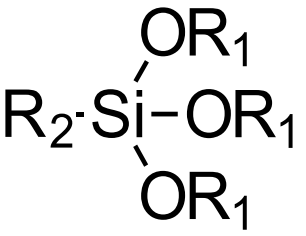
The Evolution of Trialkoxysilane Monomers to Hybrid Silicones

[1] Tom-Seung, Cheung, [2] Mike Gunther, [3]Bob Ruckle

Siltech Corporation
Toronto, ON Canada

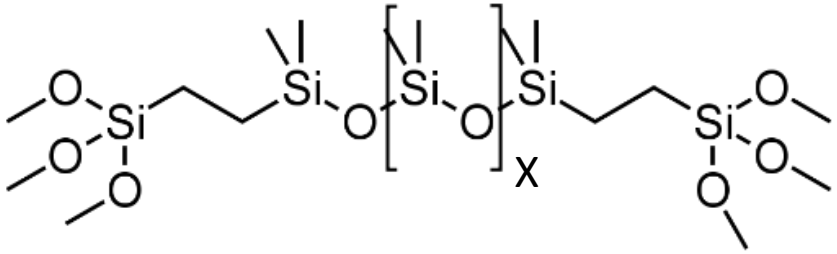
[1]Tom@siltech.com [2]Mike.Gunther@siltech.com, [3]Robert@siltech.com

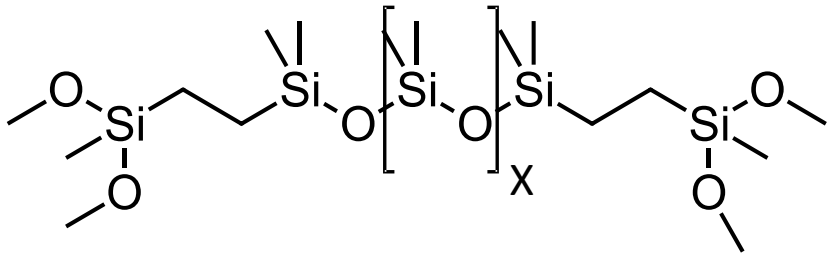
Introduction

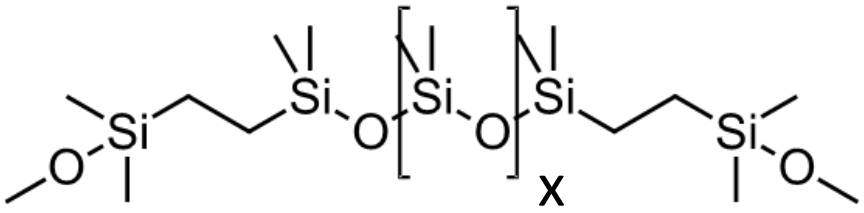


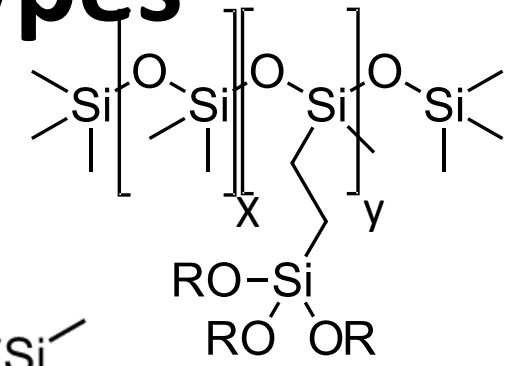
- Organofunctional silanes have been used as surface treatments, adhesion promoters, dispersants or for cross linking in condensation cured systems.
- The R^1 alkoxy groups are often methyl but ethyl, propyl, and other alcohols are used and have the effects of slowing down the reaction and liberating less toxic alcohols.
- Research in the 90's focused on increasingly more complex R^2 groups.
- A simple direction that these silanes have evolved in over the years is where the trialkoxy silane moieties are directly appended to silicone polymers forming a chemical chimera of both species.

Structures Evaluated – Reactive Alkoxy Silicones - TMS and DMS types





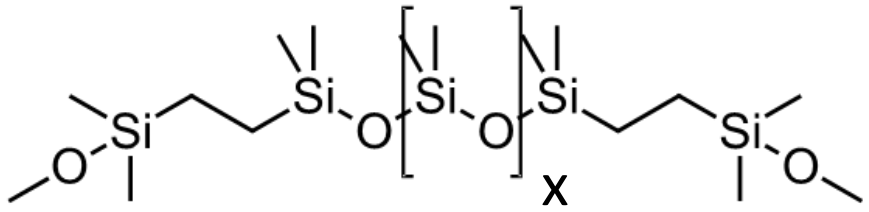




X= 0, 10, 50, 100, 400

- Hydrolyzable alkoxy groups form siloxane networks by reacting with added silanes, silanols in film formers or substrates to (of course, other M-OH groups too)
- Choice of X allows the customer to dial in the amount of silicone character needed
- Functionality on silicon, mono, di- or tri-, provides control over siloxane network density

Application Example of a Reactive Alkoxy Silicone - DMS type



X=10, 50, 100, 200, 300

- Application is concrete waterproofing – industry standard is trifunctional octyl silane
- x=50 and x=10 are both commercial products
- x=50 sales expected to 20 tons this year at one customer

SIL TECH

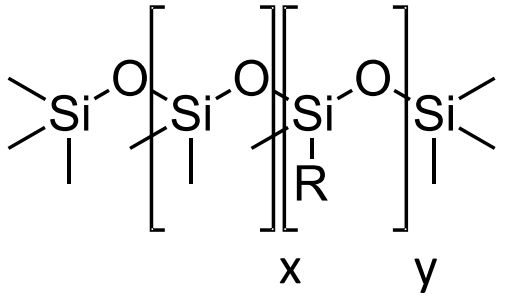
Film Forming Emulsions

- Silanol based, reactive
- Sometimes a catalyst
  - Tin
  - Titanium
  - Mineral Acid
- Hydrolysis occurs but condensation doesn't until drying on the surface

- Many variants are possible
- We explore many in this talk without many details of the differences.

SILTECH

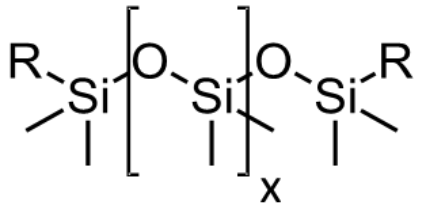
Other Reactive Silicones Evaluated



Pendant type

R Groups

Hydroxy
Dual Hydroxy
Acrylate
Acrylate with Secondary Hydroxyl (some with fluoroalkyl side chains)
Hydride
Isocyanate
Amino
Epoxide
Trimethoxysilane, Dimethoxysilane, Monomethoxysilane
Vinyl



Linear type

Reactive Alkoxy DTQ Type Resins

Type	DT	DT	DT	DTQ	DTQ	DTQ	DTQ	DTQ	TQ	T	Phenyl DT	D/T/ PhT/Q	D/T/ PhT/Q
Ratio	(75/25) 5% OMe	(50/50) 15% OMe	(25/75) 20% OMe	(25/50/25) 20% OMe/OEt	(65/25/10) 25% OMe	(25/50/25) 40% OMe	(50/25/25) 20% OMe	(25/50/25) 40% OMe	(66/33) 60% OMe	(heat cure)	20% OMe	(25/50/10/15) 20% OMe	(25/40/20/15) 20% OMe
Gloss	164	163	163	159	170	172	175	177	178	170	167	173	172
Contact angle	104	87.2	98.2	97.2	99.8	99.9	106.9	98	101.4	97.9	95.2		
Static CoF	2.648	2.918	1.999	1.326	1.302	0.527	2.579	0.436	0.353	1.334	0.817	0.531	0.526
Kinetic CoF	2.598	2.643	1.097	0.660	1.264	0.394	2.093	0.343	0.287	0.652	0.682	0.227	0.503
Mar resistance	4	4	8	8	4	4	4	8	4	6	6		
Oil resistance	9.2	9.2	9.2	9.2	9.6	9.2	9.2	9.6	9.6	9.2	9.6		
Pencil (Initial)	< 6B	< 6B	4B	4B	6B	6B	N/A	N/A	N/A	N/A	5B		
Pencil (Final)	5B	6B	8H	>9H	4H	8H	4H	9H	8H	9H	8H	6H	6H

Hardness ranges from 5B to over 9H!

Very flexible chemistry so many types of coating qualities can be targeted

Resins can be formulated with additional organofunctional silanes for enhanced properties

SIL TECH

Silicone Additives to Improve Adhesion of Alkoxy Cured Silicone Sealants – acid catalyzed

Commercial Sealant	Additive A (2.5%	Additive B (2.5%)	Rating 10 the best
Sikasil SG-10			0
Sikasil SG-10	Silmer TMS Di-10		1
Sikasil SG-10	Silmer TMS Di-10	Phenol mod Silicone	1
Sikasil SG-10	Siltech C-2053		1
Sikasil SG-10	Phenol modified Silicone		2
Sikasil SG-10	TMS type X=8		2
Sikasil SG-10	Silmer NCO Di-10		2
Clear Silicone II	Silmer TMS Di-10	Eugenol	3
Clear Silicone II	Silmer TMS Di-10	Silube FF108-16	3
Sikasil SG-10	Eugenol		3
Sikasil SG-10	Silicone Alkyl Polyether		3
Sikasil SG-10	Silmer TMS Di-0		3
Sikasil SG-10	Silmer NH Di-8		4
Clear Silicone II	Silmer TMS Di-0	Silamine D2 EDA	5
Sikasil SG-10	Silamine D2 EDA		5

Aminosilicones are the most effective here.

Cured with NACURE 4000: an alkyl acid phosphate catalyst

None of these performed as well as those cured with a tin catalyst

SIL TECH

Silicone Additives to Improve Adhesion of Alkoxy Cured Silicone Sealants – Tin catalyzed

Commercial Sealant	Additive A (2.5%)	Additive B (2.5%)	Rating 10 the best
Clear Silicone II			0
Sikasil SG-10	Silmer NCO Di-10		2
Clear Silicone II	Silmer TMS Di-10	Eugenol	3
Sikasil SG-10	Eugenol		3
Sikasil SG-10	Silube FF108-16		3
Sikasil SG-10	Silmer TMS Di-8		3
Sikasil SG-10	Silmer NH Di-8		3
Sikasil SG-10	Silmer TMS Di-10	Phenol mod Silicone	4
Sikasil SG-10	Phenol mod Silicone		4
Clear Silicone II	Silmer TMS Di-10	Silube FF108-16	5
Sikasil SG-10	Silamine D2 EDA		6
Sikasil SG-10	Silmer TMS Di-10		7
Sikasil SG-10	Silmer TMS Di-0		7
Clear Silicone II	Silmer TMS Di-10	Silamine D2 EDA	7.5
Sikasil SG-10	C-2053		8

Aminosilicones are again the most effective.

DBTDL catalyst

SIL TECH

Silicone Additives (5%) Improve Adhesion of Alkoxy Cured Silicone Caulks and Sealants

Commercial Sealant	TMS type Additive A	Silane type Additive B	A/B Ratio	Rating 10 best
Clear Silicone II	Silmer TMS Di-10	aminopropyltrimethoxysilane (no cat)	1:1	7
Clear Silicone II			1:2	7
Clear Silicone II			2:1	10
Clear Silicone II		aminopropyltriethoxysilane (K-Kat 675)	1:1	9
Clear Silicone II		aminopropyltriethoxysilane (K-Kat 651)	1:1	10
Clear Silicone II		aminopropyltriethoxysilane (K-Kat 678)	1:1	10
Clear Silicone II		aminopropyltriethoxysilane (K-Kat 670)	1:1	10

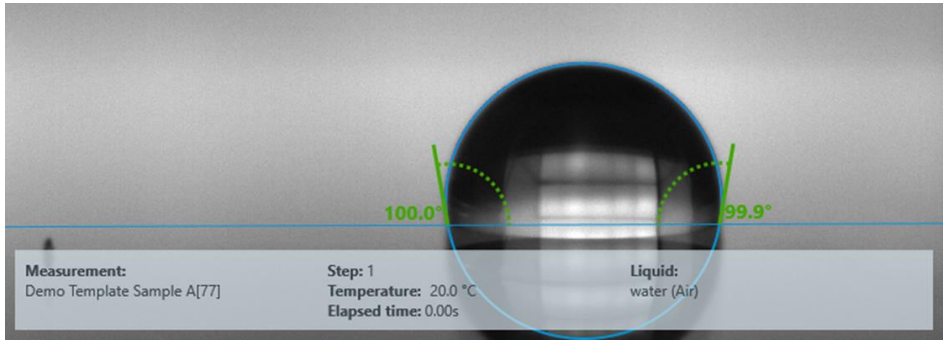
These TMS Di-10 with silane formulations far out performed all others in this study

The sample with 2:1 TMS type to silane has good adhesion on PVC substrate without the use of additional catalyst

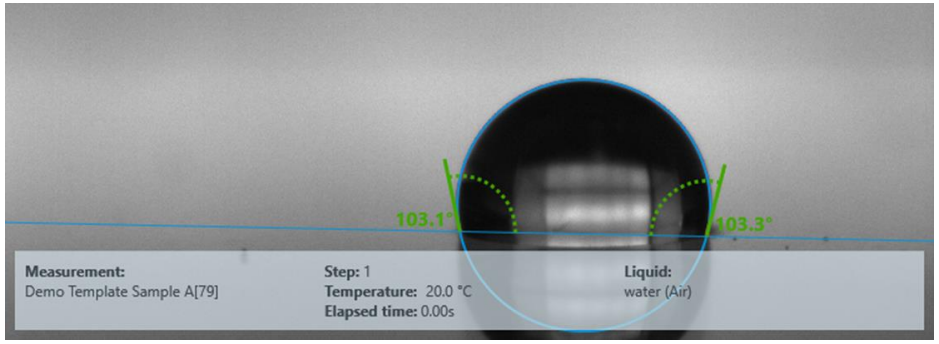
The sample 1:1 of triethoxy silane has good adhesion on PVC substrate with all catalysts tested

SIL TECH

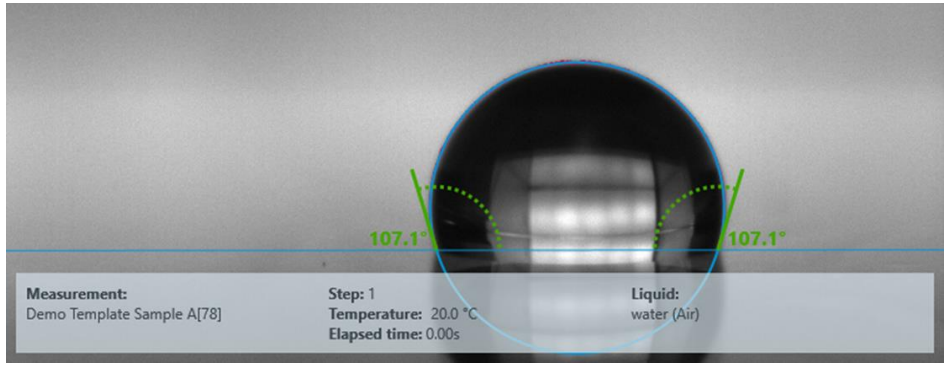
Contact angle increase



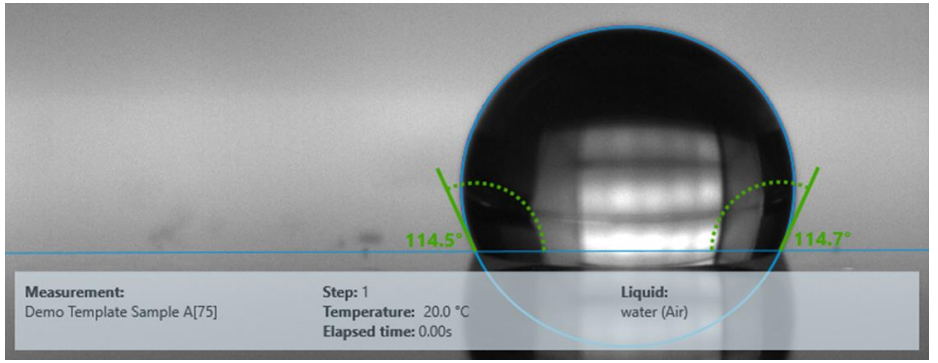
TMS, X=0 angle 100° on glass



TMS, X=10 angle 103°



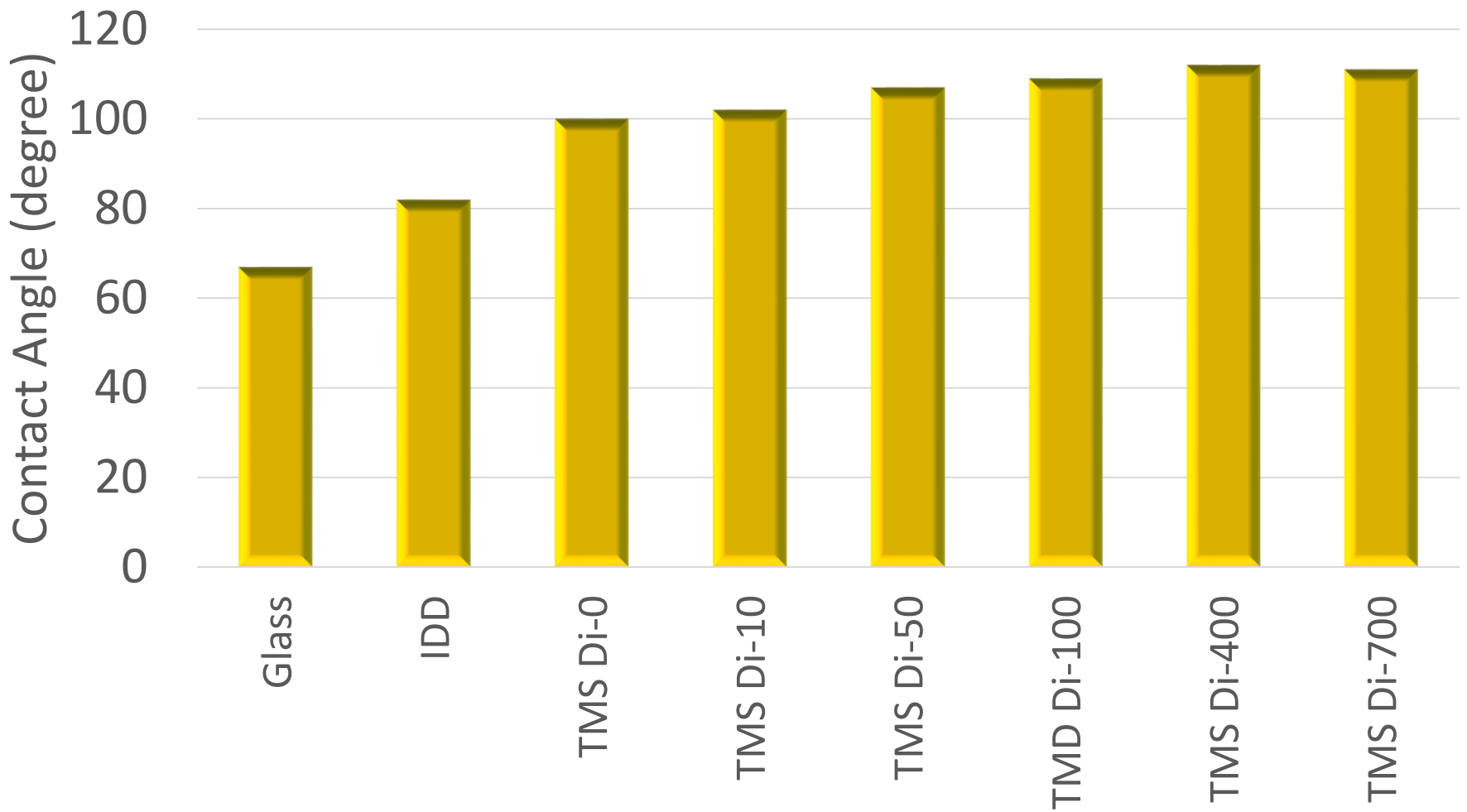
TMS, X=50 angle 107°



TMS, X=400 angle 115°

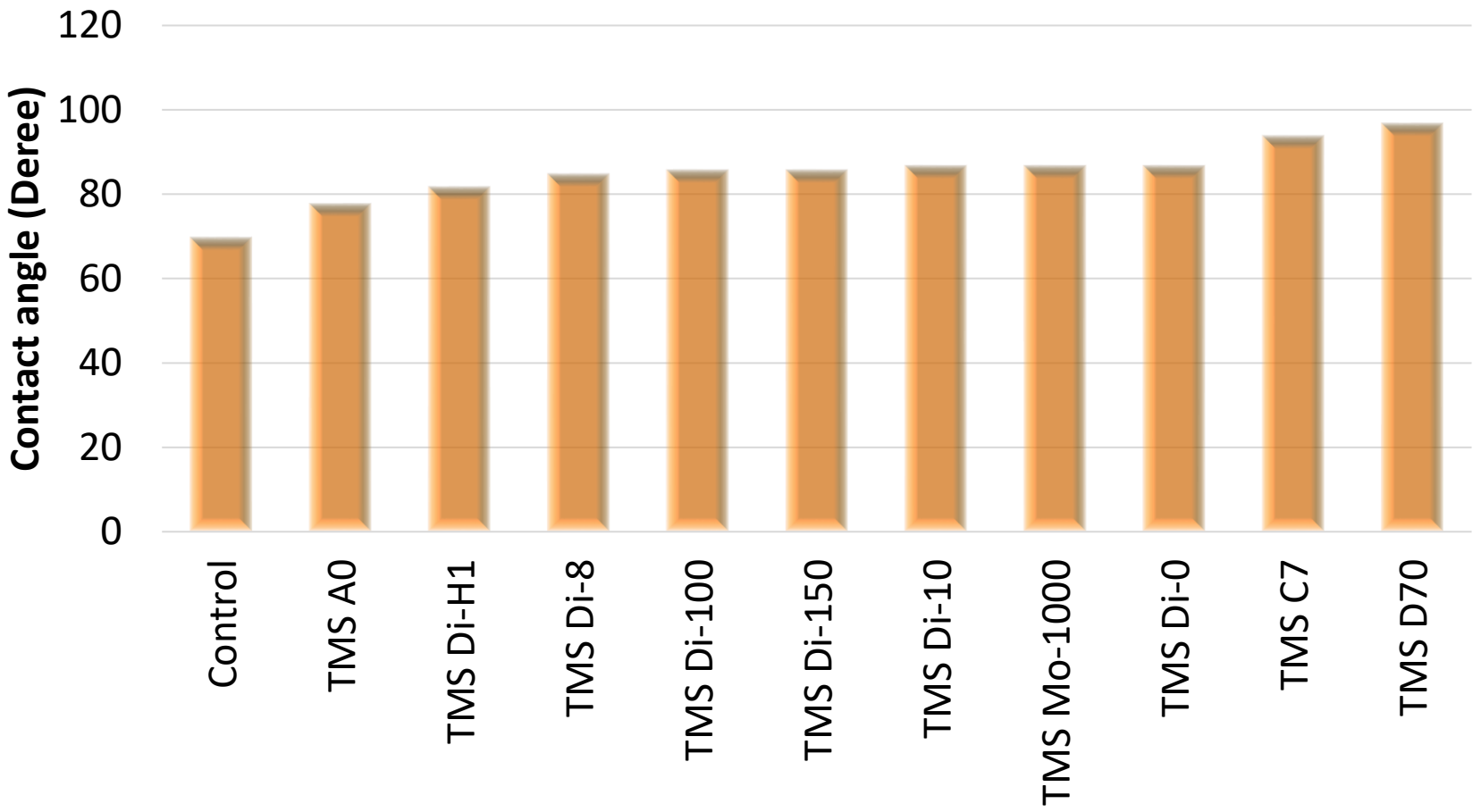
SIL TECH

Contact Angle of TMS Type Polymers on Glass



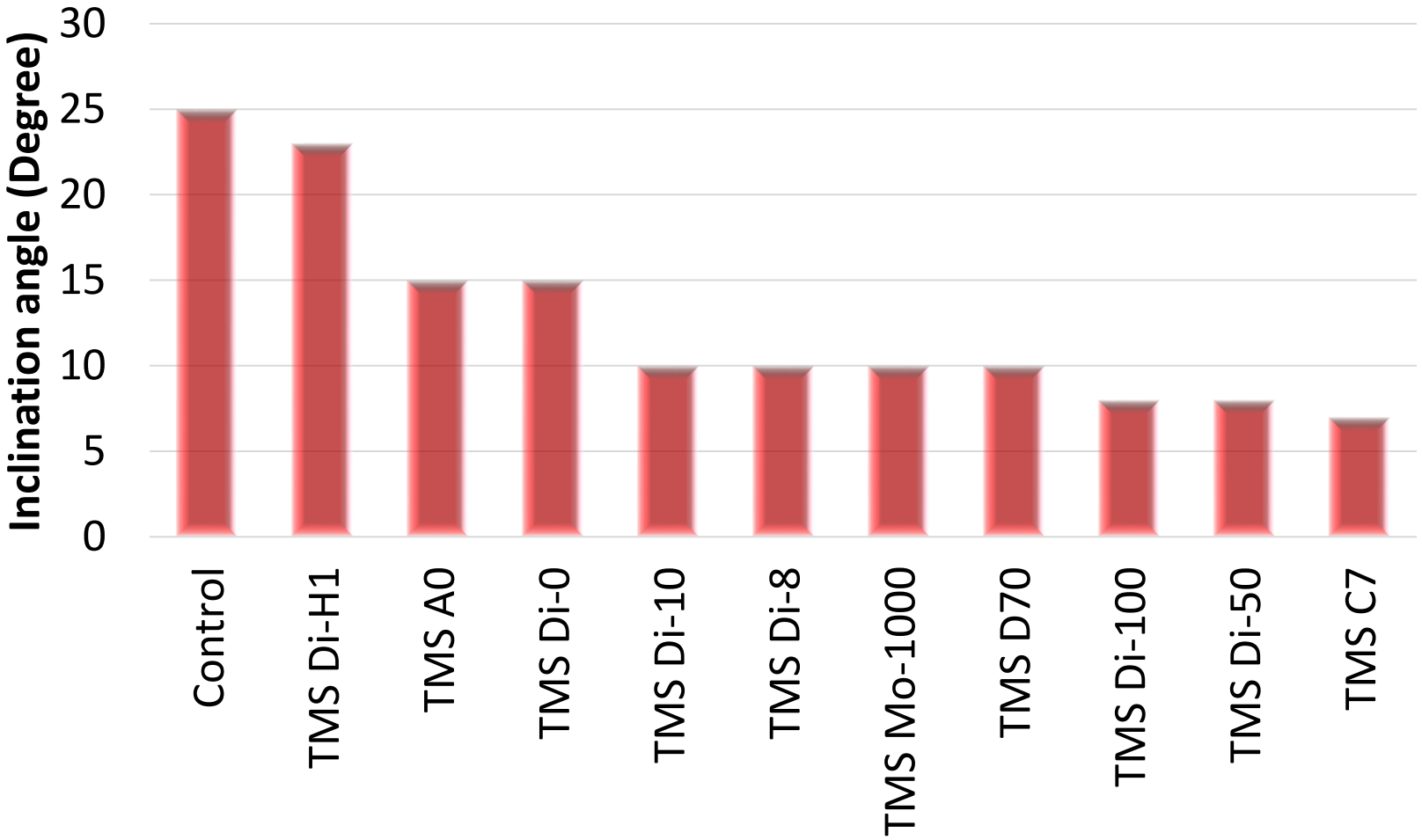
SIL TECH

Contact Angles of Water on Al Panels Coated with TMS types



The contact angles of all the samples treated with TMS types are higher than the control .

Inclination Angles of Water on Al Panels Coated with TMS Types

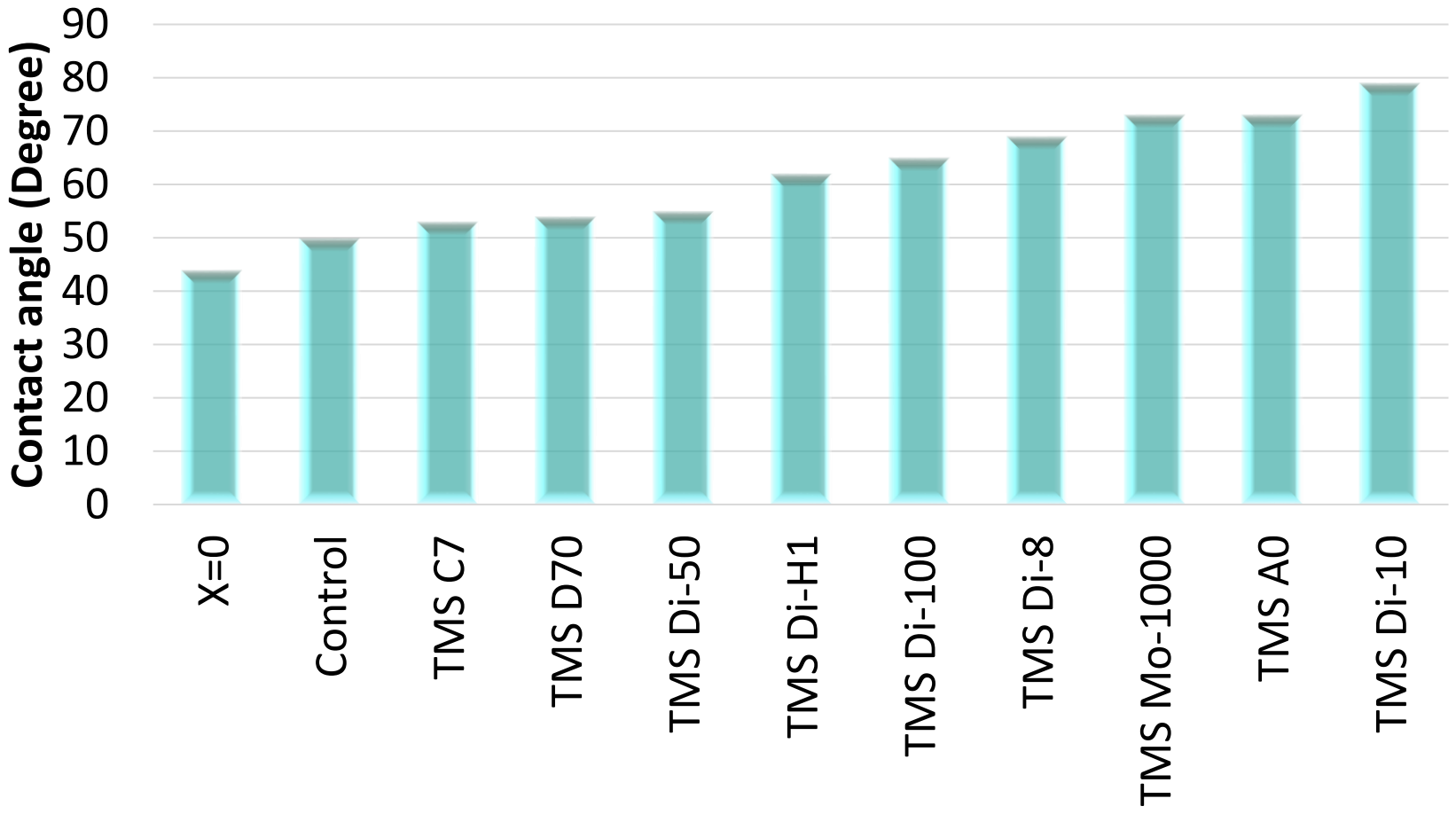


The inclination angles of all the samples treated with TMS products are lower than the control

The best of these give excellent water repellency for hard surfaces

SIL TECH

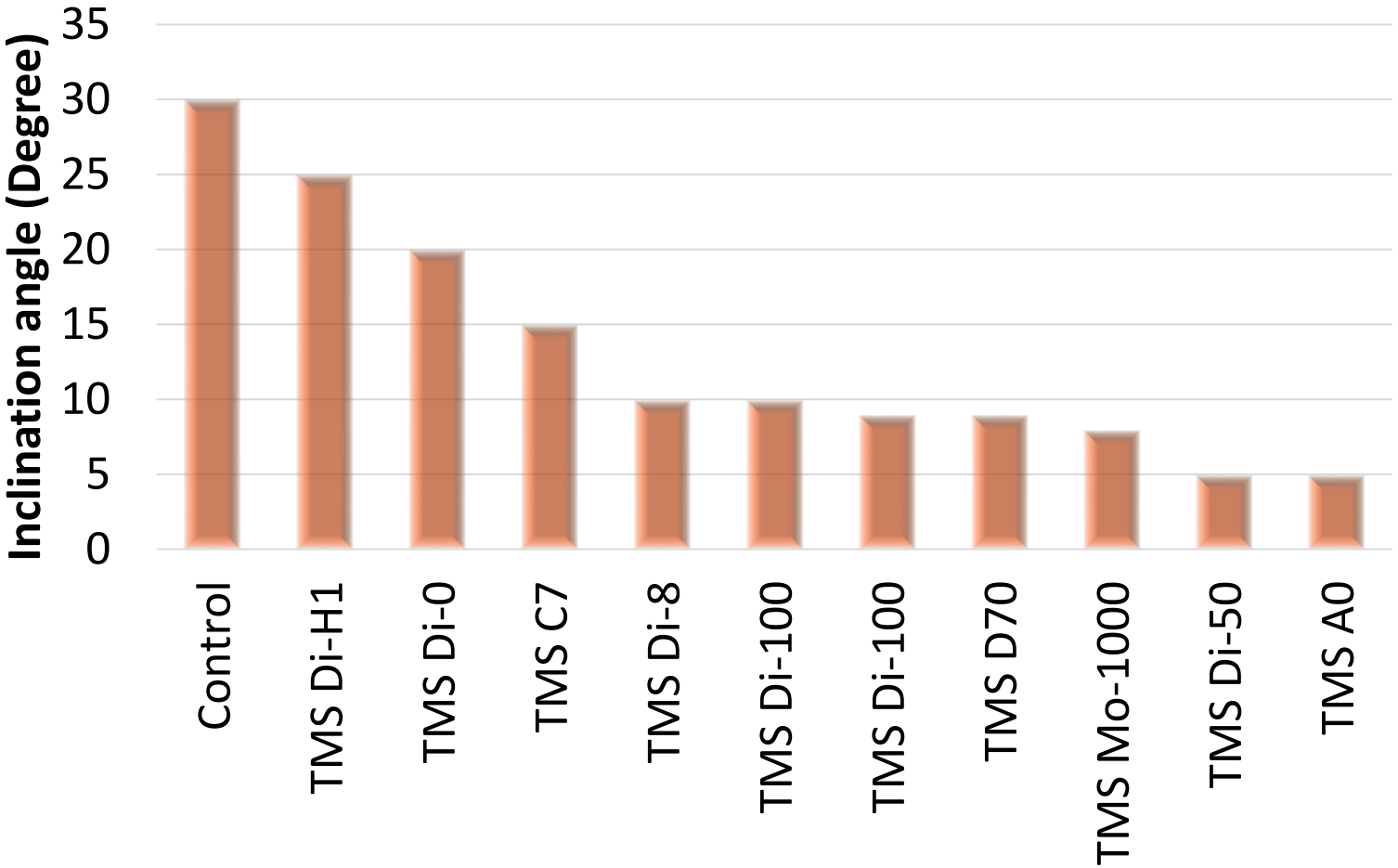
Contact Angles of Water on Leneta Paper Coated with TMS Types



The relative contact angle and inclination angle of all samples coated of TMS are better than the control.

The paper coated by X=10 has the largest contact angle at 79 degree and X=0 has the smallest at 44 degree

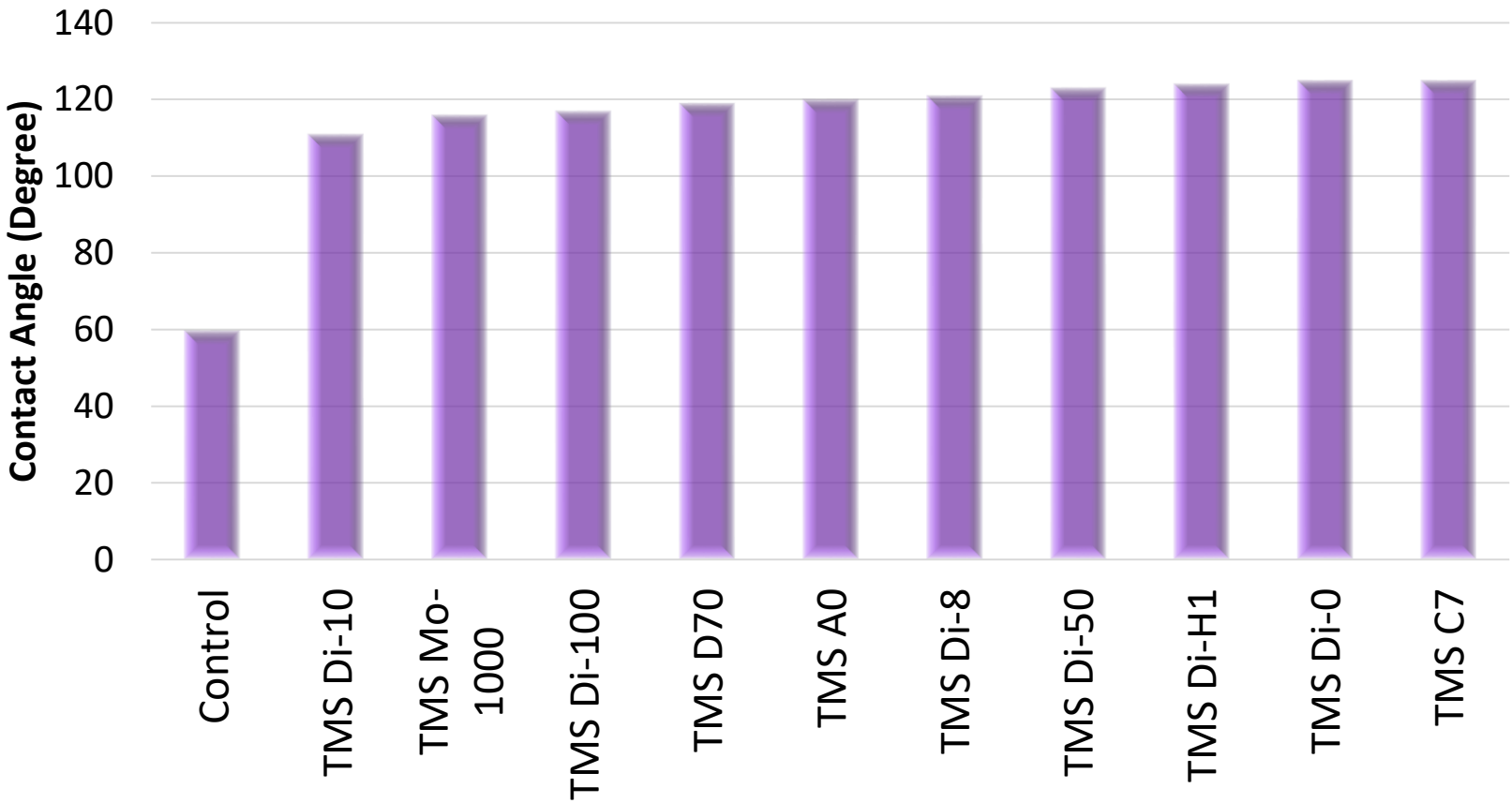
Inclination Angles of Water on Leneta Paper Coated with TMS Types



The paper coated by Silmer TMS Di-H1 has the largest inclination angle at 25 degree and TMS Di-50 and Silmer TMS A0 share the smallest at 5 degree

SIL TECH

Contact Angle 5% TMS Types on Fabric



Fabric coated with TMS type Silmer TMS C7 has the largest contact angle at 125°

TMS Di-10 has the smallest at 111°

All samples had high contact angles with excellent water repellency

Waterproofing Glass Beads with Silicone Additives

1% additive	Dry Wt.	Wet Wt.	Water Pick Up (gm)	Pick UP, %	Rating
E-2178	20.39	21.59	1.2	5.9%	9.0
E-2171	20.26	22.18	1.9	9.5%	8.1
Octyl Trimethoxy Silane	20.18	23.10	2.9	14.5%	7.5
TMS Di-50	20.93	23.99	3.1	14.6%	7.5
TC10-21 Exp Emulsion	20.04	23.4	3.4	16.8%	7.0
E-2158	20.43	24.00	3.6	17.5%	6.8
Silquat 3180	20.03	23.72	3.7	18.4%	6.7
TMS A0	20.45	24.35	3.9	19.1%	6.6
C-2053	19.92	24.24	4.3	21.7%	5.7
Silquat C-18	20.14	24.92	4.8	23.8%	5.3
E-2152	20.00	25.58	5.6	27.9%	3.9
Control (no additive)	20.01	28.59	8.6	42.9%	0

Emulsion F, which has octyl silane included, is the best product.

The TMS types are only moderately effective here

SIL TECH

Superhydrophobic Coatings with Reactive Silicones

	TC12-109A	TC12-109C	TC12-109D	TC12-109B	TC12-109E	TC12-109F	TC12-109G	TC12-109H
Aerogel (g)	0.2			0.2				
Nano SiO_2 (g)		0.2	0.2		0.2	0.2	0.2	
Aminoethylaminopropyltrimethoxysilane (g)	20	20	20					
C-2053 (g)				20	20	20	20	20
Dabco T-12				0.02	0.02	0.02	0.02	0.02
Toluene (g)	50	50	50	50	50	50	50	50
Cure temperature	Ambient for 1 hour			110ºC for 1 hour/R.T. Overnight				
Appearance	Gel particles stick to each other	Unstable Dispersion	Unstable Dispersion	Gel particles too large for spraying	Unstable Dispersion	Unstable Dispersion	Unstable Dispersion	Clear Solution
No. of coating	0	1	2	0	1	2	3	1
Hydrophobicity (10 best)	ND	1	1	ND	6	9	8	5
Dry Adhesion	ND	Good	Good	ND	Good	Good	Good	Good
Wet Adhesion	ND	No Good	No Good	ND	Good	Good	Good	Good

Super-hydrophobicity was achieved by spraying Nano SiO_2 particles with hydrolysate of TMS Di-10 as binder

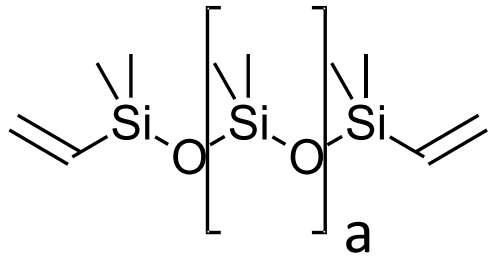
The hydrophobicity is very much dependent on the degree of roughness of the surface and can be reduced if the surface is too smooth or too rough

SIL TECH

Water Repellency Of Fabric Treated With 2K VIN/SiH, TMS Type And Vinyl Silane

	Formulation
VIN 10000/Simler VQ 93 resin 1:1	41.11%
VIN 10000	14.23%
Karstedt Catalyst	0.01%
Ti-2-Ethylhexoxide	0.21%
Silmer HQ 30 resin	3.43%
TMS Di-10	40.91%
VTMO (vinyl silane)	0.10%
Total	100.00%

VIN 10000
a= 10,000



The best sample was VIN10,000/ Q Resin/ HQ resin blended with TMS type X=10

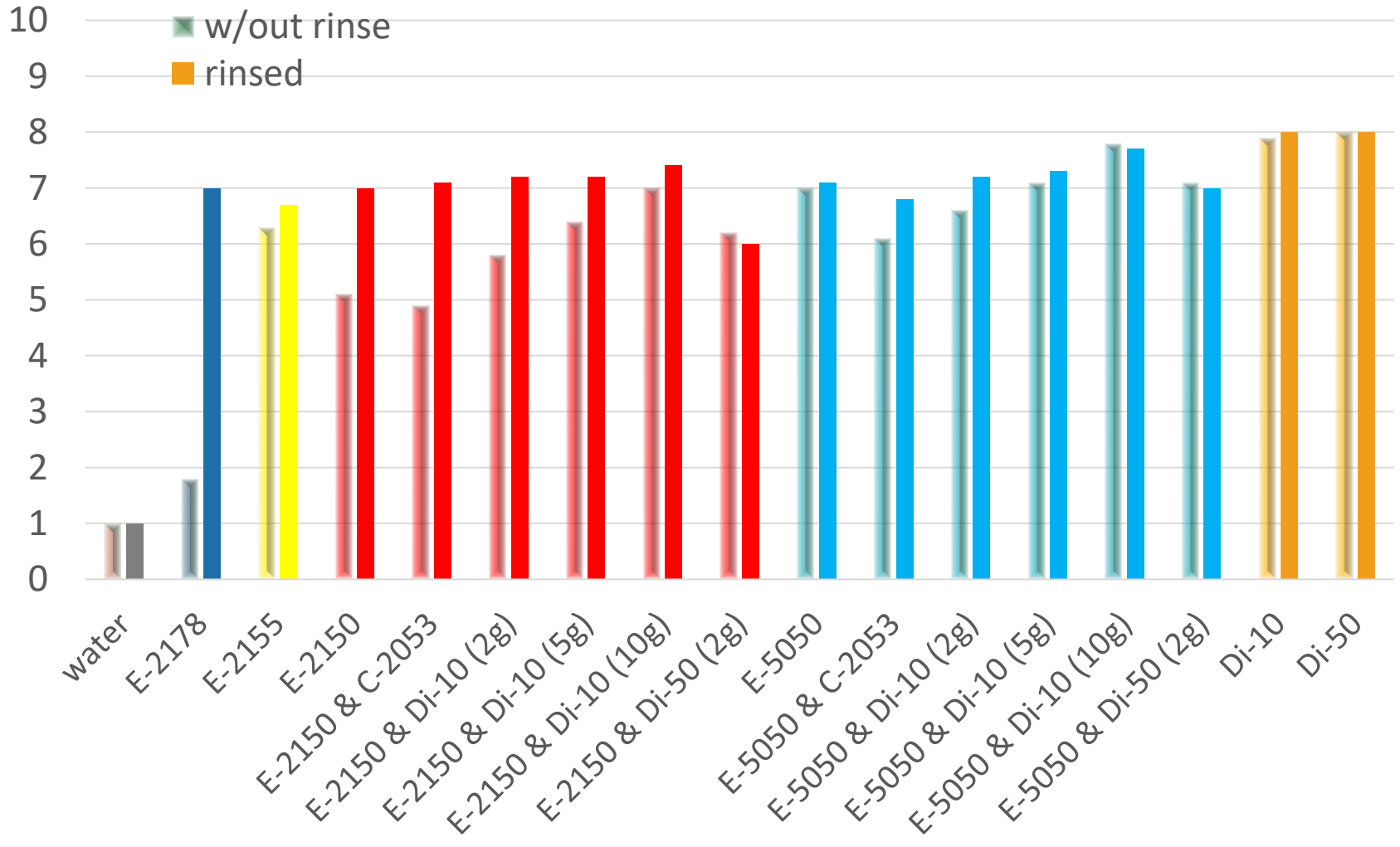
2K system applied from IDD

Water repellency was judged to be very close to that of a fluoro-based material on fabric

One example of Dual Cure technology

SIL TECH

Fabric Water Repellency Using Film Former Emulsions Enhanced with TMS type



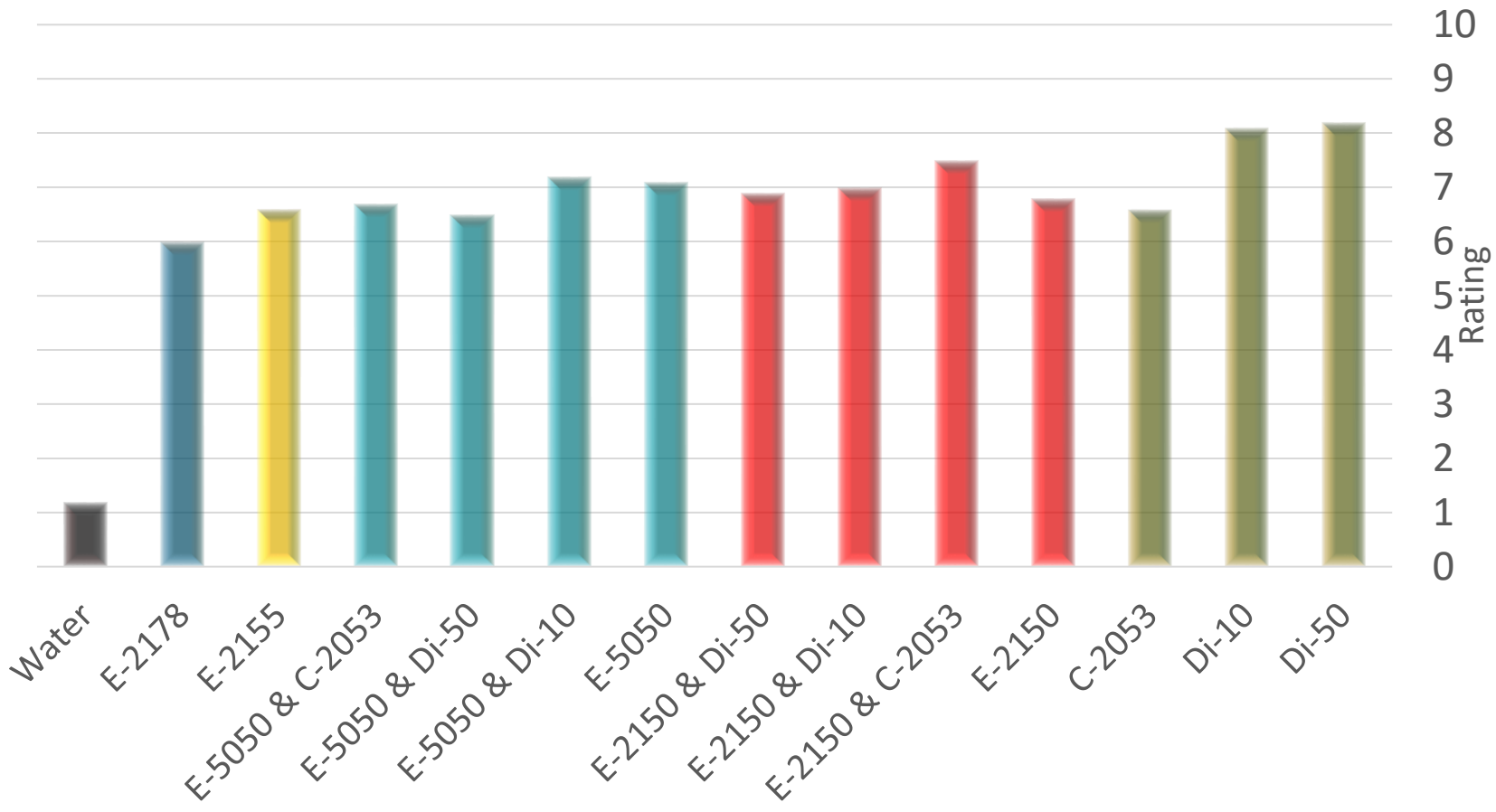
The film forming emulsions gave good water repellency over the control

The addition of TMS types with catalyst gave a slight improvement

The TMS types alone gave the best performance

SIL TECH

Fiberglass Water Repellency Using Film Former Emulsions Enhanced with TMS type



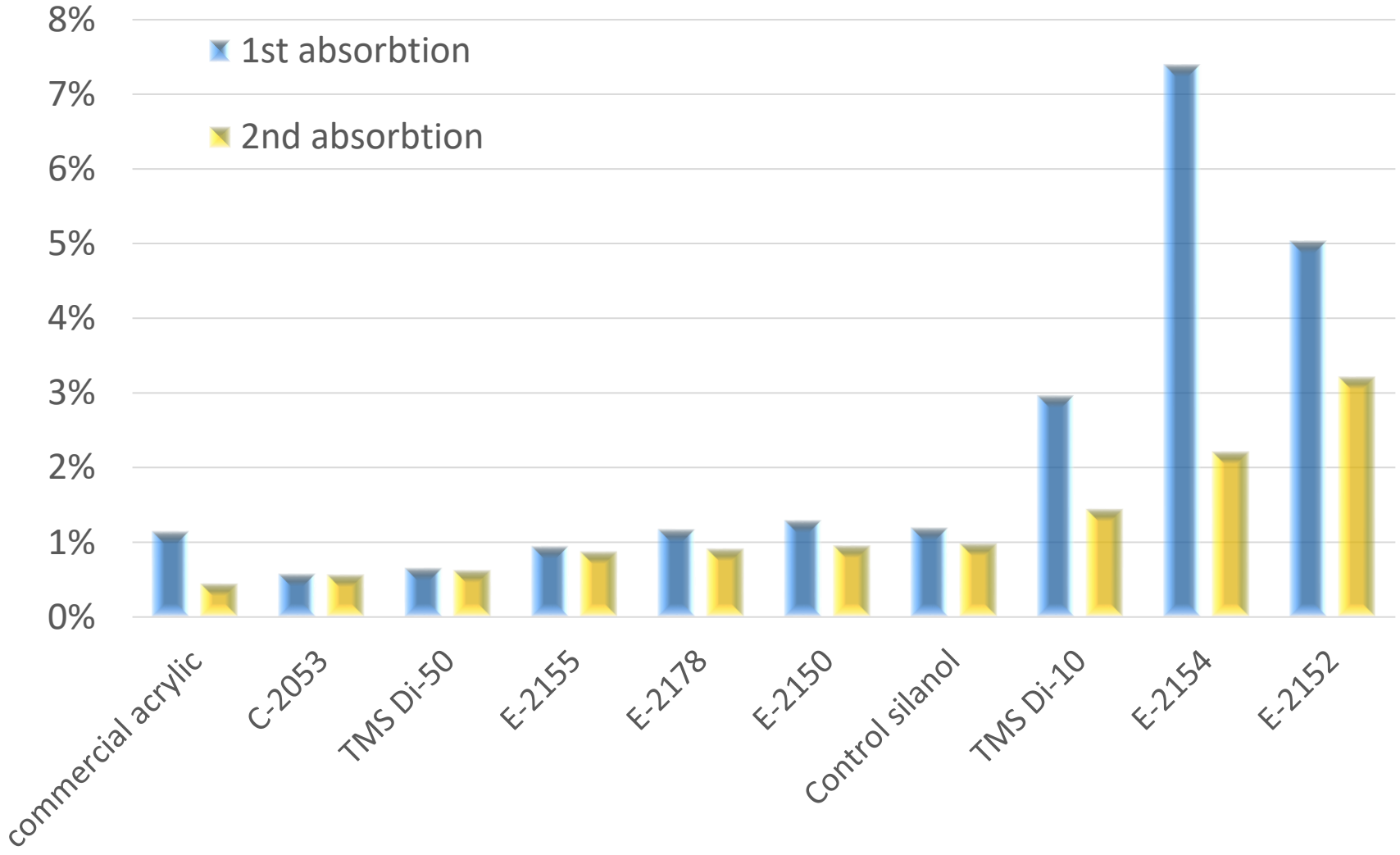
The film forming emulsions gave good water repellency over the control

The addition of TMS types with catalyst gave a slight improvement

The TMS types alone gave the best performance

SIL TECH

Water Pickup on Treated Concrete Tiles

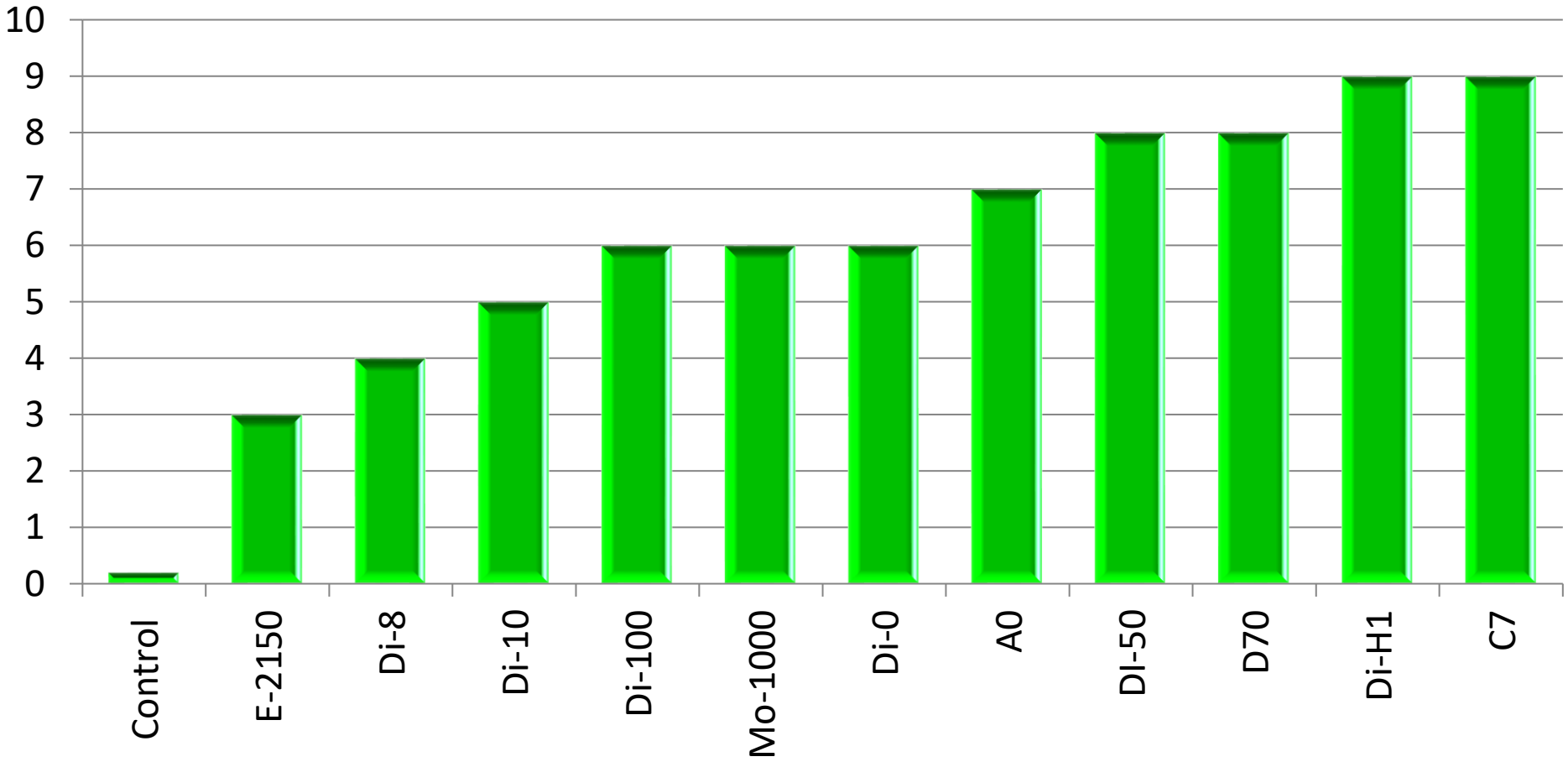


The TMS Di-50 and hydrolysate of Di-10 are similar to commercial product.

Some of the film forming emulsions are also close

SIL TECH

Waterproofing Concrete with TMS Types

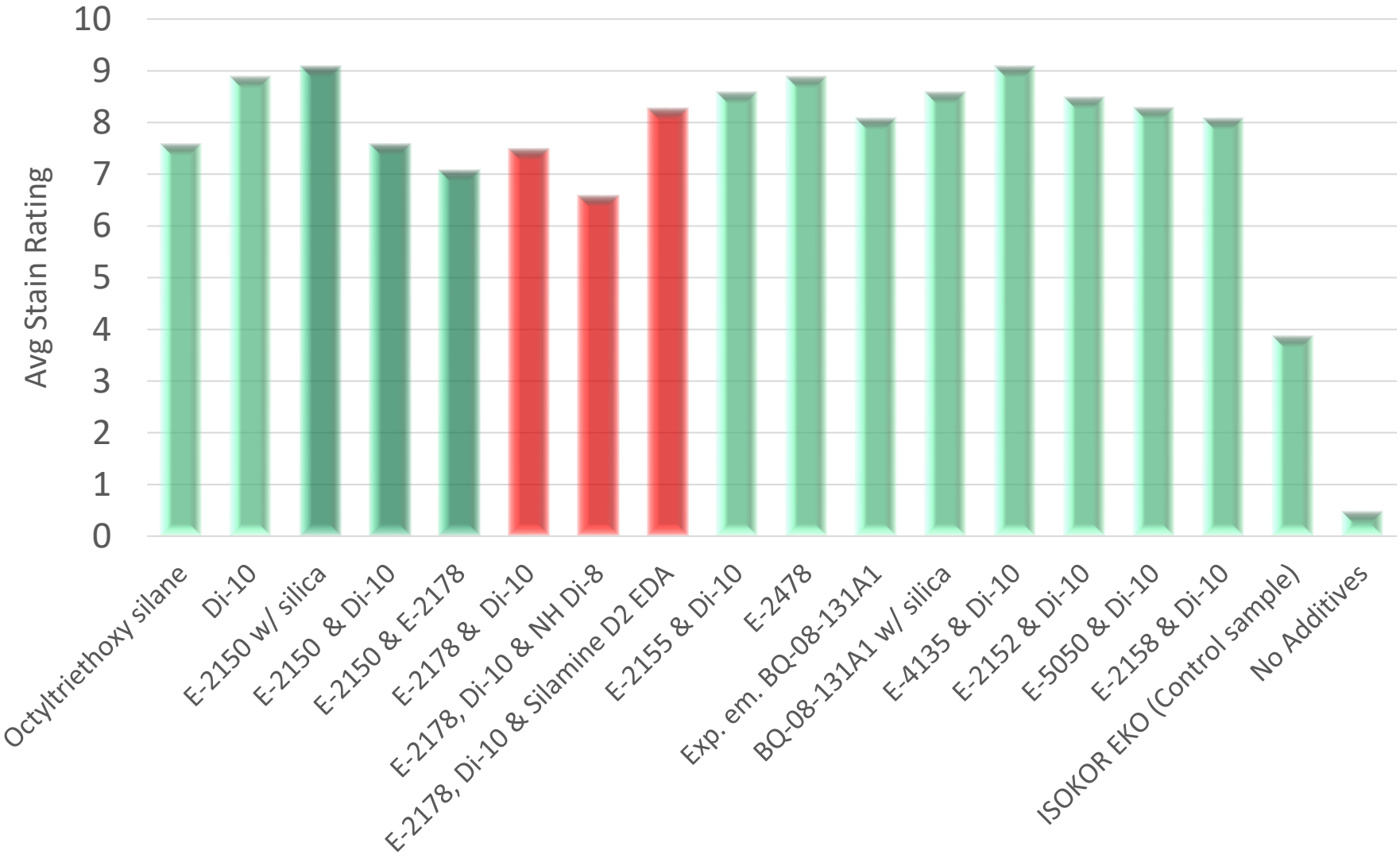


All samples treated with TMS types are much better than control

TMS C7 and TMS Di-H1 give the best water beading rating on concrete

SIL TECH

Silicone Additives to Improve Stain Resistance of Tile Sealant

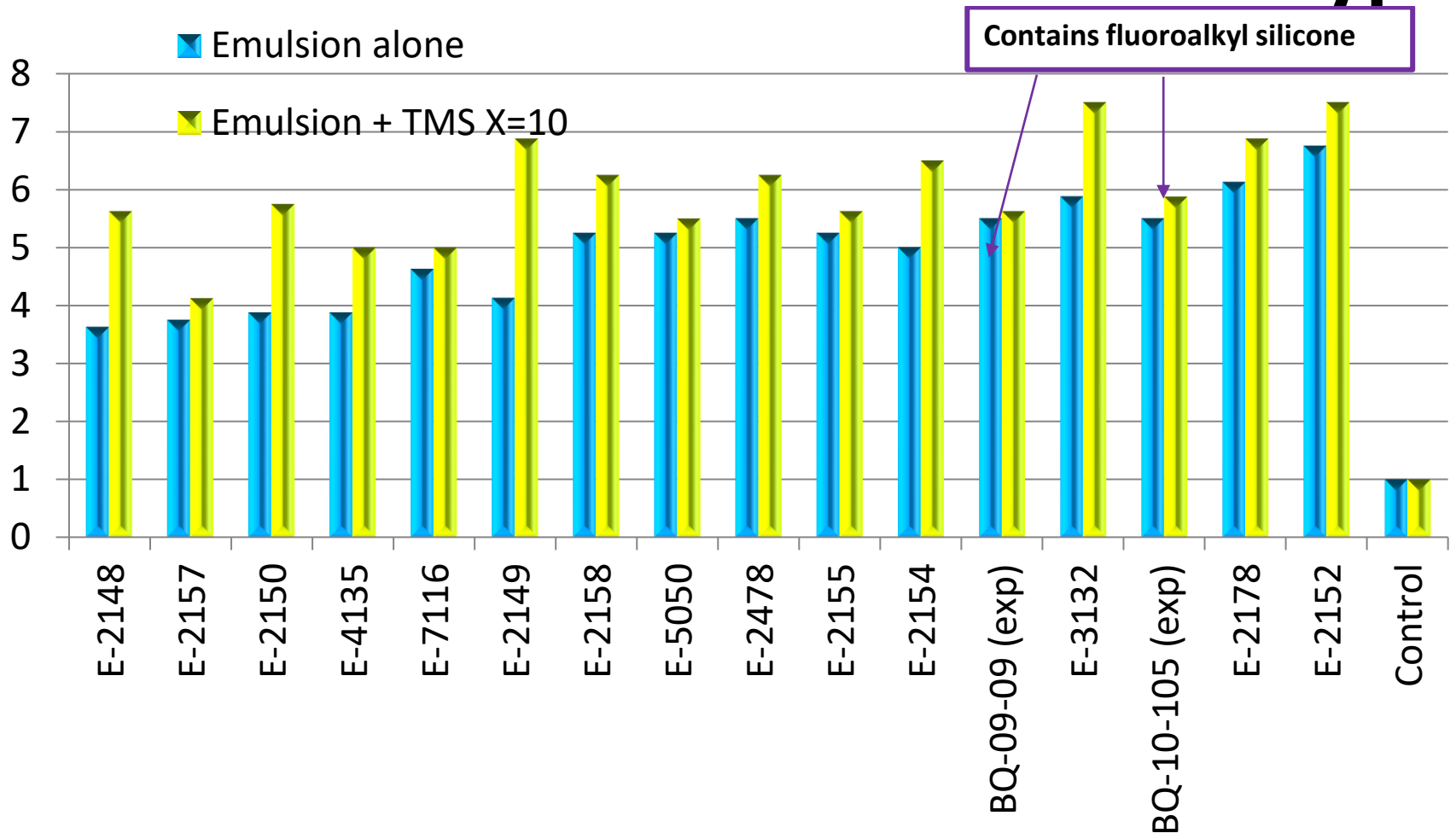


TMS Di-10 is excellent alone

Many of the combinations are better than OTS treatment

The addition of silica helps in some cases

Stain Resistance Of Fabric Treated With Siltech Emulsions Alone & With 7% TMS Type X=10



All samples with added TMS Di-10 show improved stain resistance

Marker Resistance On Al Panel Coated With Various TMS Types and Epoxy Silane - experimental

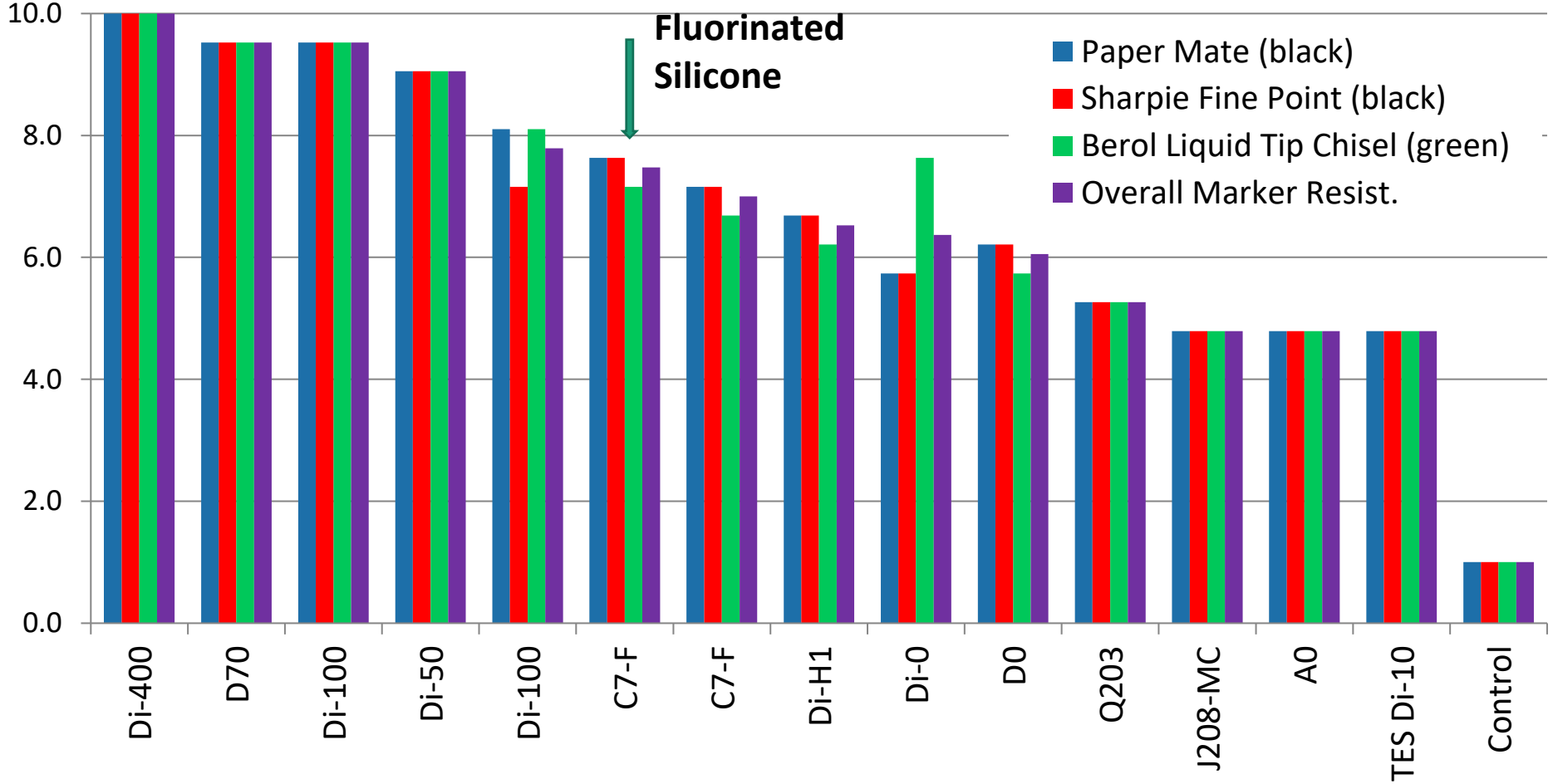
	Part A	Part B
Xylene	61.74%	98.26%
TMS type	34.78%	0.00%
3-Glycidoxypropyl methyldimethoxysilane adhesion promoter	3.48%	0.00%
Titanium Diisopropoxide Bis(ethylacetoacetate)	0.00%	1.74%
Total	100.00%	100.00%

Mix ratio of Part A: Part B = 1:1

Titanium Diisopropoxide Bis(ethylacetoacetate) added as a hydrolysis/ condensation catalyst

SIL TECH

Marker Resistance of TMS Types Coated on Al Panels (10 is the best)



Marker resistance improved as the length of TMS siloxane chain increased

Several non-fluorinated TMS types performed better than TMS type fluorosilicone

SIL TECH

Final Thoughts

- The technology has moved beyond monomeric, highly functionalized alkoxysilanes.
  - In same cases these are still the best options.
- Film Forming, cured silanol alkoxysilane emulsions often offer superior water repellency and stain resistance.
- Pre-hydrolyzed silanes solutions often provide best properties.
- TMS functional silicones provide excellent water repellence for fabric, concrete, glass, cardboard, leather and many other substrates.
  - Lower molecular weight TMS polymers are highly compatible with most organic binders, emulsions, silanes, silanols, and PU dispersions.
  - Higher molecular weight TMS polymers give excellent stain and solvent resistance. Very durable coatings can be obtained.
- Super hydrophobicity can be achieved with TMS products and nano-silica.

SIL TECH

SILTECH