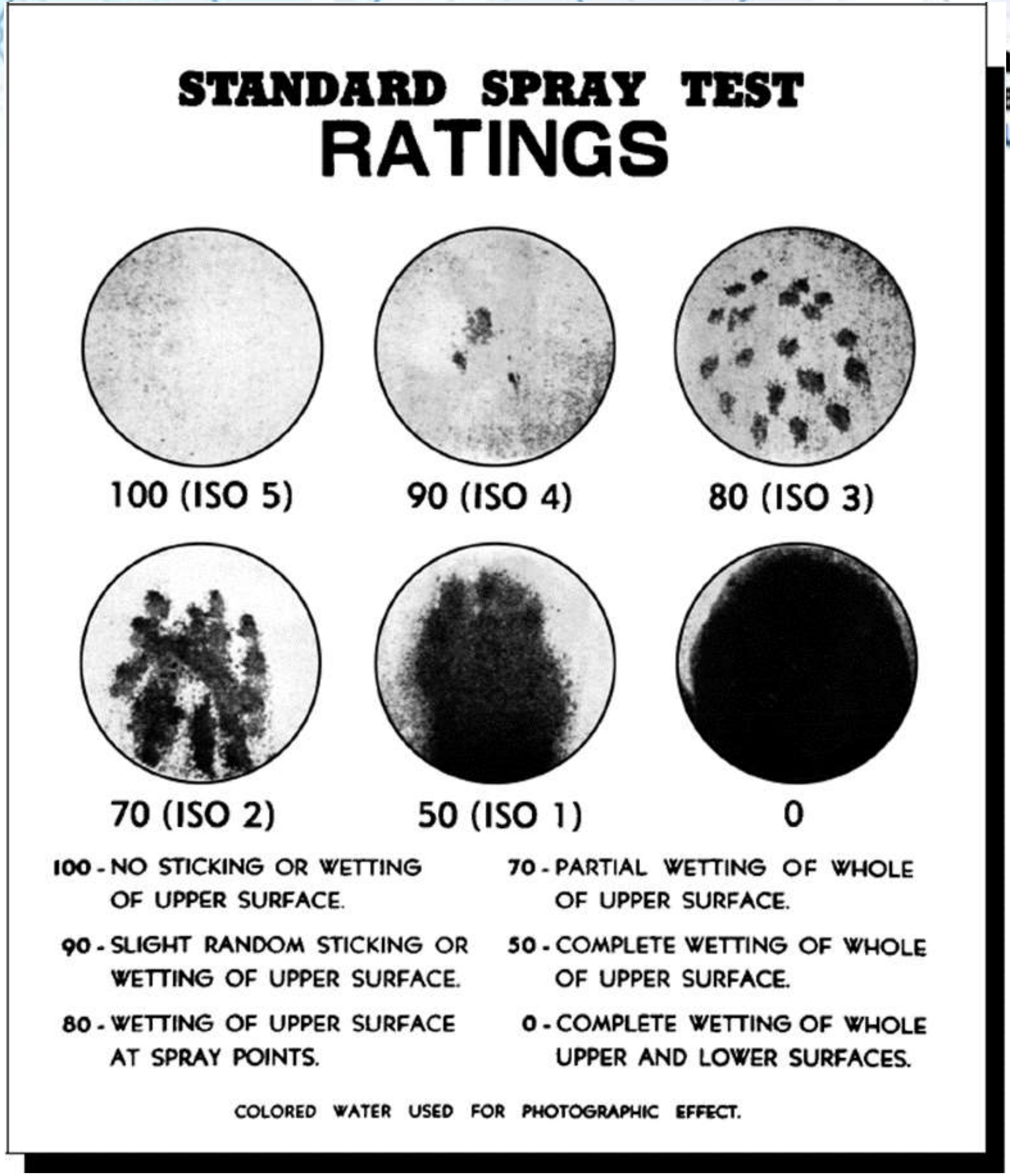
X=50 angle 107°



X=400 angle 115°

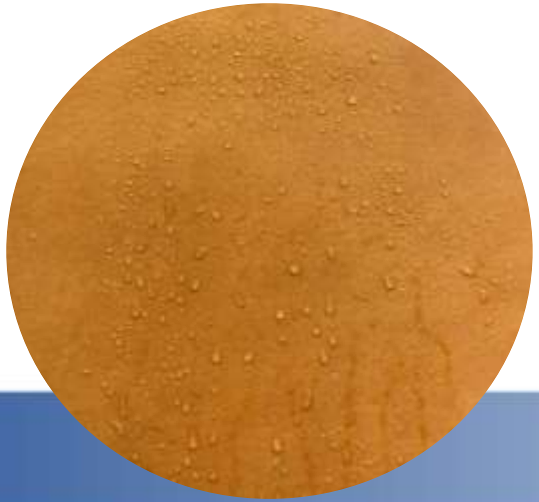
115°

AATCC 22 Standard Spray Test



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

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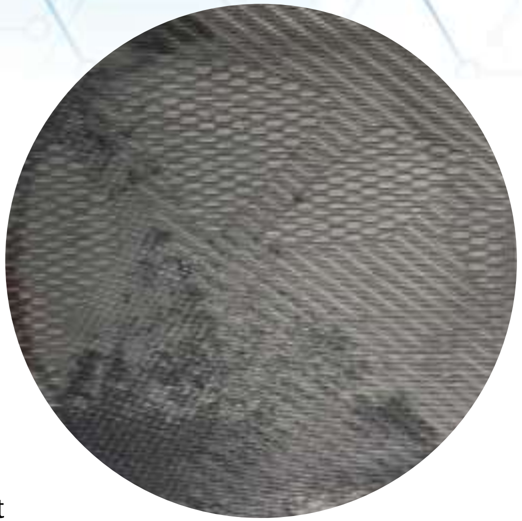
Grey

Benchmark water repellent

Rating: 90 (ISO 4)

front

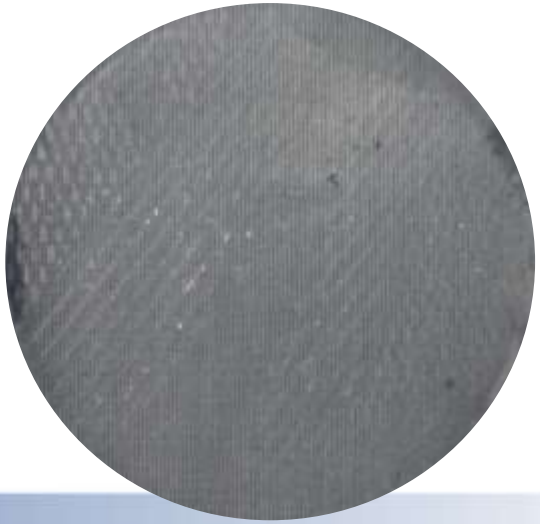


back

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

142° (on leather)

Glass Contact Angle QT Resins in Solvent

108°

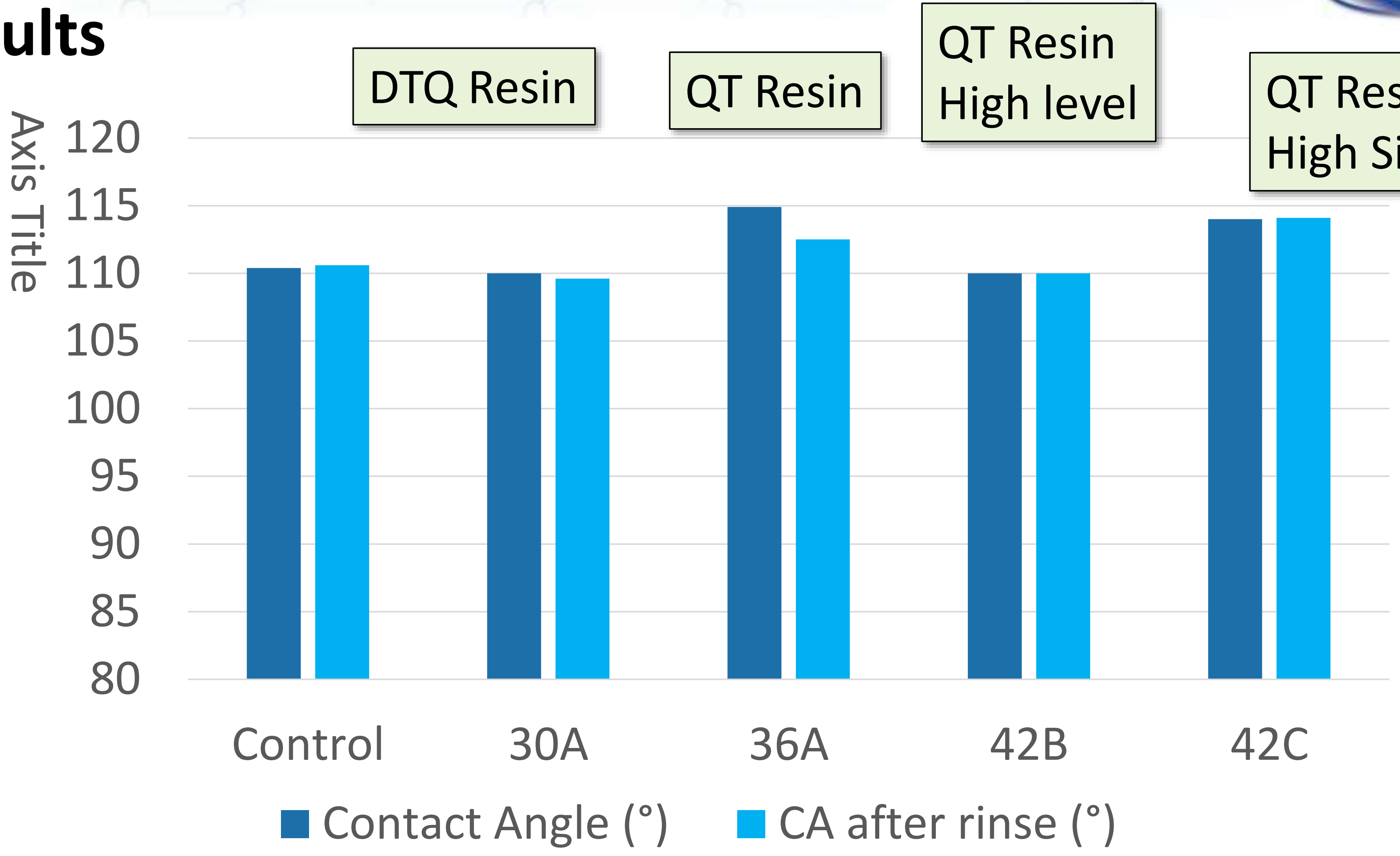
Sample	WCA	sliding angle
Blank	84°	22°
Benchmark	109°	6.5°
YL7-143B	108°	27°

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

Results

115°



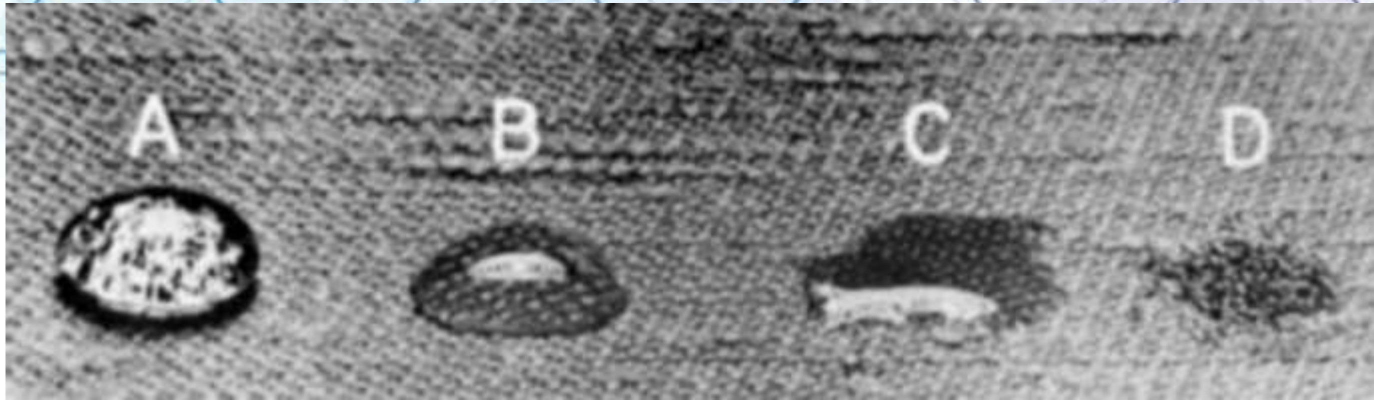
Durability is determined by contact angle lost after rinsing under a 25°C flow of water for 1 minute.

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.

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

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

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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

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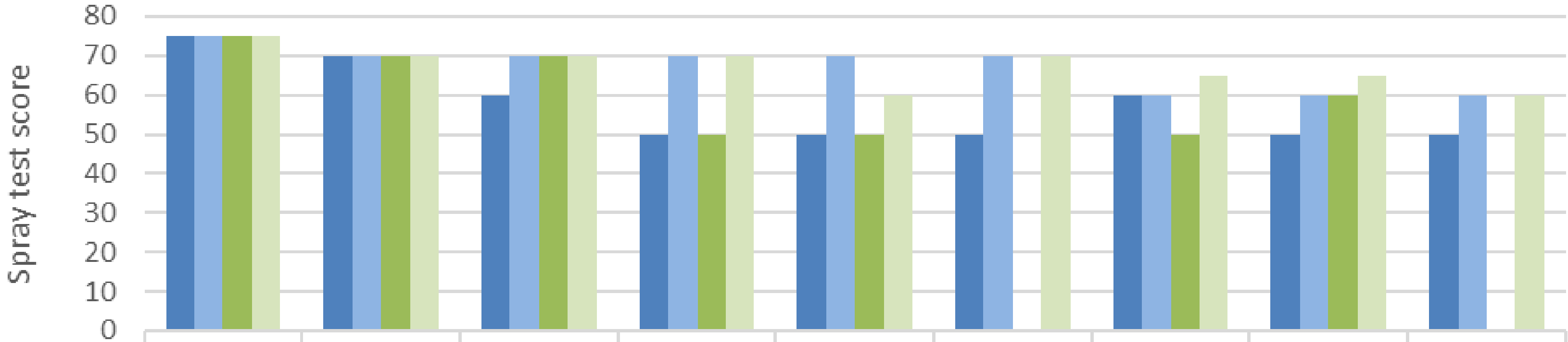
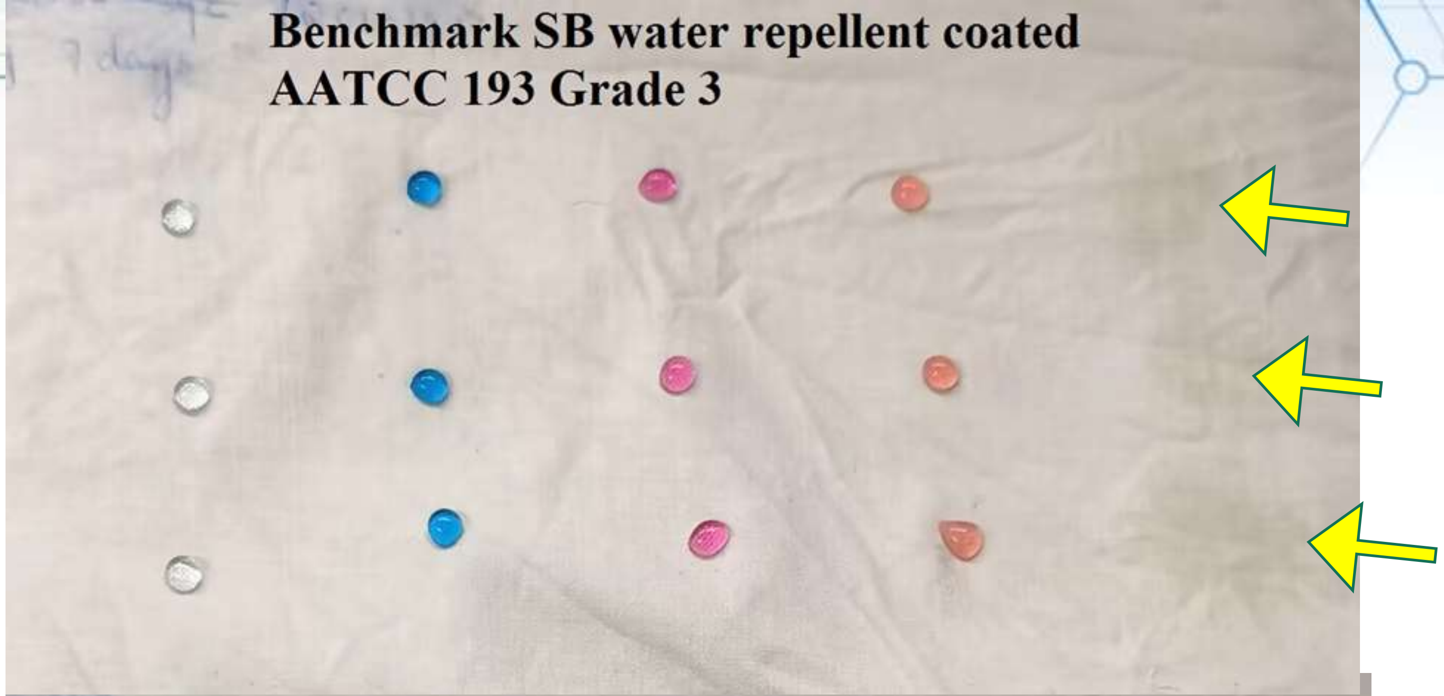
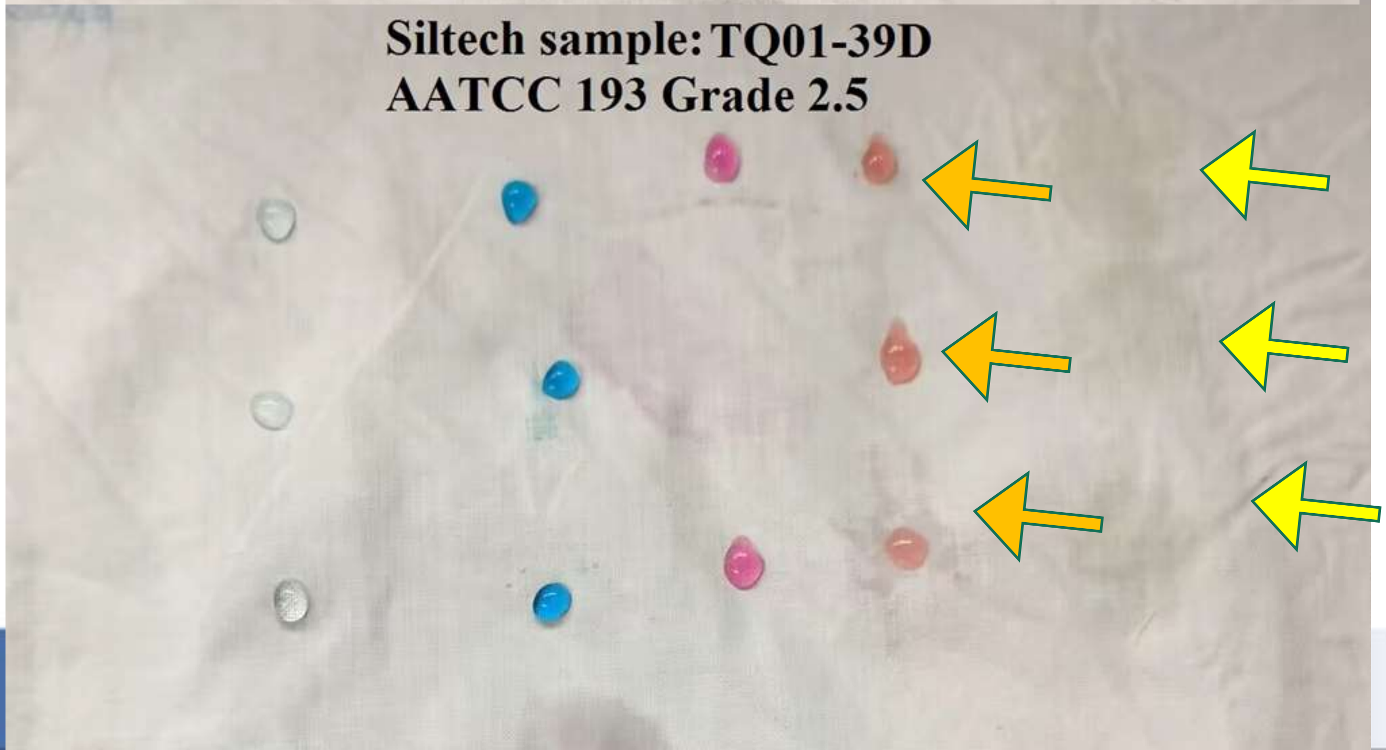
AATCC 22 spray test result for heat cured and R.T. cured sample before and after rinse



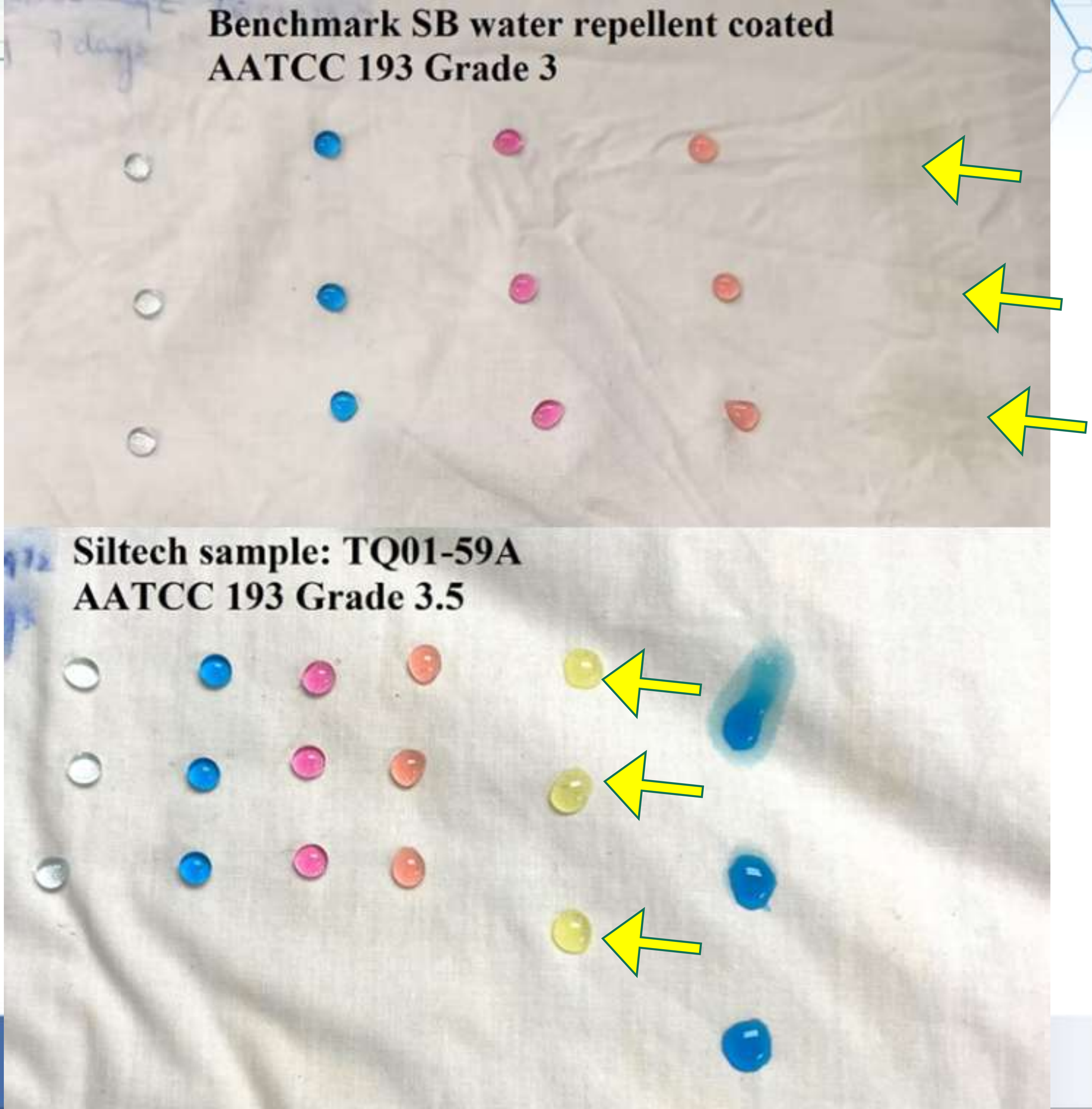
	Benchmark solvent-based silicone water repellent	TQ01-39D	TQ01-59A	TQ01-55A	TC15-87F	BQ-19-187	TQ01-16A	TQ01-16G	TQ 01-41C
heat cure-before rinse	75	70	60	50	50	50	60	50	50
heat cure-after rinse	75	70	70	70	70	70	60	60	60
R.T. cure-before rinse	75	70	70	50	50	0	50	60	0
R.T. cure-after rinse	75	70	70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

Sol-Gel QT Resins: Glass Contact Angle

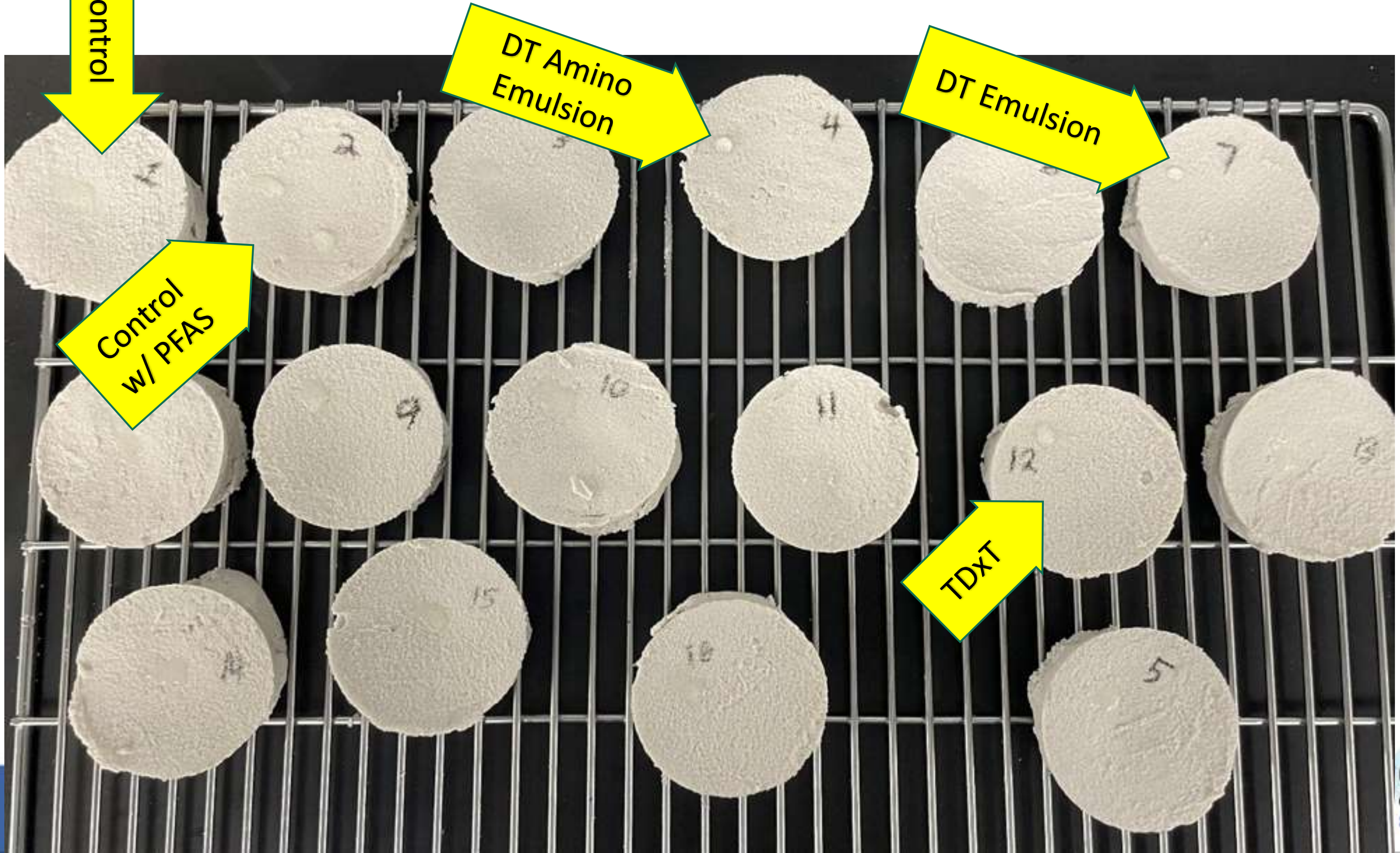
114°

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°

Oleophobicity

- Early results here show several approaches with promise.
  - Film Forming DT Systems
  - T-Dx-T
  - Waxy SPE and Silicone Hydrocarbons
  - A new composition

Oleophobicity: Sunflower Oil on Grout Plugs



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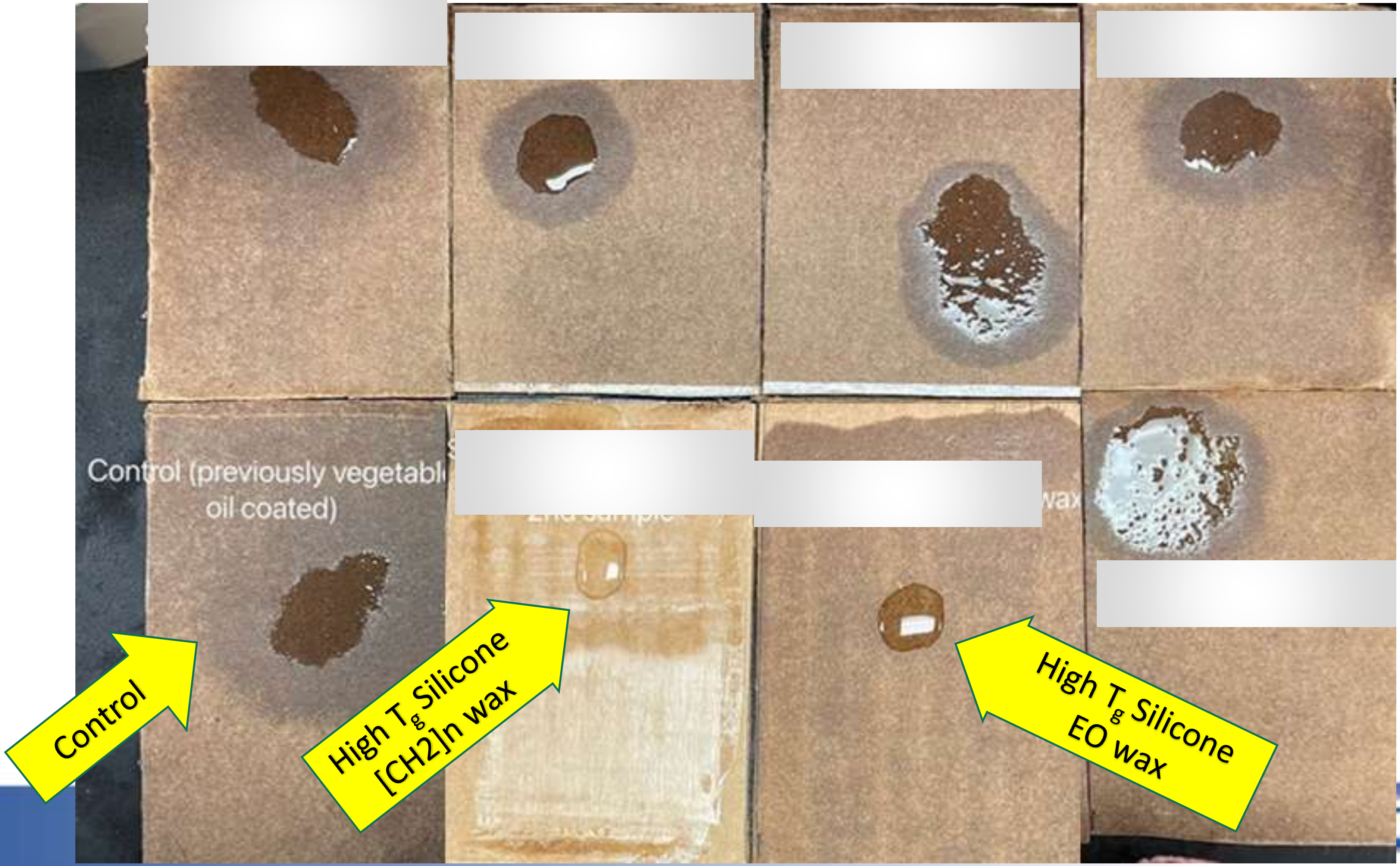
Oleophobicity: Vegetable Oil on Cardboard

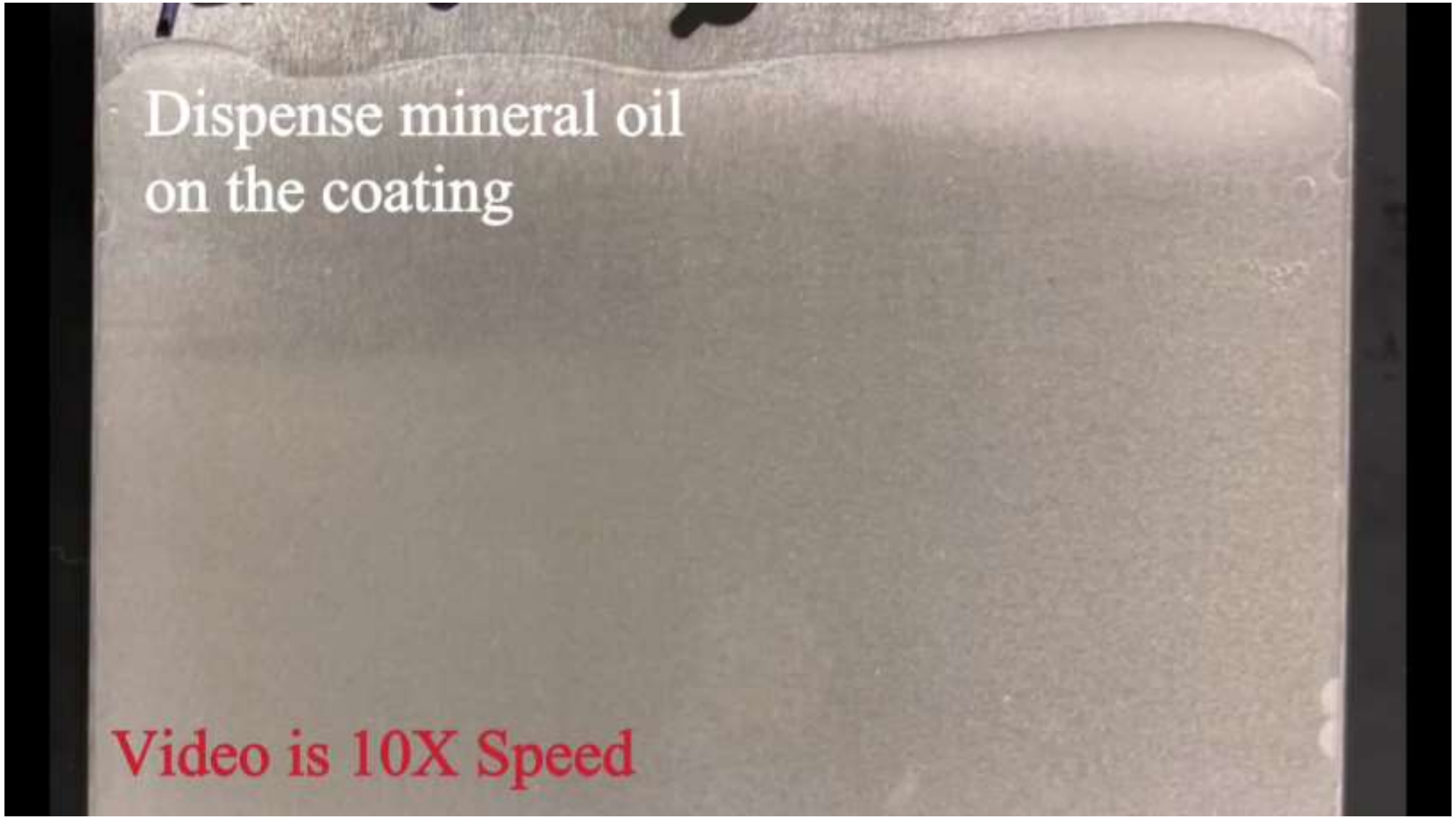


Oleophobicity: Vegetable Oil on Cardboard

A New Compound for UV: Beading MO

Close Up

Video



Chemical Resistance

1 **H** 1.008							2 **He** 4.0026
3 **Li** 6.94	4 **Be** 9.0122	5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180

- PFAS compounds are very strongly bonded and resistant to acids, etc.
- PDMS based materials are very labile to acid/base hydrolysis.
  - This is why they degrade in the environment.
- Some unique species such as TQ resins are likely to be somewhat chemically resistant.
- We are not going to be able to obtain the chemical stability of PFAS.

Conclusions

- Surface Tension of standard PDMS materials is the next best thing to PFAS - and is good enough for nearly all applications.
- Water Repellency of 115° on glass is possible via multiple approaches of PDMS and related materials.
- Oleophobicity is plausible with some newer specialty silicon – based materials.

BUT

- Chemical Resistance is Futile

90
Th
232.04

79
A
196.97

7
N
14.007

19
K
39.098

39
Y
88.90

8
O
15.999

92
U
238.03