The Use of Modern Silicon Cross-linking Moieties to Confer Water and Oil Repellency, Release and Protection Properties to Surfaces.

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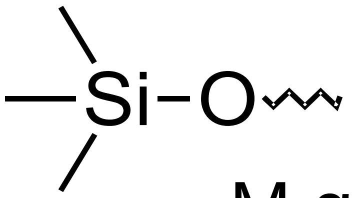
A series of reactive Q and T resins, $Si(OR)_4$ and $R'(SiOR)_3$ based units respectively, are formulated with reactive silicone polymers. The systems are evaluated in various fabric, leather, or hard surface treatments primarily for water and oil repellency. Release and protection properties are also evaluated in basic coatings systems.

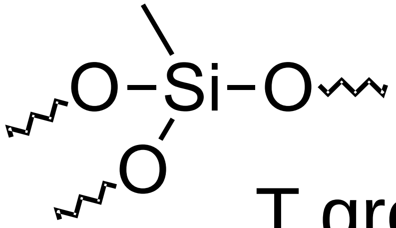
Agenda

- Brief Silicone Background
- Replacing PFAS?
- ST and COF
- Hydrophobicity
- Oleophobicity
- Stain Resistance
- Chemical Resistance
- Conclusions

Silicon Nomenclature

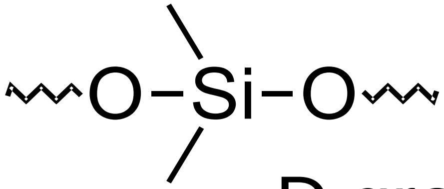


M group



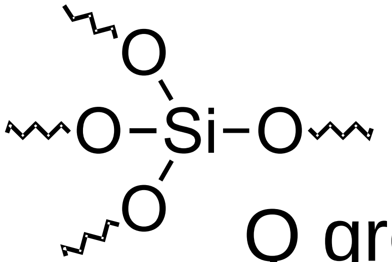
T group

Trialkoxy silanes are T groups



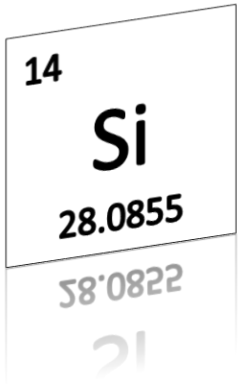
D group

MD_xM is the standard formula for silicone



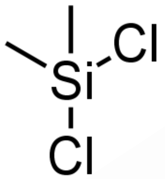
Q group

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

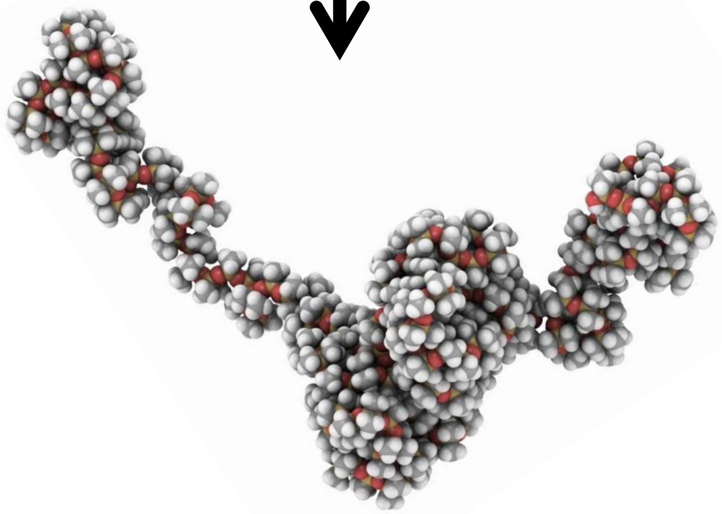
Catalysts:
From the Earth



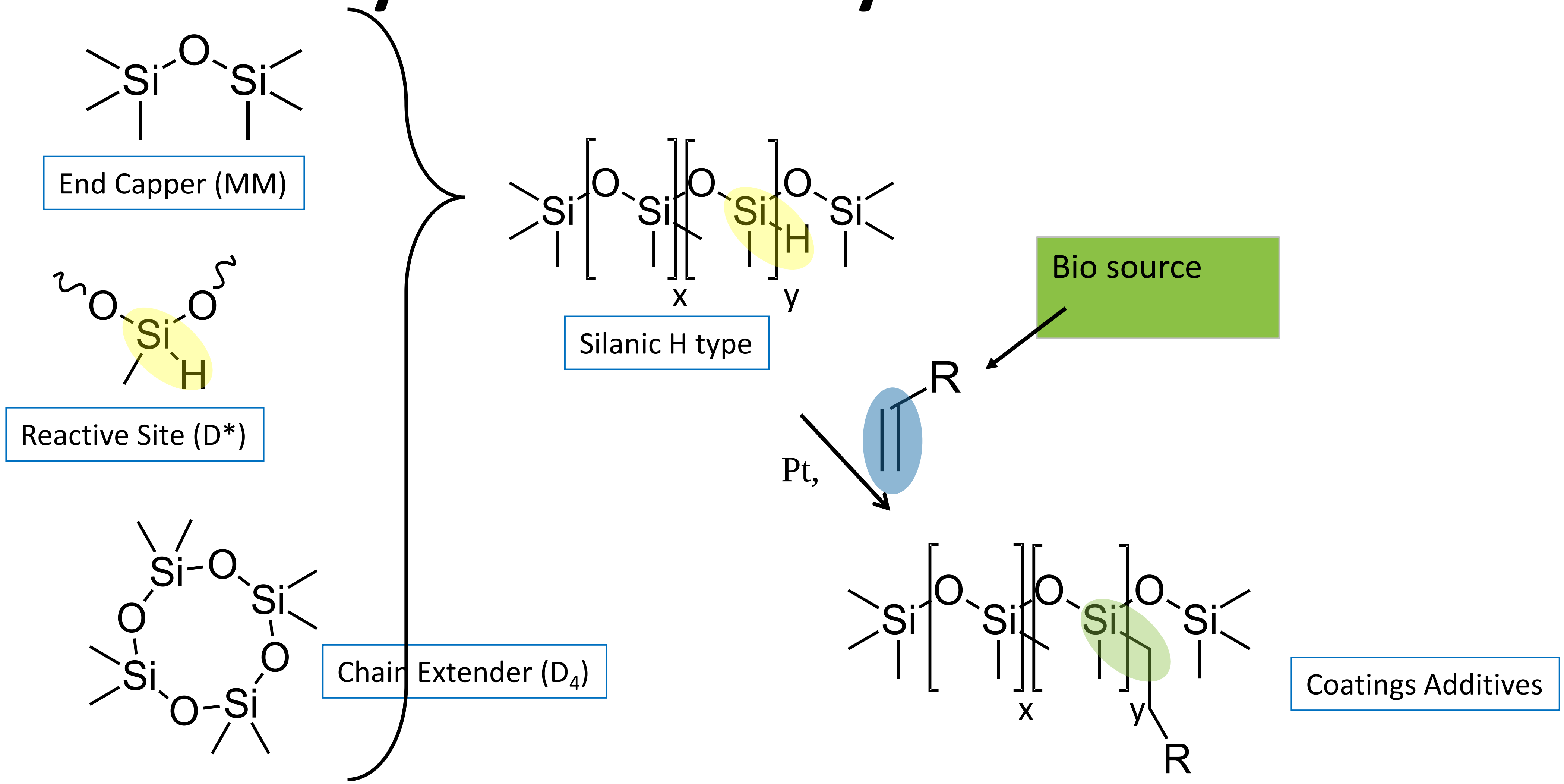
A variety of **chlorosilanes**: man-made, highly reactive intermediates. These are only used by chemical companies.

Water:
Natural

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



Silicone Hybrid Chemistry



PFAS

EPA and ECHA are acting to heavily regulate compounds with ~$(CF_2)_n$ where $n \geq 2$ (EPA) or $n \geq 1$ (EU).

Timing is 2024 for EPA

Many End Users are Attempting to Formulate These Out.

- 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:

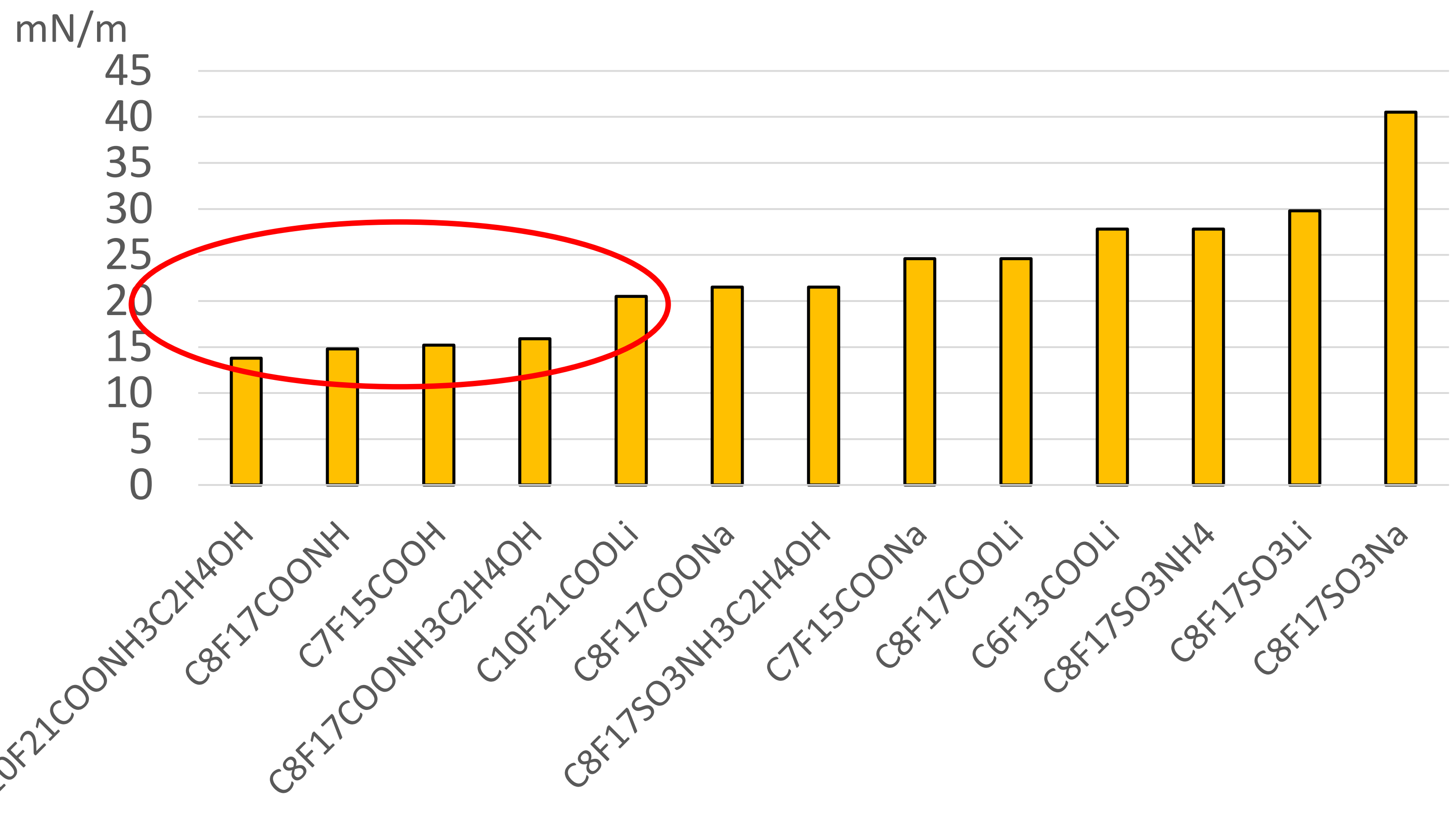
ST 20-30 mN/m

Water Repellency

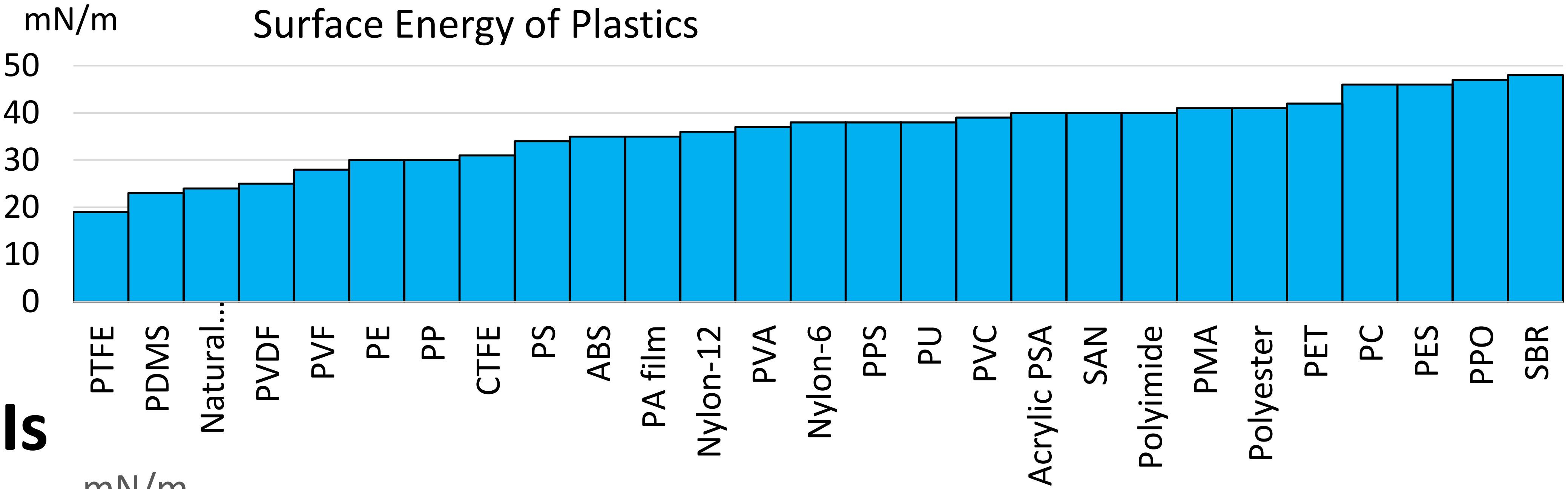
Can we develop Oil Repellency?

- 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.

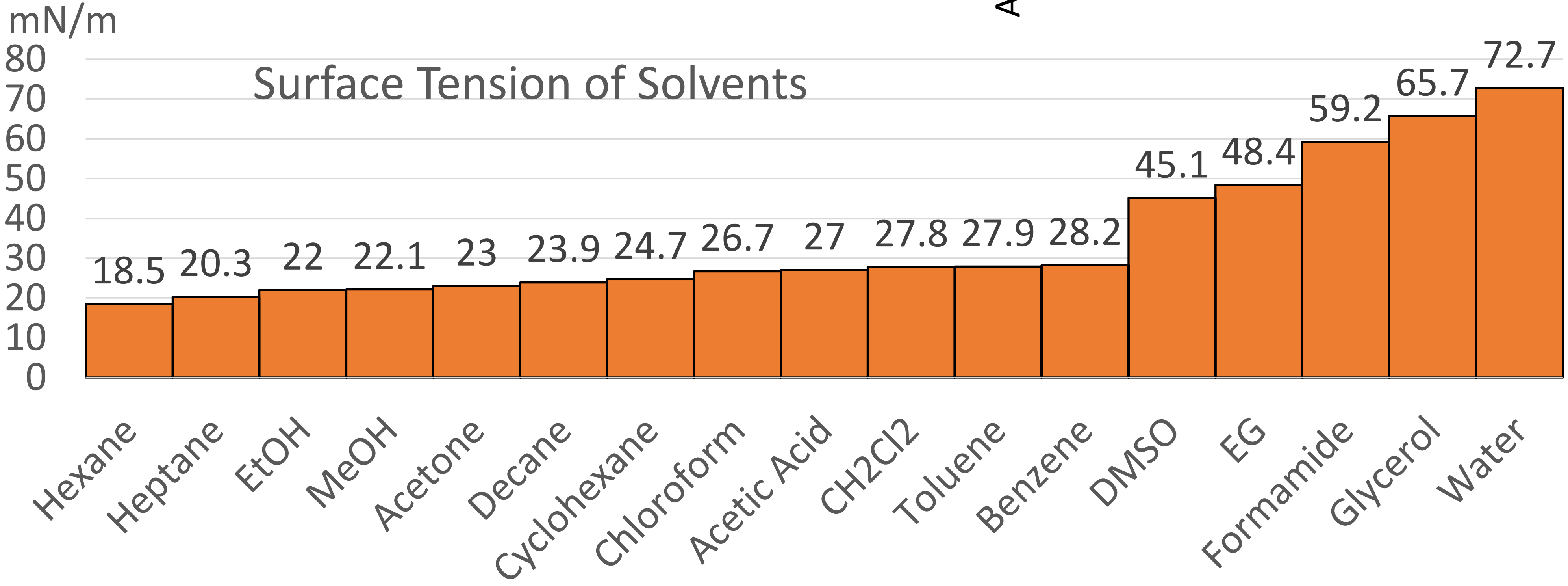
ST of PFAS Surfactants in Water



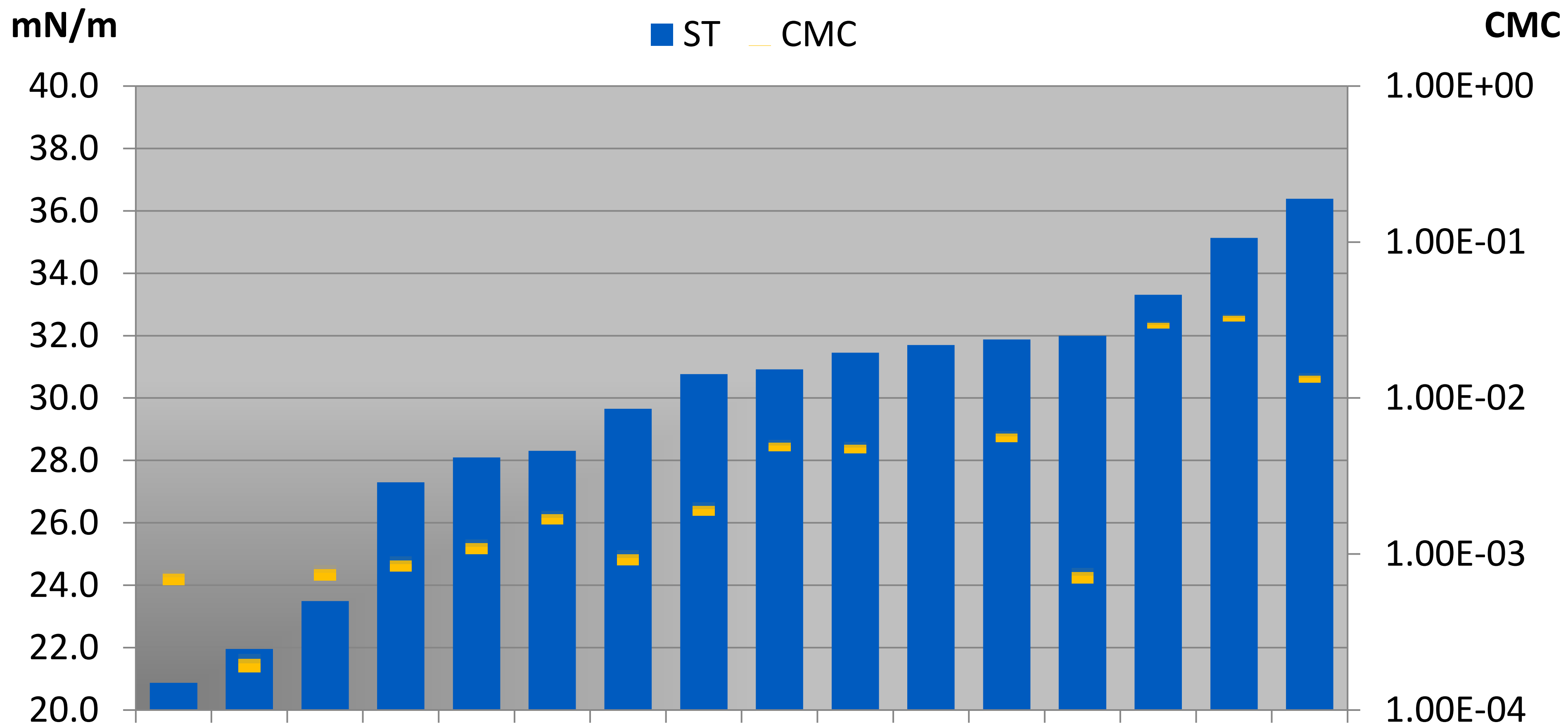
AdvancesinColloidandInterfaceScience210(2014)65–71



What ST Is Needed?



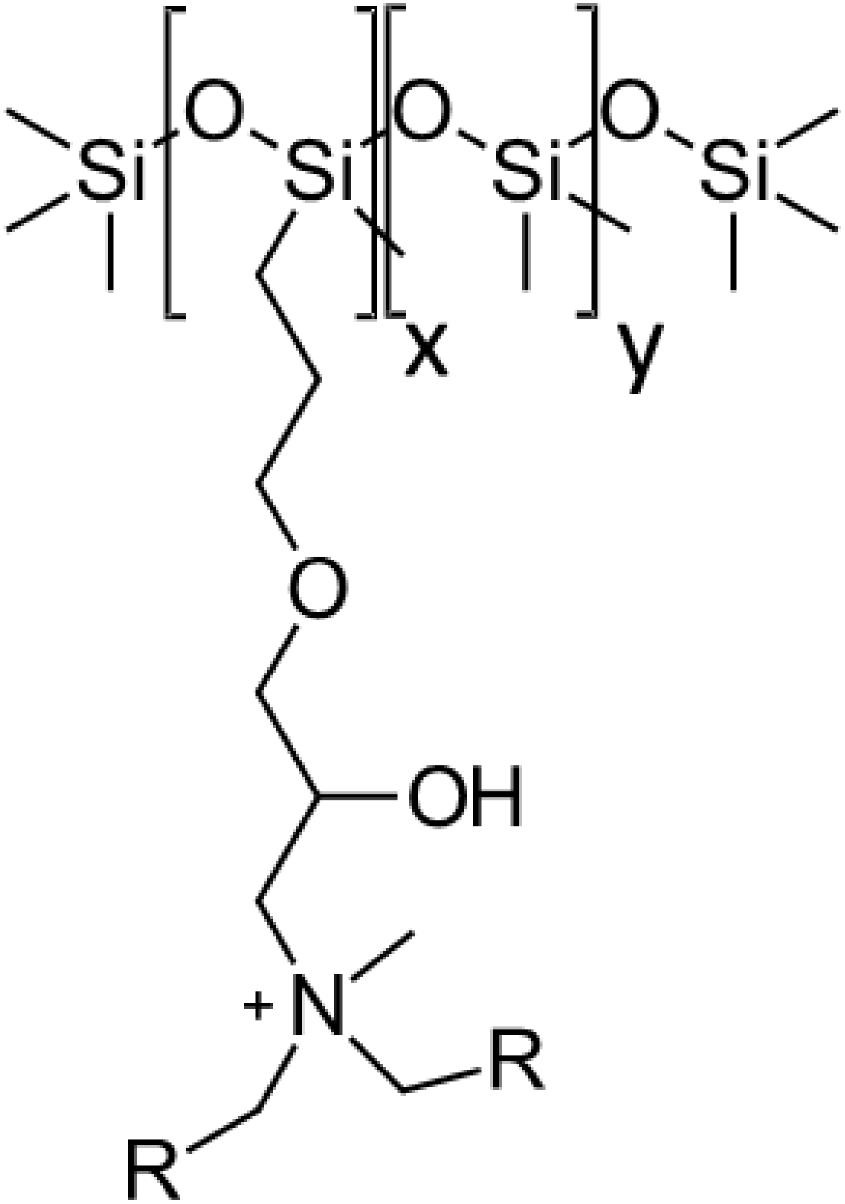
Silicone Surfactant ST in Water



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

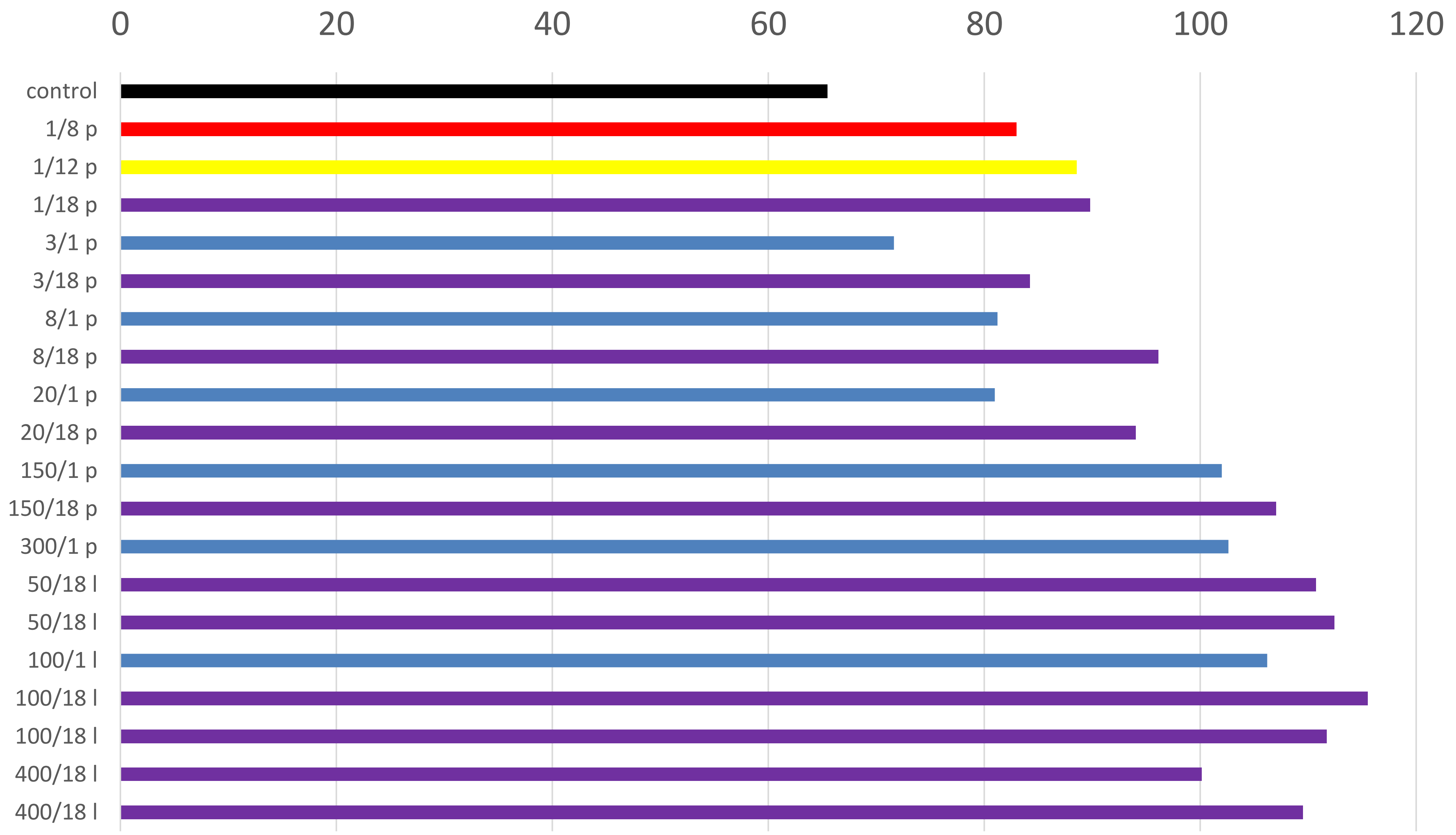
Pendant Dialkyl Quaternium Silicone Structure



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

Glass Contact Angle: DiAlkyl Silicone Quats

116°



DT Resin Emulsions

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

Result WB DT Emulsions

~ 80°

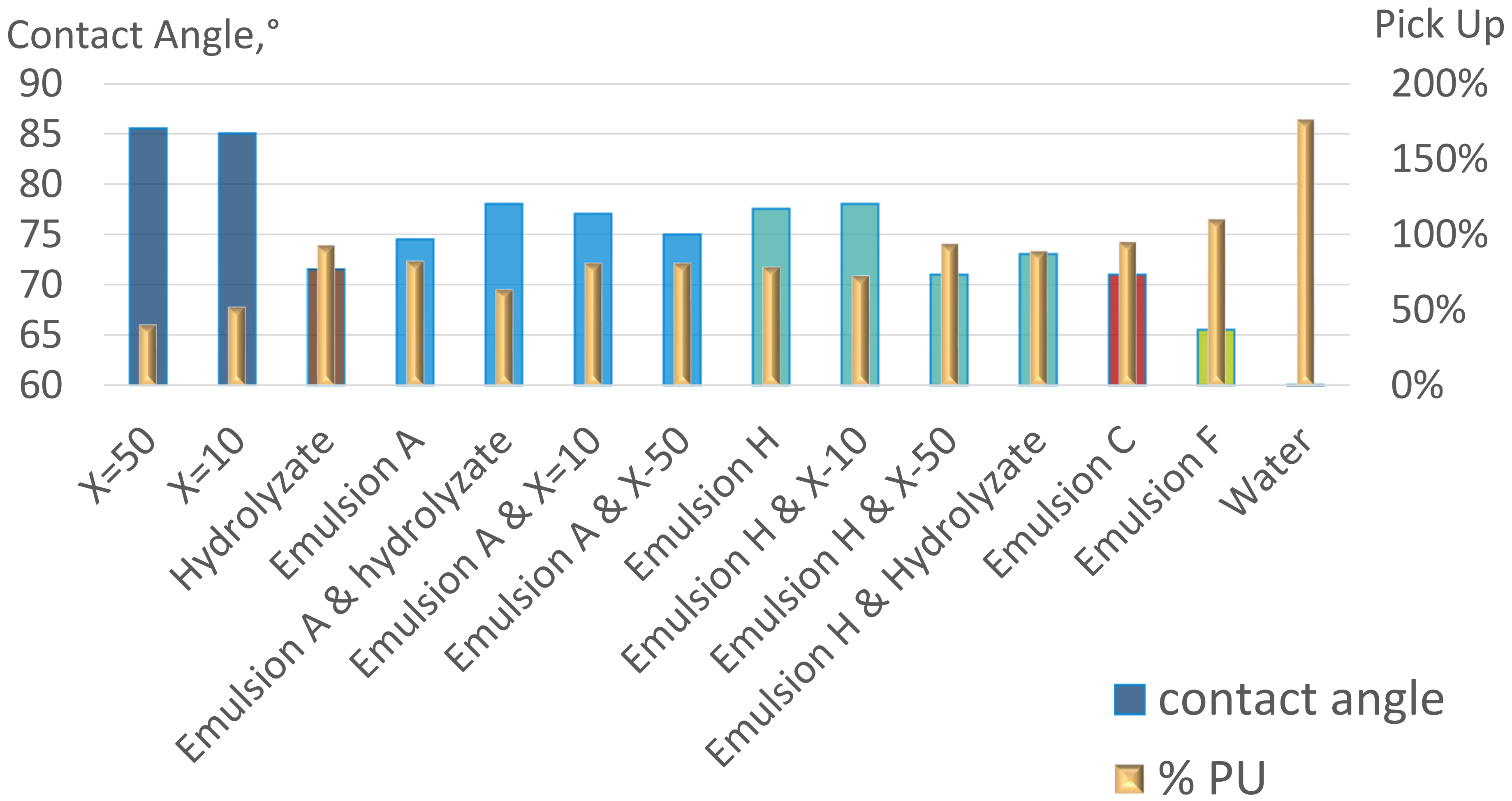
Typically ~80°

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.

Fiberglass Water Repellency: Film Forming Emulsions and TMS type

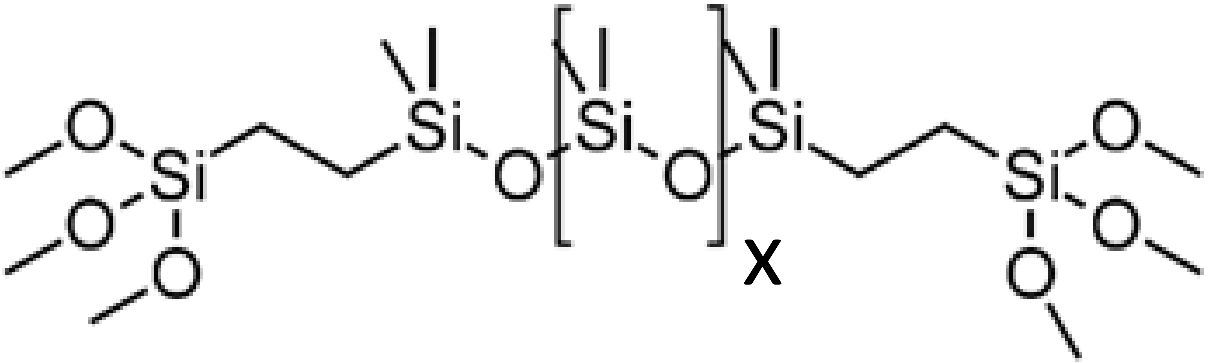


The emulsions add water repellency

Adding TMS types give a slight improvement

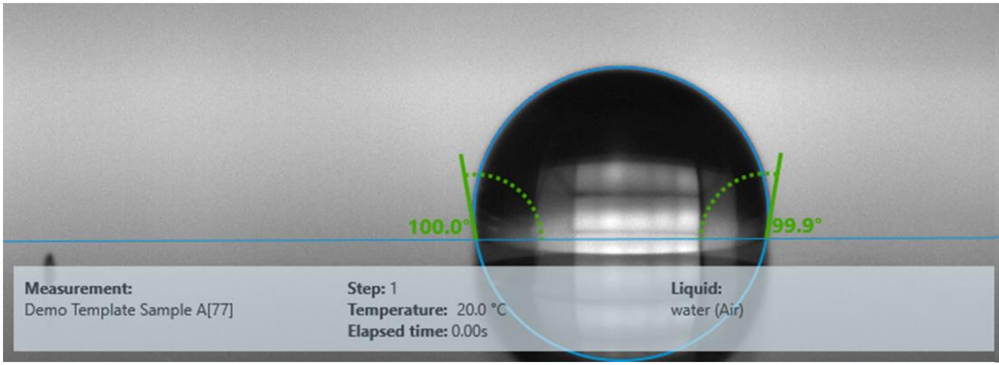
The TMS types alone give the best performance

TDxT

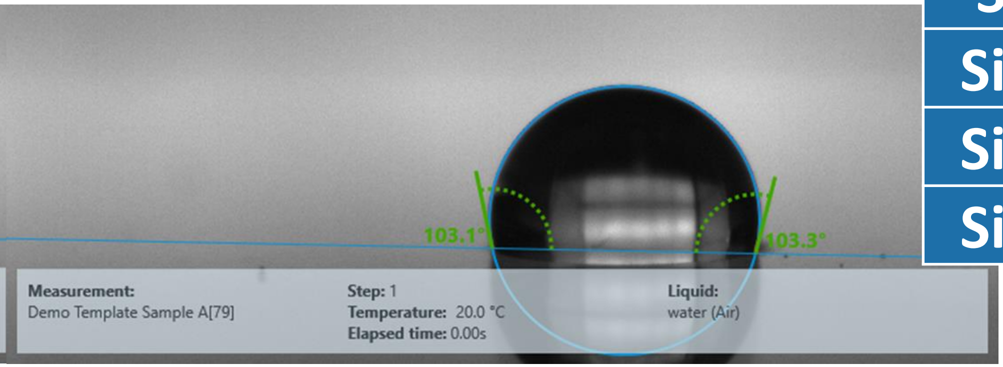


TD_xT Silicones Used Alone

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

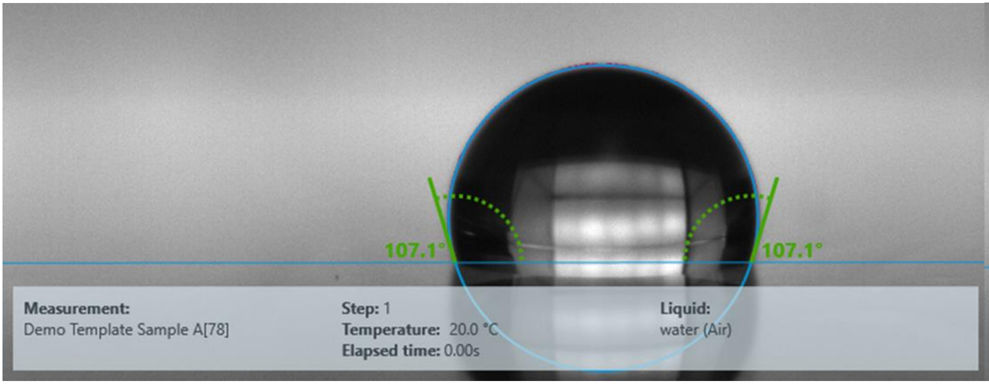


X=0 angle 100° on glass

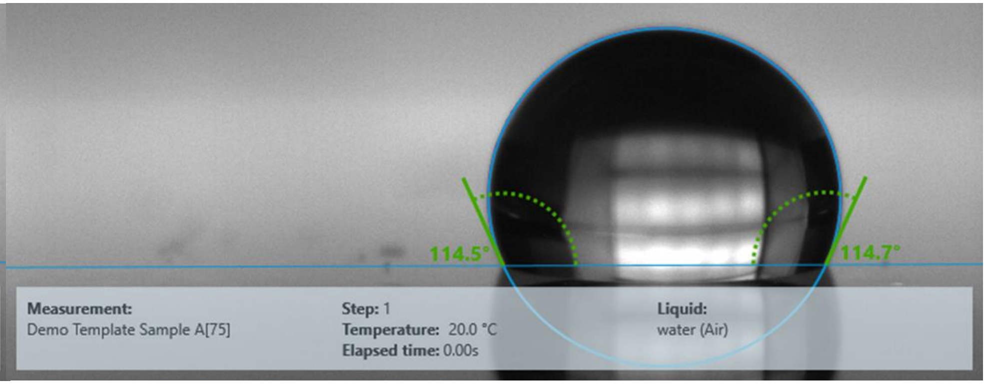


X=10 angle 103°

115°

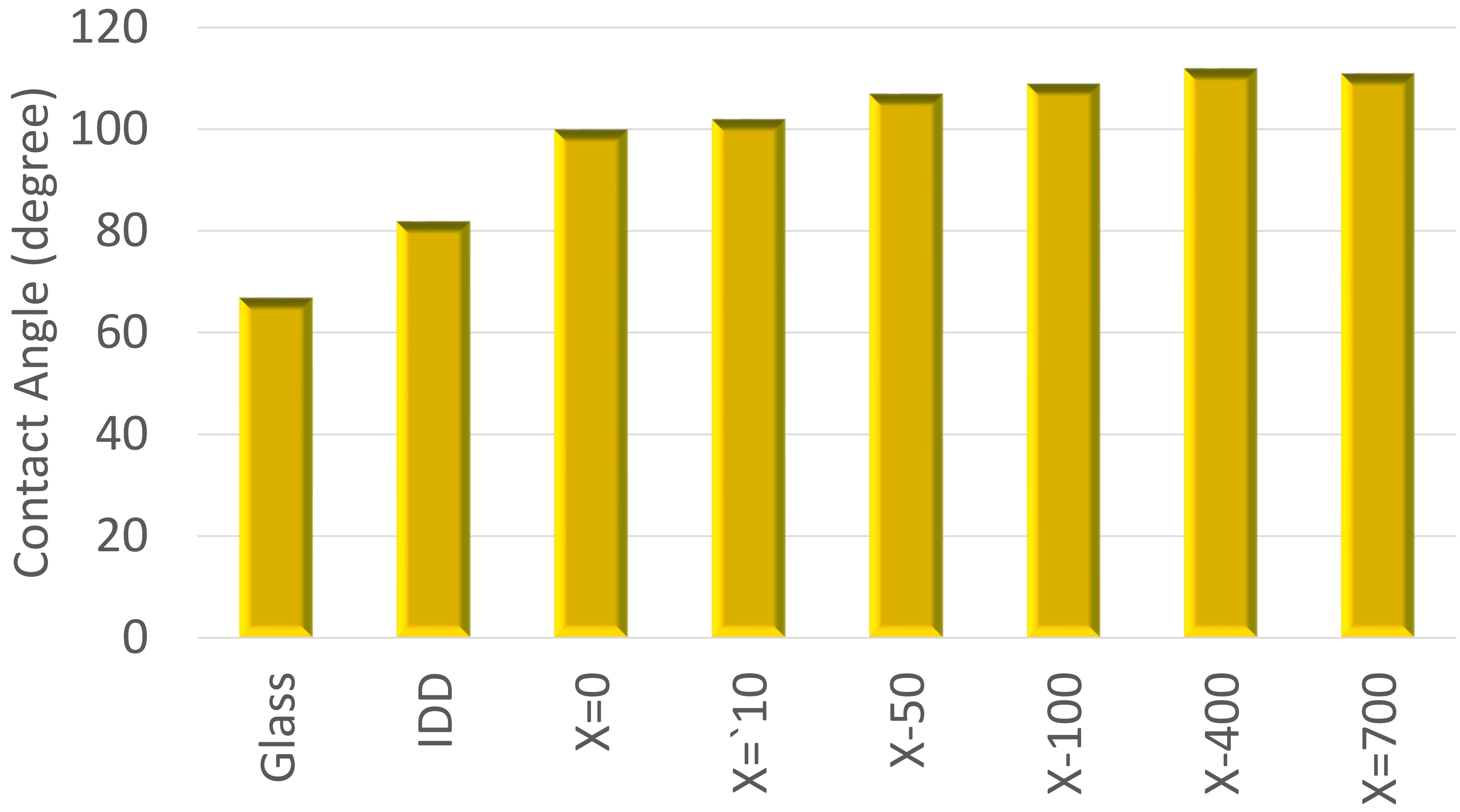


X=50 angle 107°

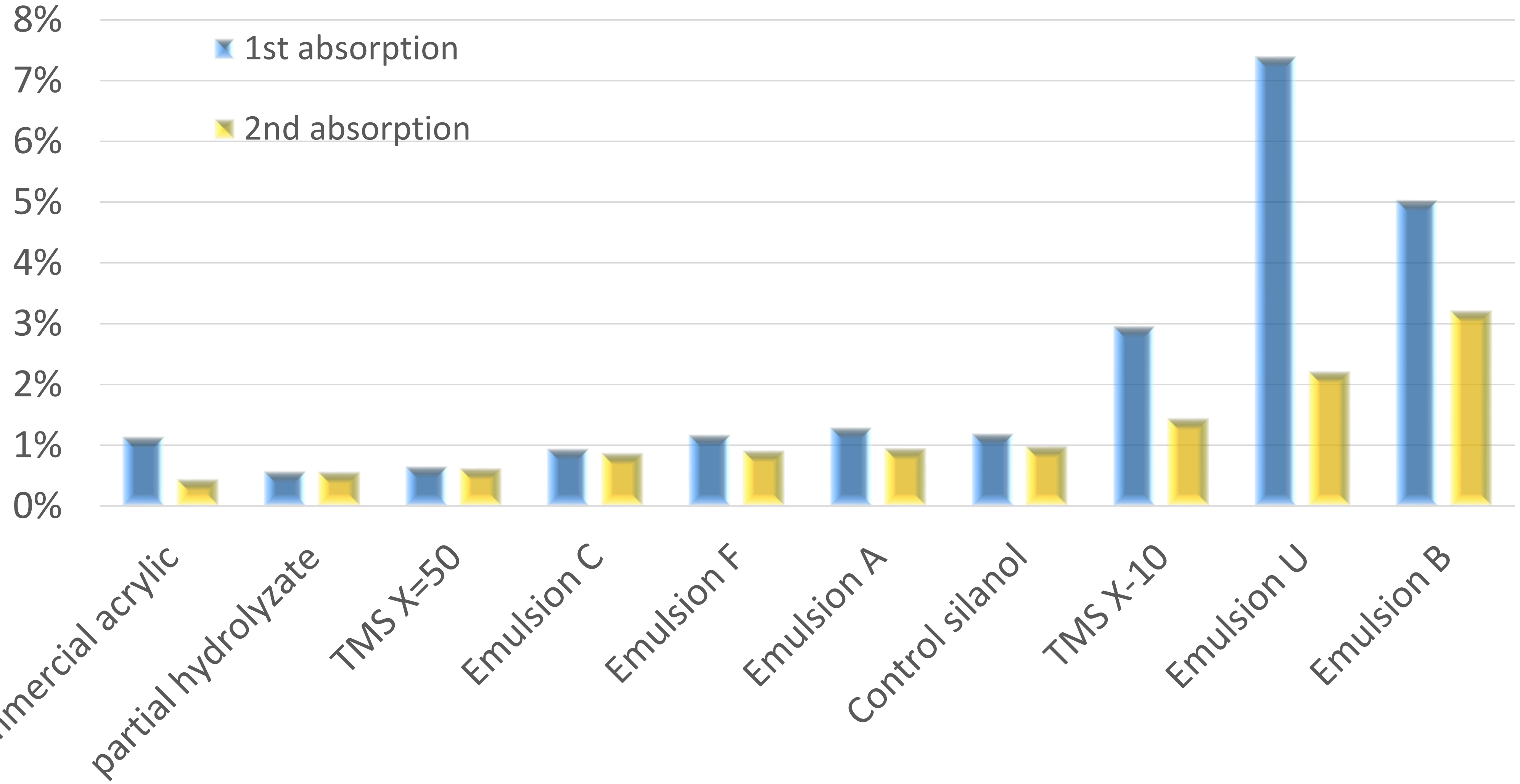


X=400 angle 115°

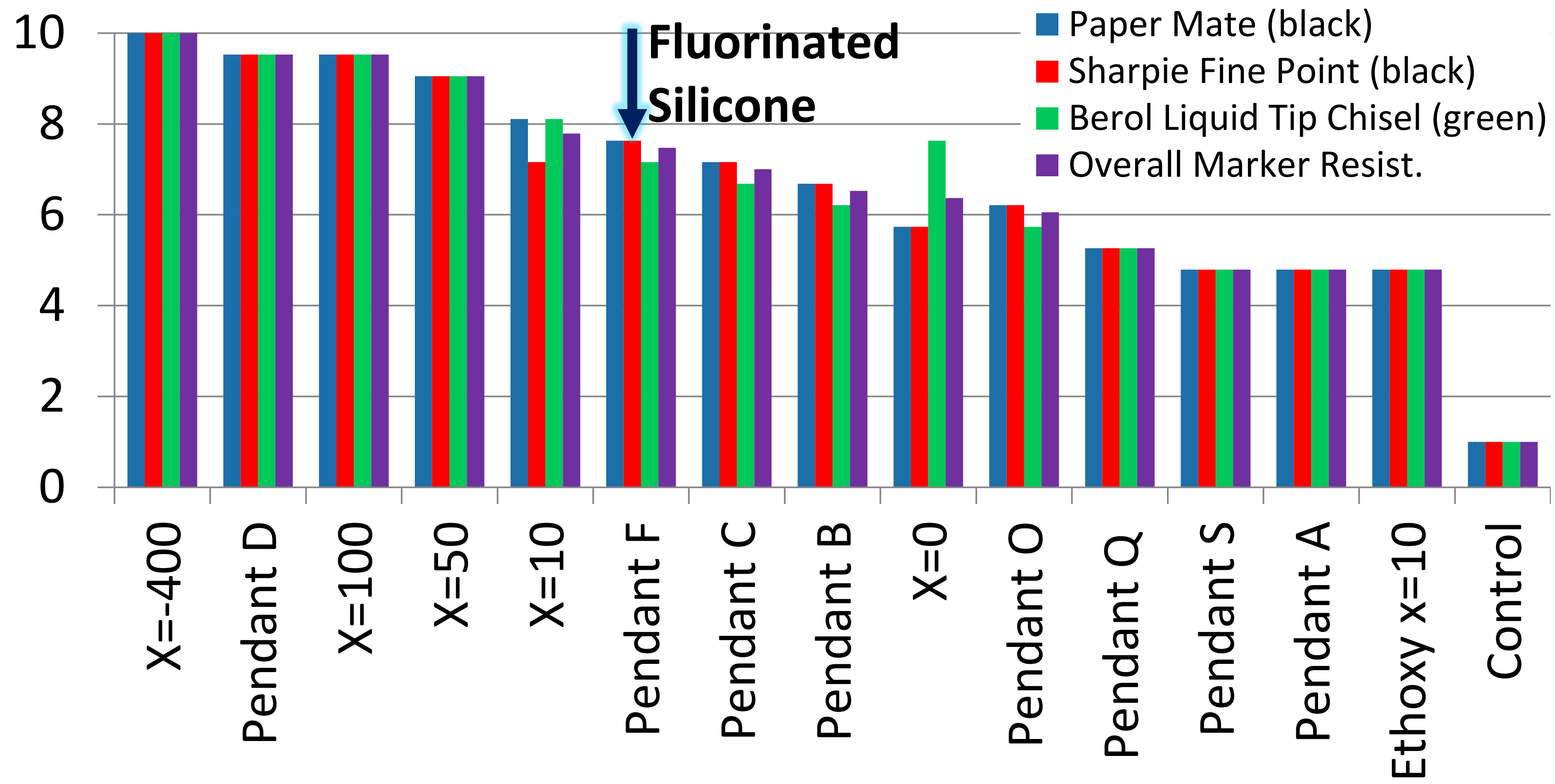
Contact Angle of TDxT Type Polymers on Glass



Water Pickup: Concrete Tiles

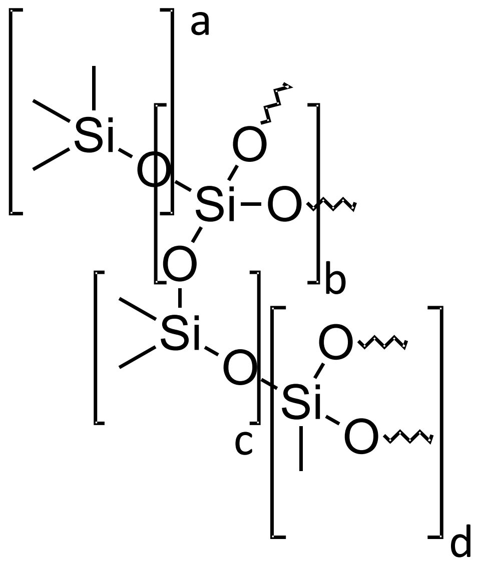


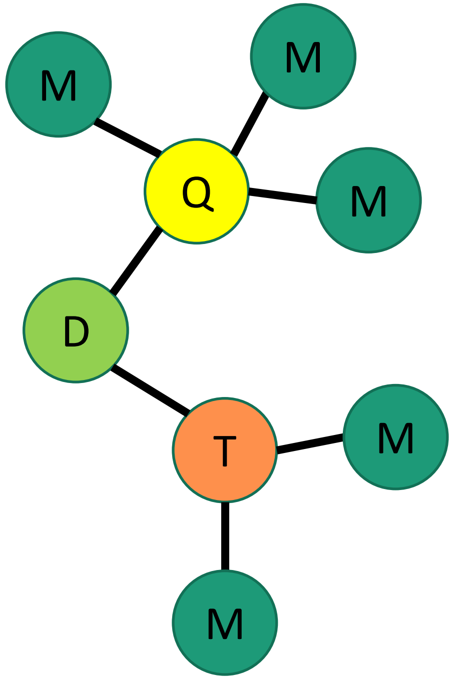
Marker Resistance: Al Panels W/ TDxT types



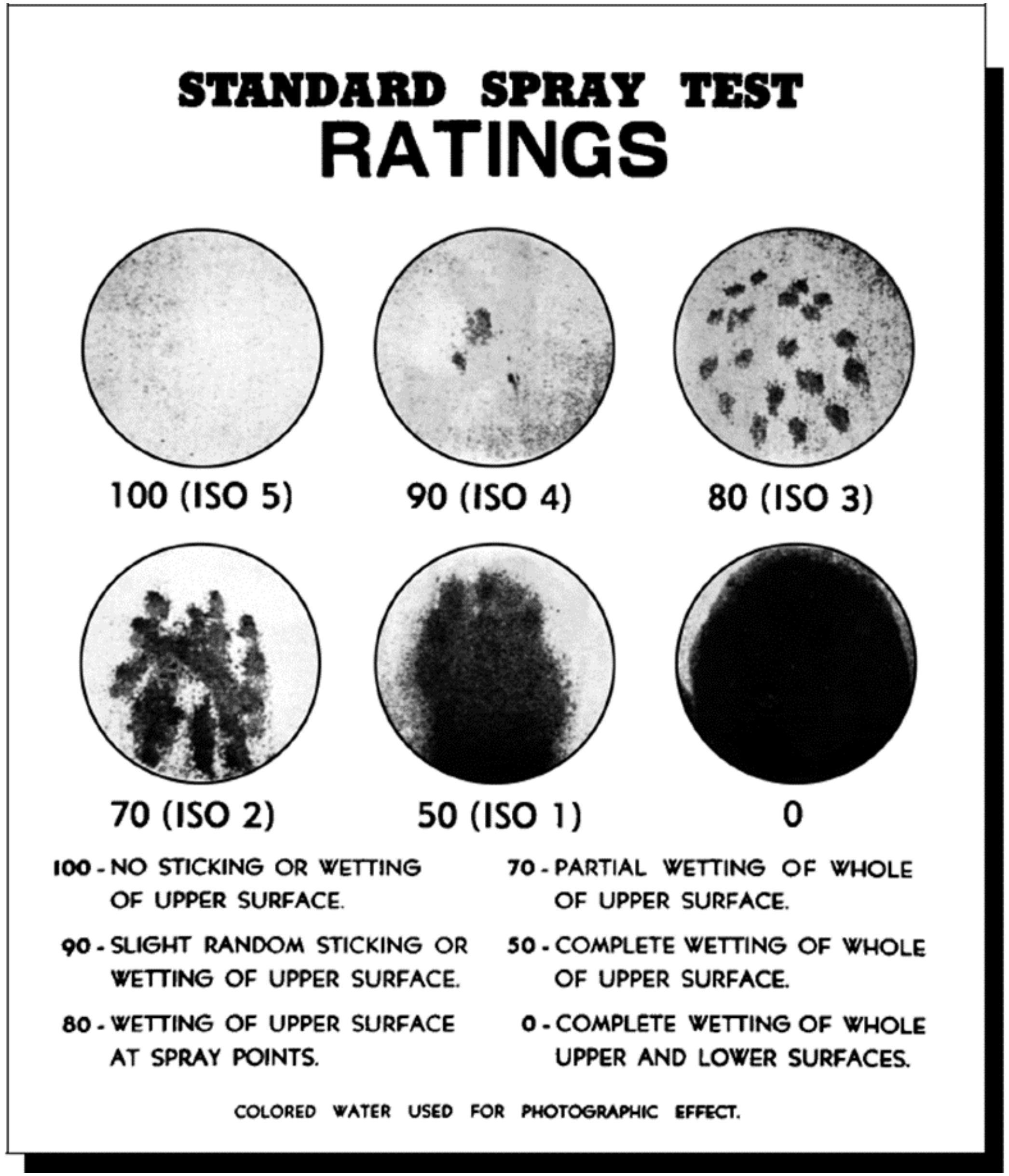
Marker resistance improved with higher MW

MDTQ Resins





AATCC 22 Standard Spray Test



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)

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

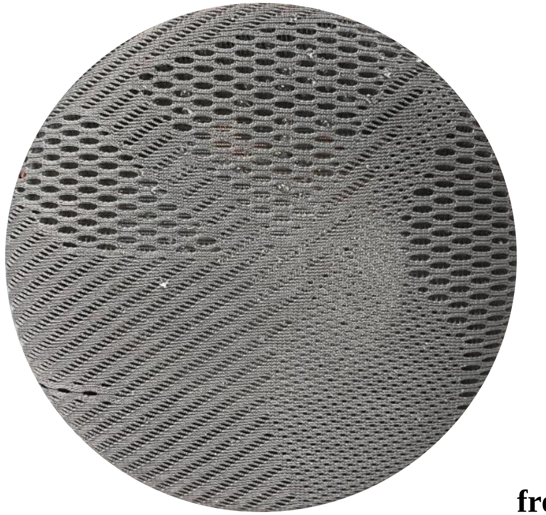
Suede

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

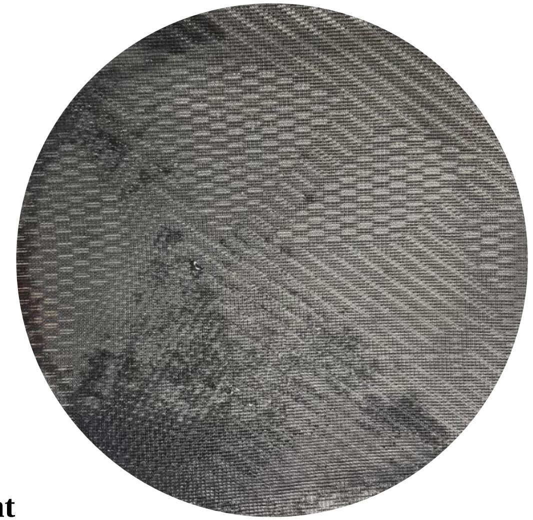
Brown

Benchmark water repellent

Rating: 90 (ISO 4)



front



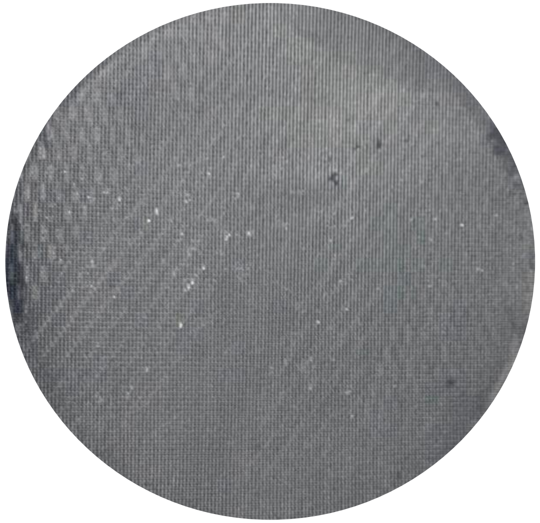
back

Grey

Siltech YL7-53B

Rating: 90 (ISO 4)

front



back

Glass Contact Angle QT Resins in Solvent

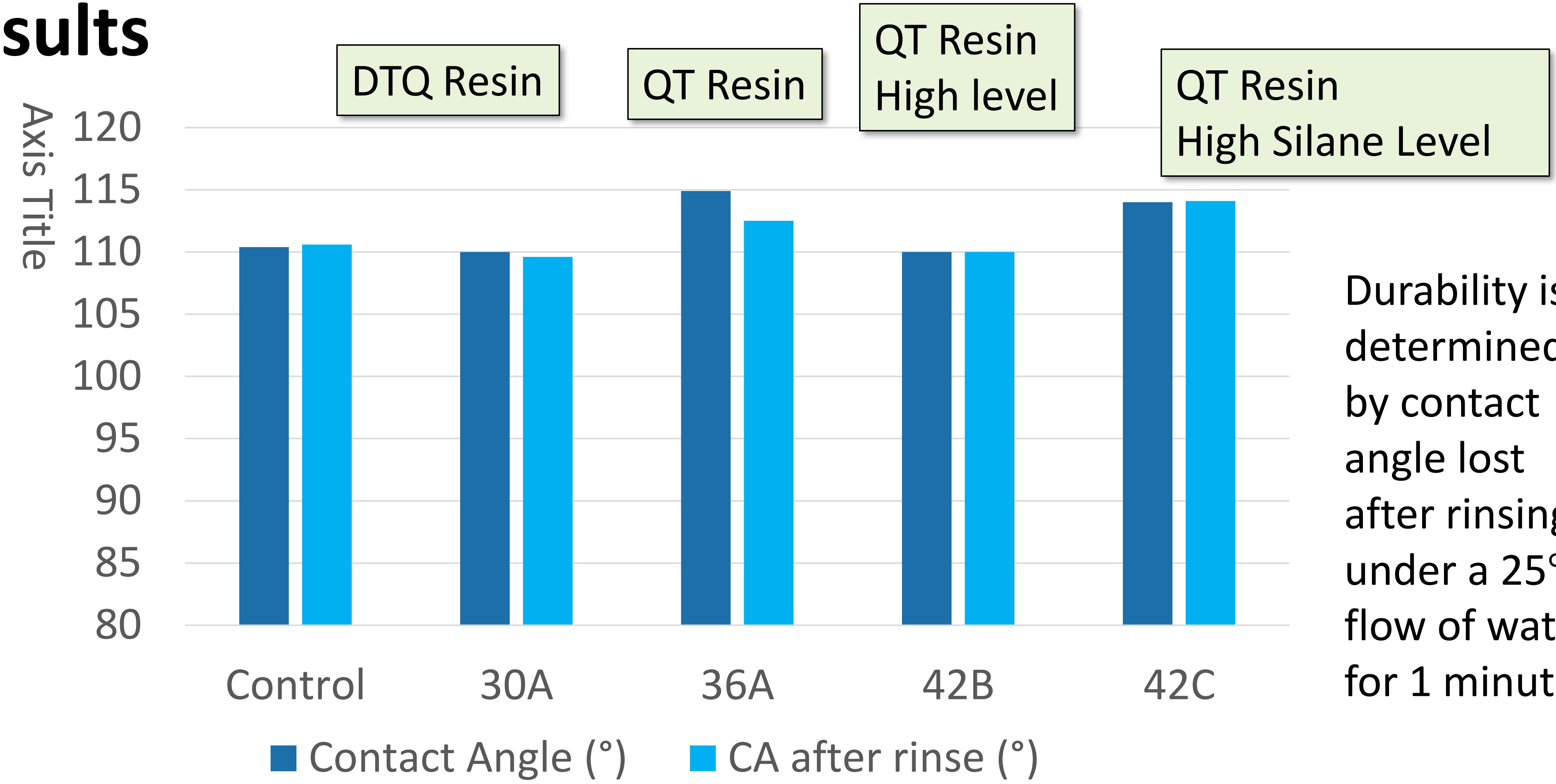
Sample	WCA	sliding angle
Blank	84°	22°
Benchmark	109°	6.5°
YL7-143B	108°	27°

108°

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°

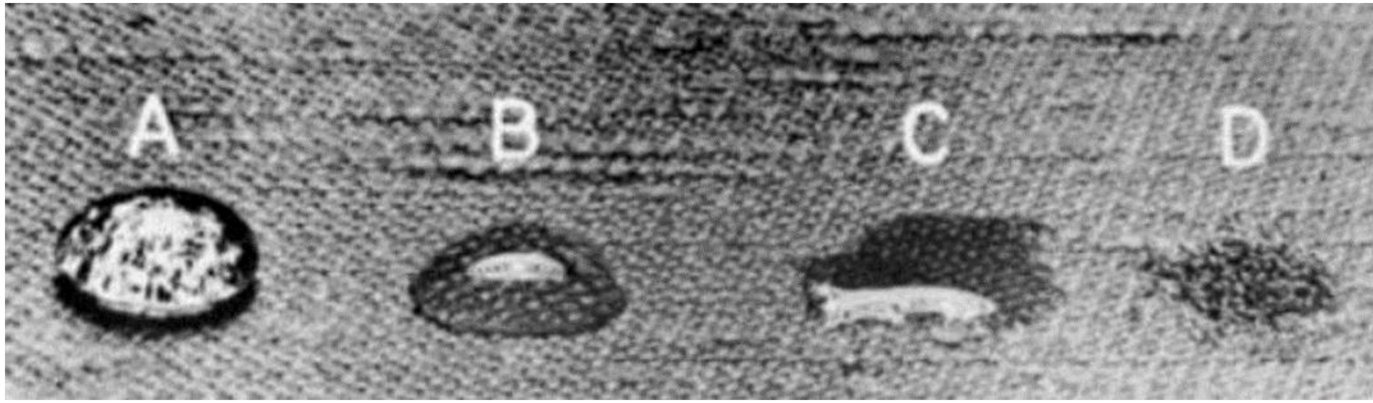
Durability is determined by contact angle lost after rinsing under a 25°C flow of water for 1 minute.

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

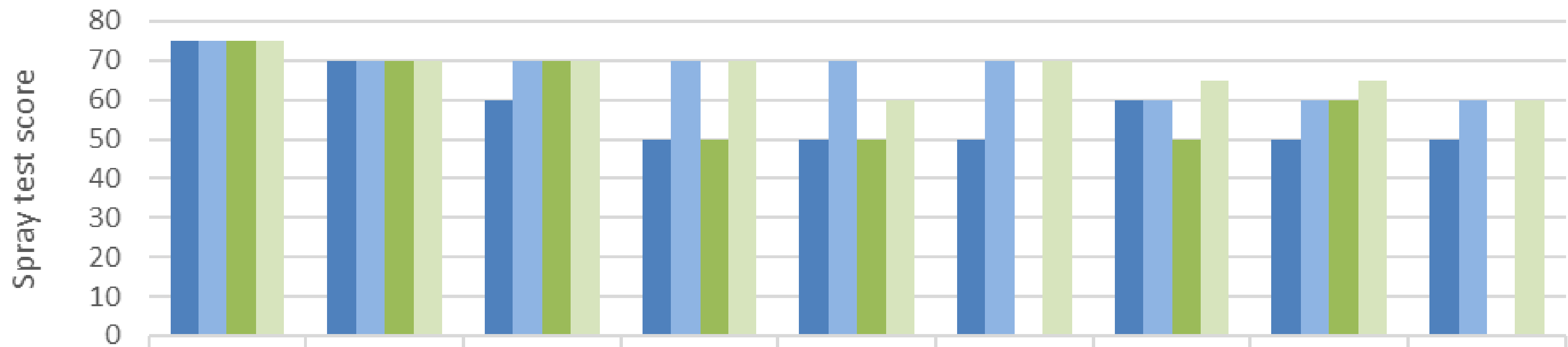


AATCC 193 Standard Test Liquids			
AATCC Aqueous Solution Repellency Grade (0-5 best)	Color	Water/IPA (vol/vol)	Surface Tension (mN/m)
0	None	100:0	72
1	Blue	98:2	59
2	Pink	95:5	50
3	Orange	90:10	42
4	Yellow	80:20	33
5	Dark Blue	70:30	28

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

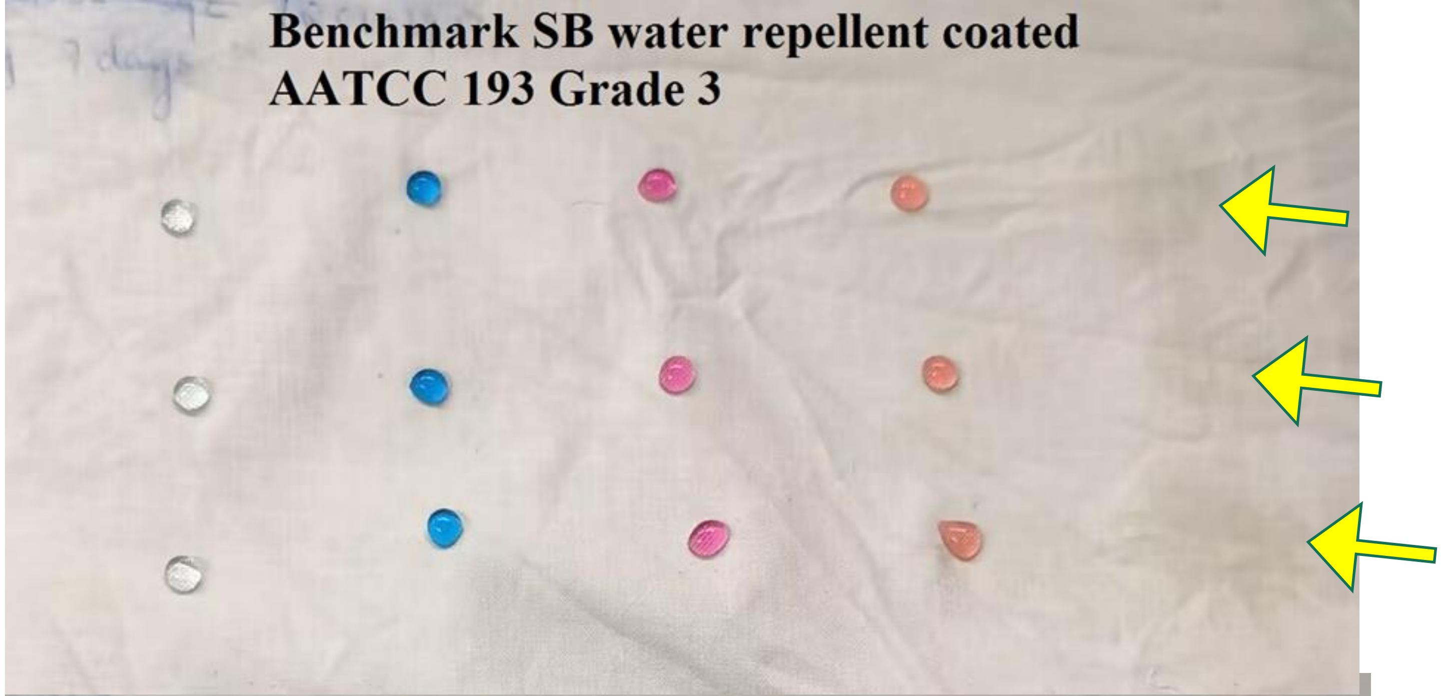
Sample	Description	AATCC 22 Rating	AATCC 193 Rating
Control	Commercial product	75	3
87F	Sol-gel base	70	na*
55A	Sol-gel + QT resin	70	na
39D	Sol-gel + QT + aminosilicone 1	70	2.5
59A	Sol-gel + QT + aminosilicone 2	70	3.5
187	QT resin **emulsion**	70	na
28A	Silane modified silicone **emulsion**	50	na
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

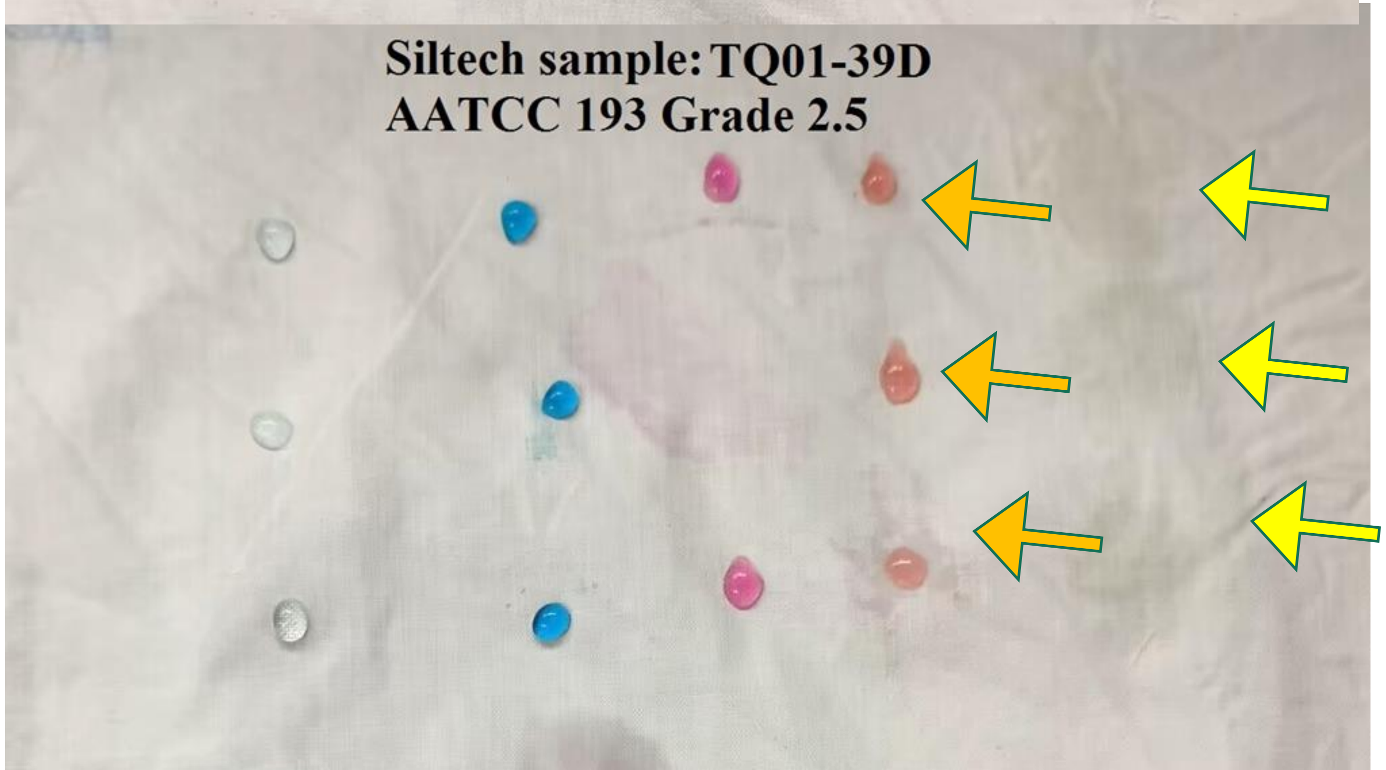
AATCC 22 spray test result for heat cured and R.T. cured sample before and after rinse



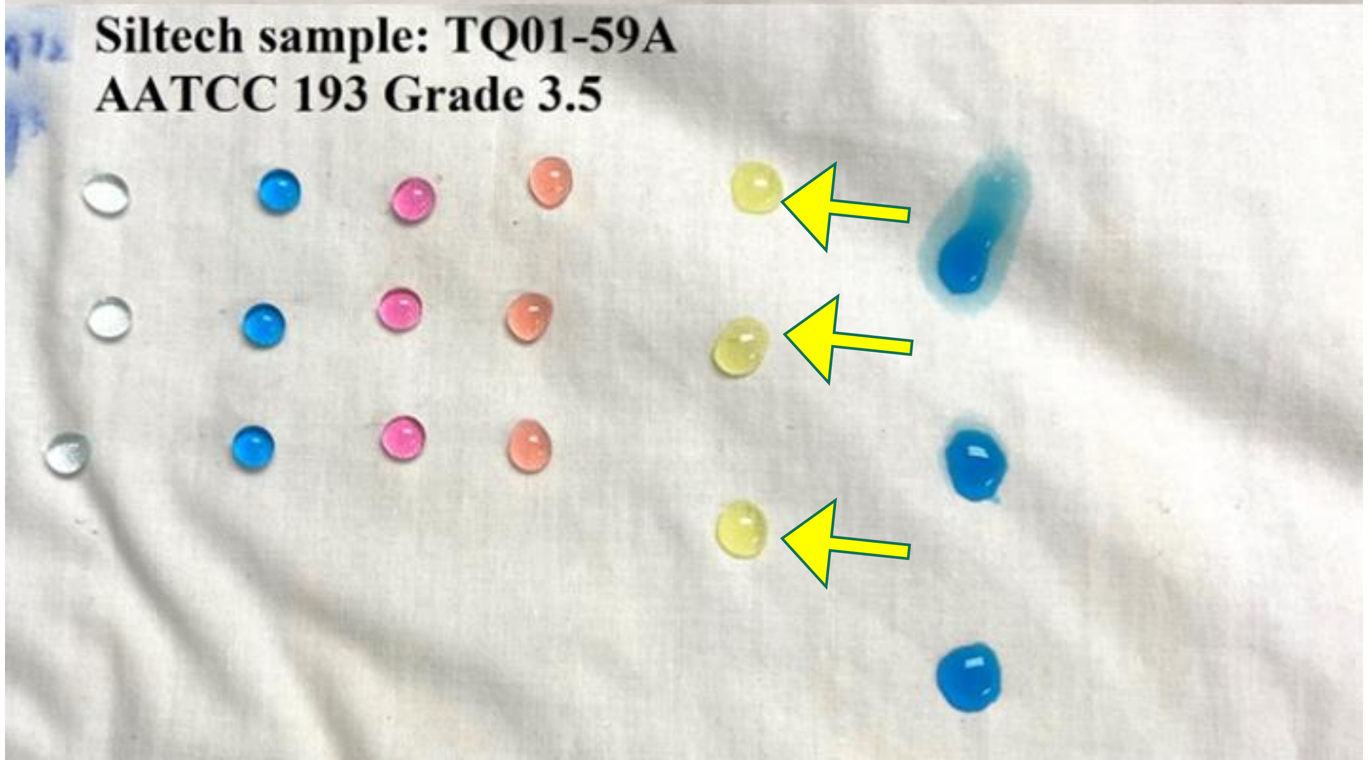
	Benchmark solvent-based silicone water repellent	TQ01-39D	TQ01-59A	TQ01-55A	TC15-87F	BQ-19-187	TQ01-16A	TQ01-16G	TQ 01-41C
heat cure-before rinse	75	70	60	50	50	50	60	50	50
heat cure-after rinse	75	70	70	70	70	70	60	60	60
R.T. cure-before rinse	75	70	70	50	50	0	50	60	0
R.T. cure-after rinse	75	70	70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

Sol-Gel QT Resins: Glass Contact Angle

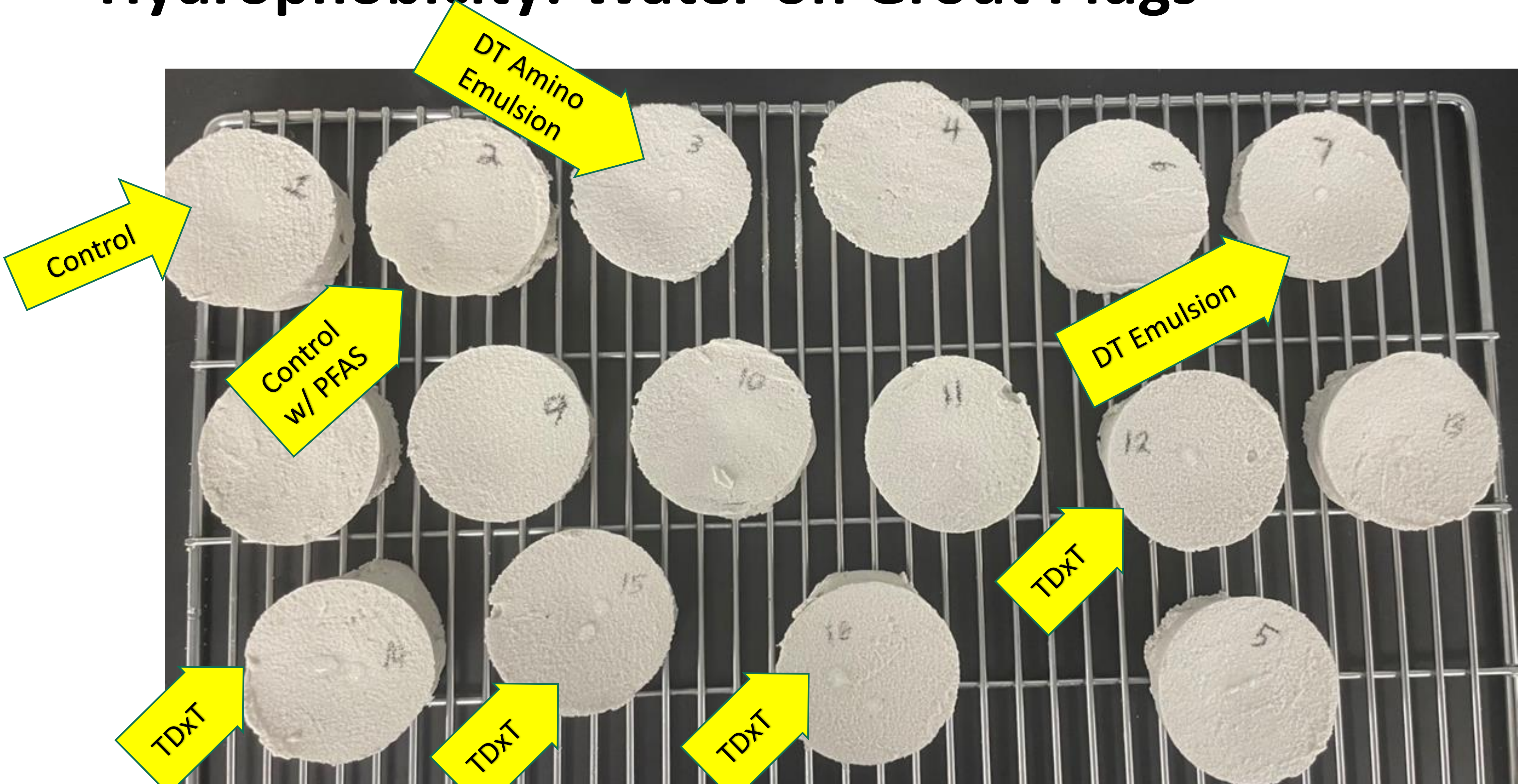
114°

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°

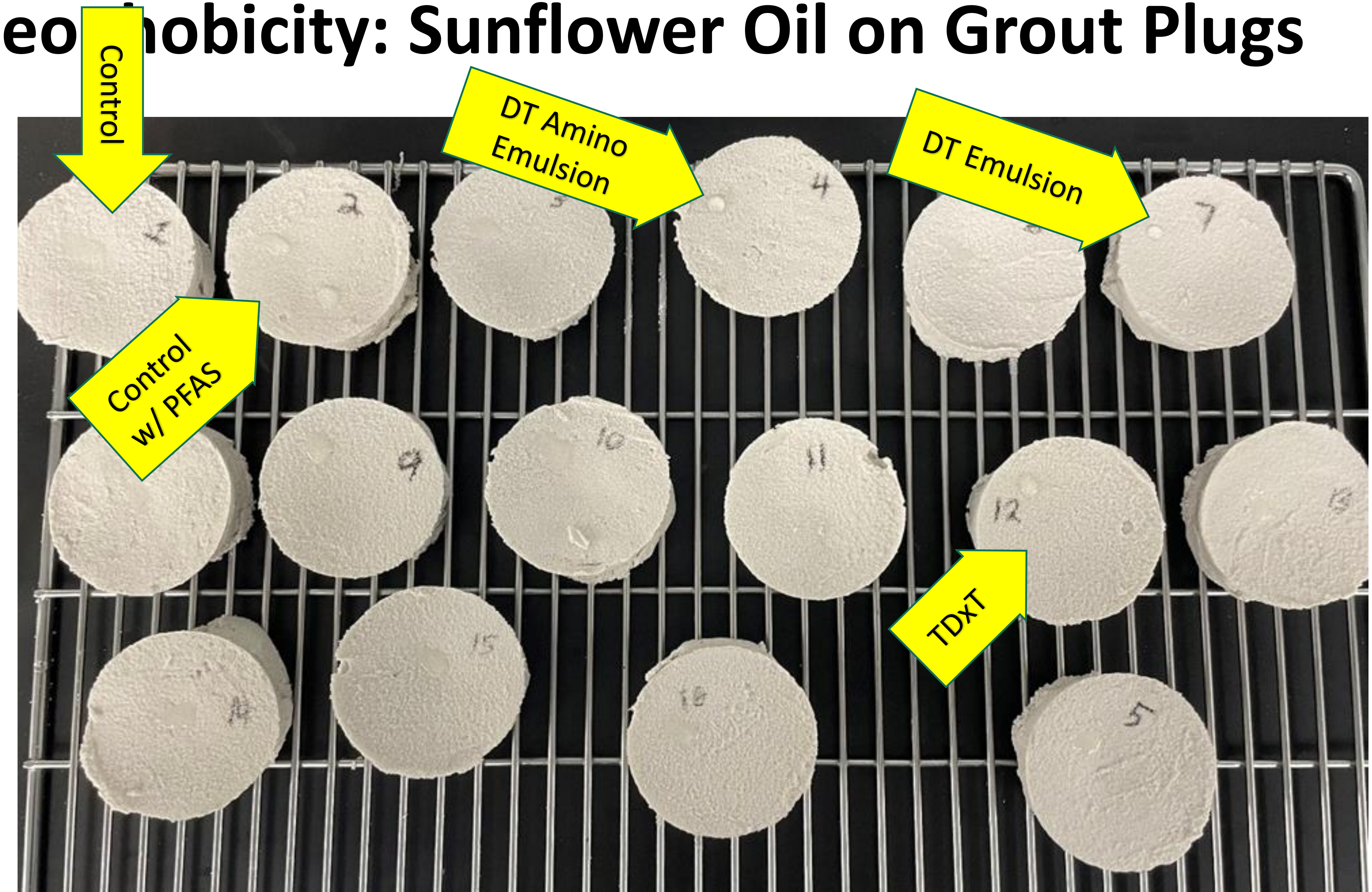
Oleophobicity

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

Hydrophobicity: Water on Grout Plugs

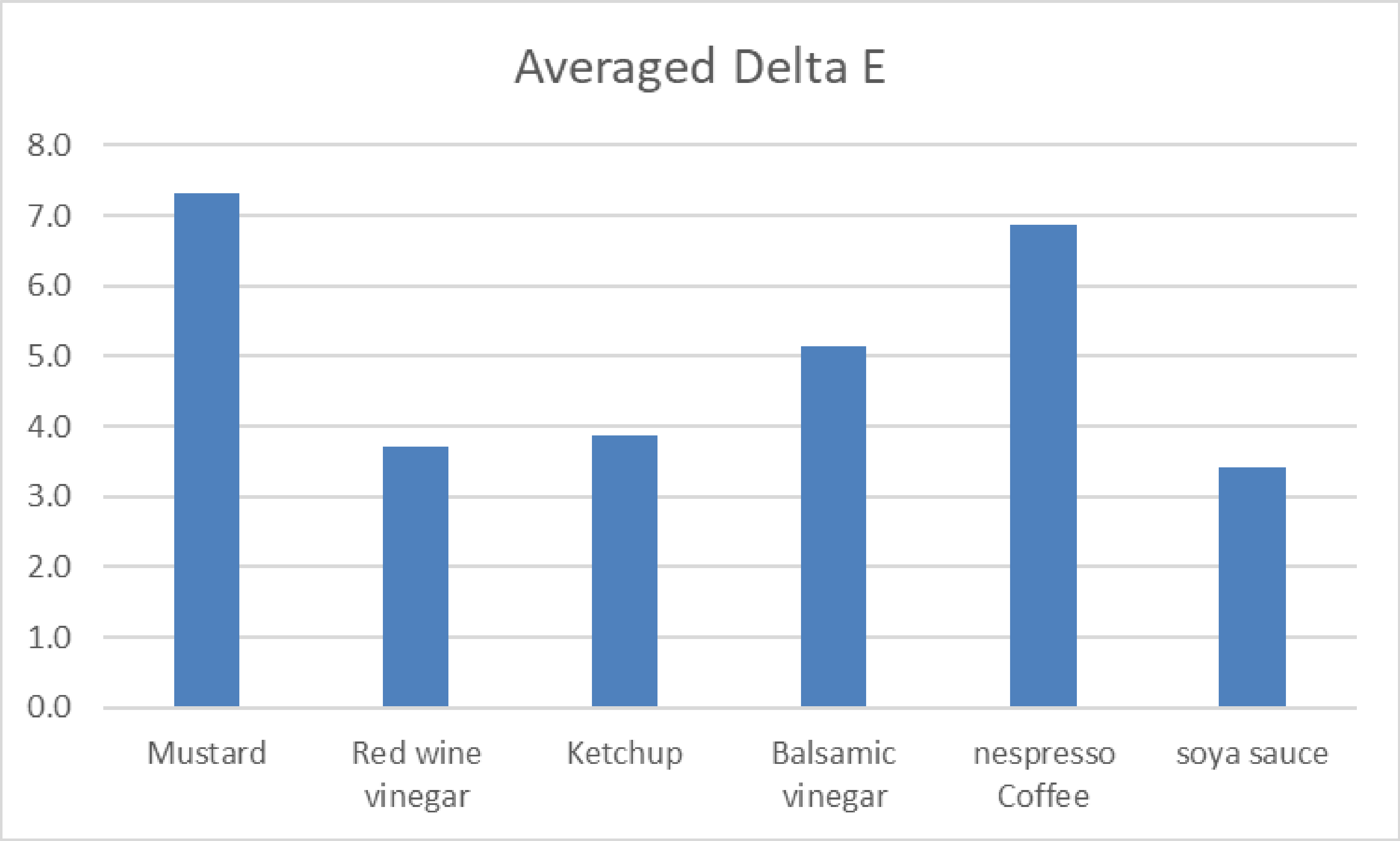


Oleophobicity: Sunflower Oil on Grout Plugs

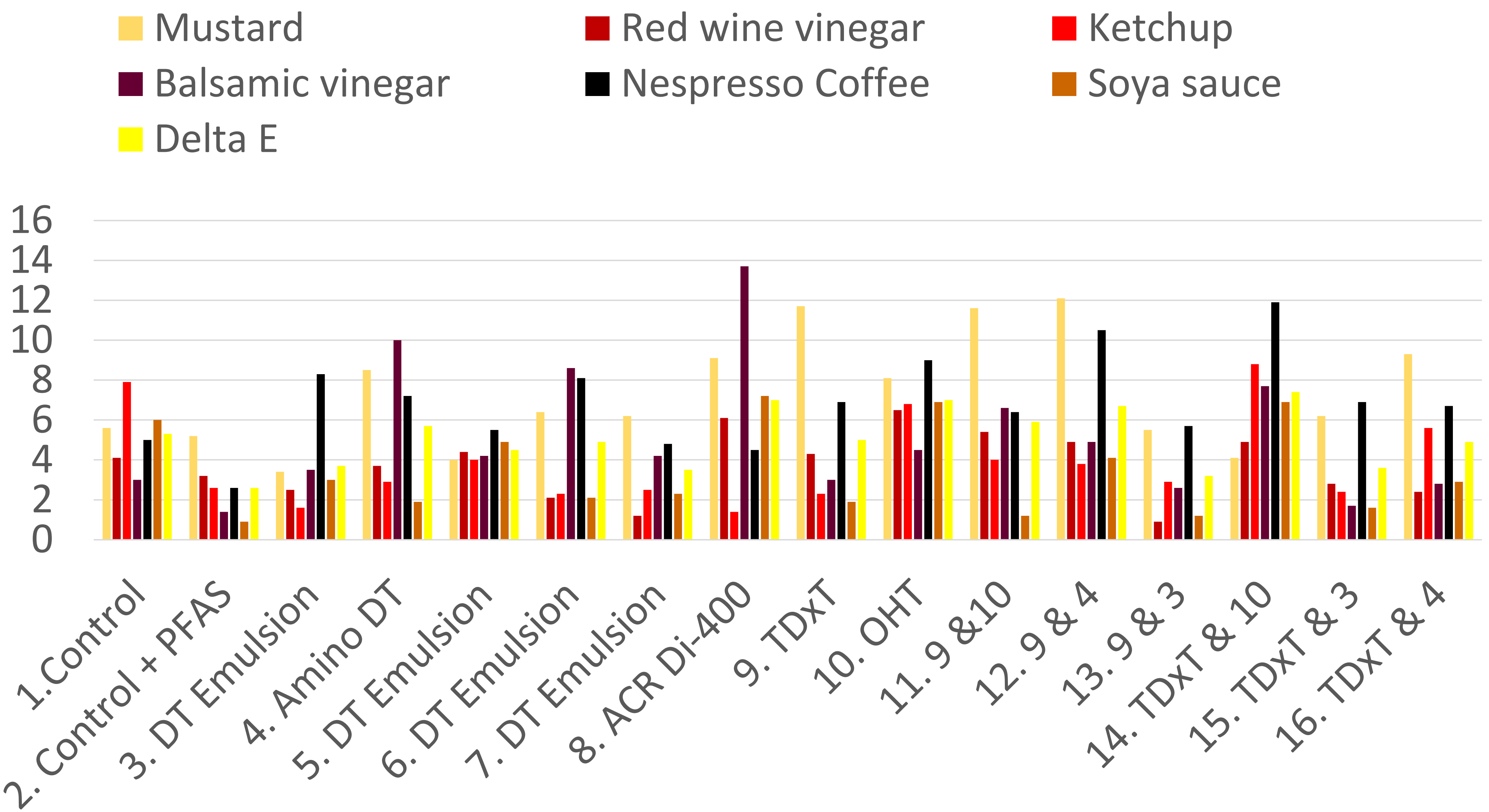


Stain Resistance

Stains

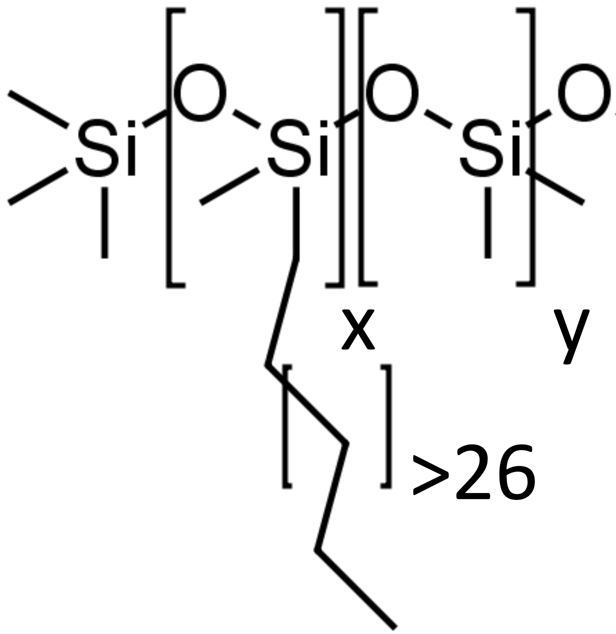

Averaged Delta E
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Mustard
Red wine vinegar
Ketchup
Balsamic vinegar
nespresso Coffee
soya sauce

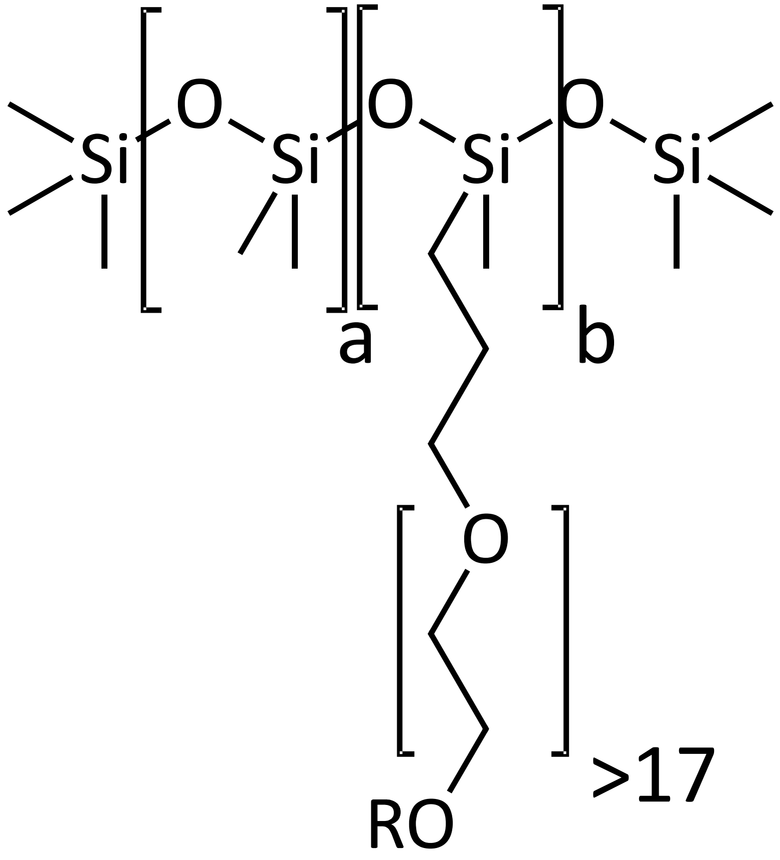
Delta E data



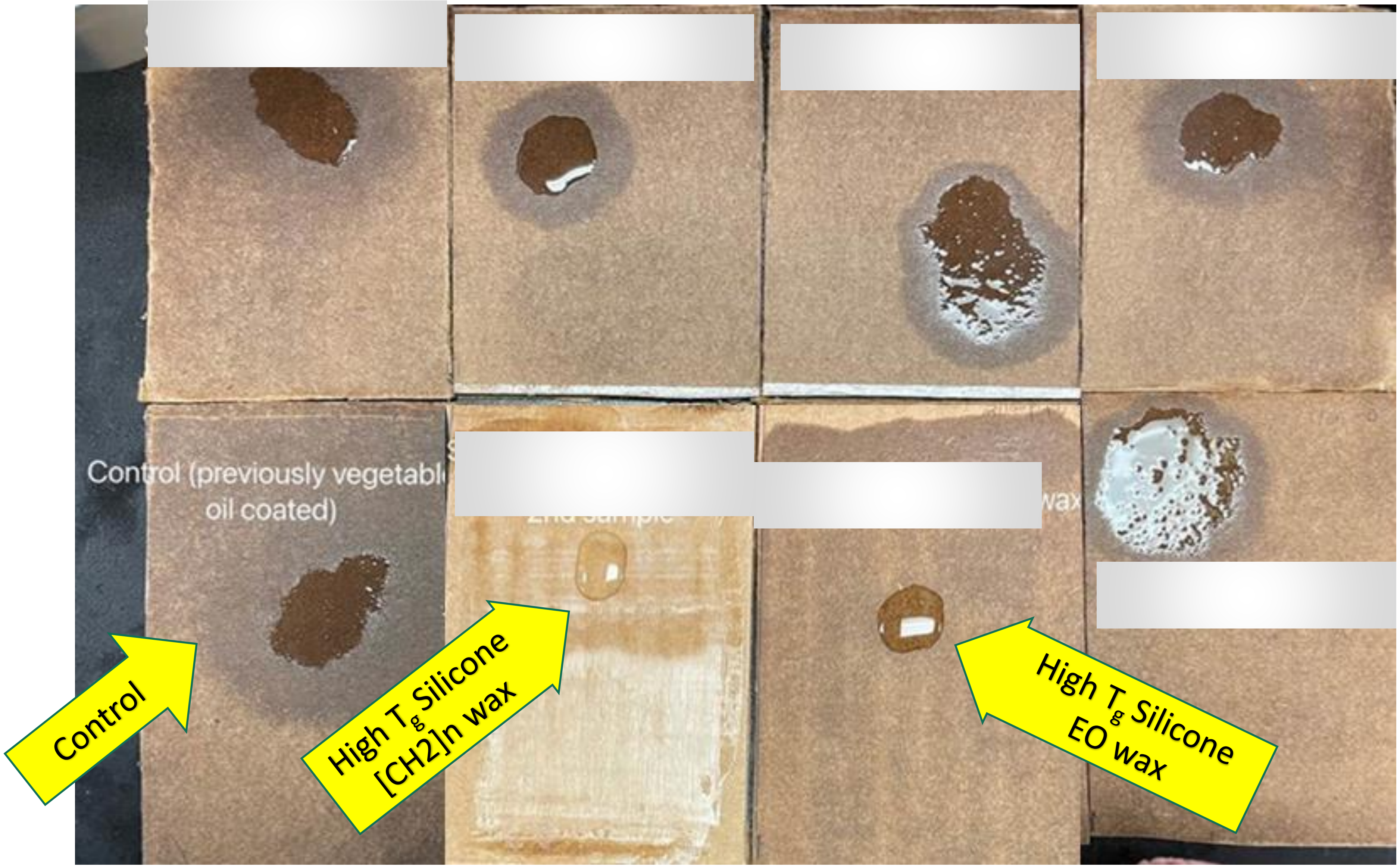
Mustard
Red wine vinegar
Ketchup
Balsamic vinegar
Nespresso Coffee
Soya sauce
Delta E
16
14
12
10
8
6
4
2
0
1.Control
2. Control + PFAS
3. DT Emulsion
4. Amino DT
5. DT Emulsion
6. DT Emulsion
7. DT Emulsion
8. ACR Di-400
9. TDxT
10. OHT
11. 9 &10
12. 9 & 4
13. 9 & 3
14. TDxT & 10
15. TDxT & 3
16. TDxT & 4

Silicone Waxes





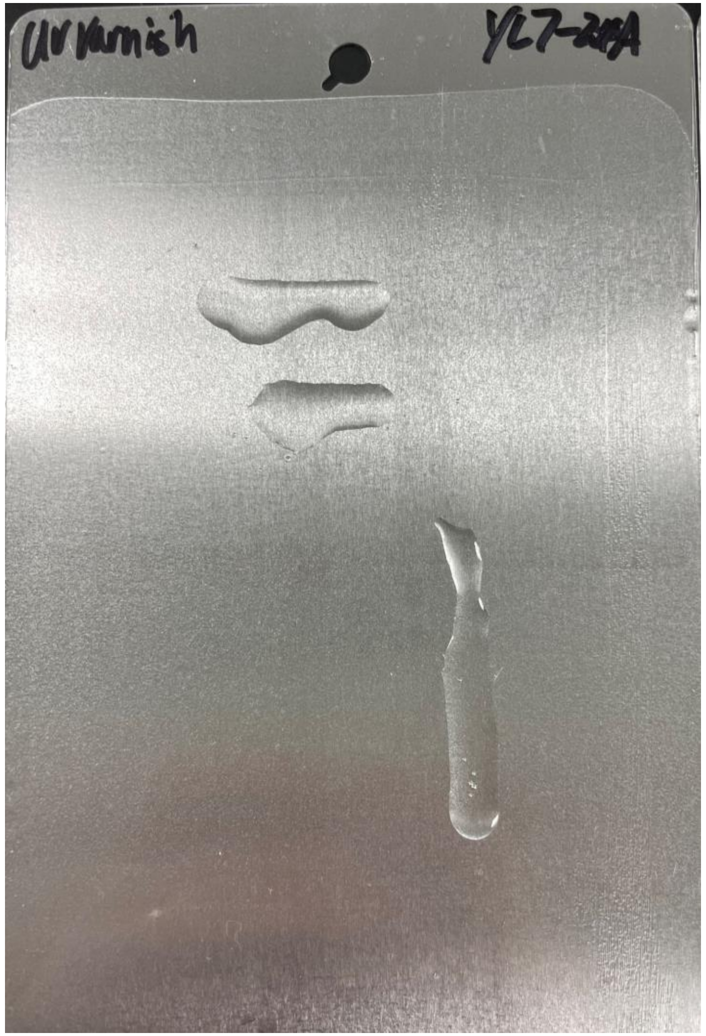
Oleophobicity: Vegetable Oil on Cardboard



Oleophobicity: Vegetable Oil on Cardboard

A New Compound for UV: Beading MO

Close Up



Video

Chemical Resistance

1 **H** 1.008							2 **He** 4.002 6
3 **Li** 6.94	4 **Be** 9.012 2	5 **B** 10.81	6 **C** 12.01 1	7 **N** 14.00 7	8 **O** 15.99 9	9 **F** 18.99 8	10 **Ne** 20.18 0

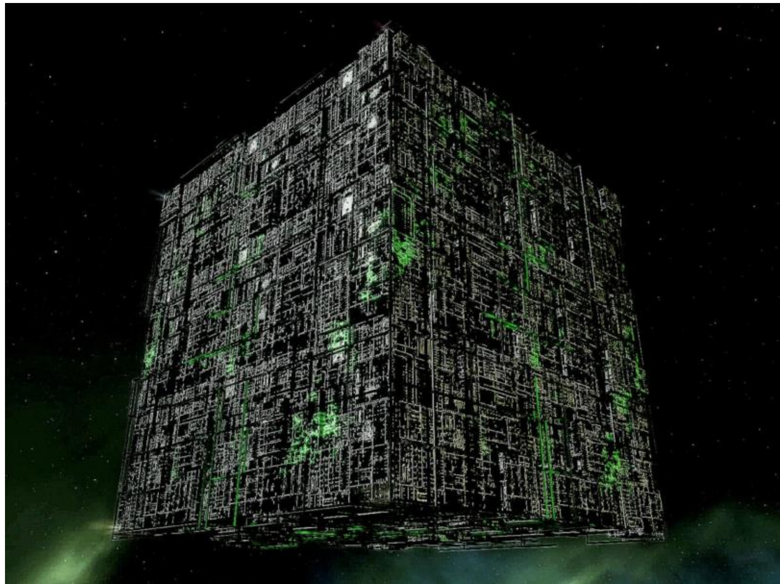
- PFAS compounds are very strongly bonded and resistant to acids, etc.
- PDMS based materials are very labile to acid/base hydrolysis.
  - This is why they degrade in the environment.
- Some unique species such as TQ resins are likely to be somewhat chemically resistant.
- We are not going to be able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