The Evolution of Trialkoxysilane Monomers to Hybrid Silicones

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

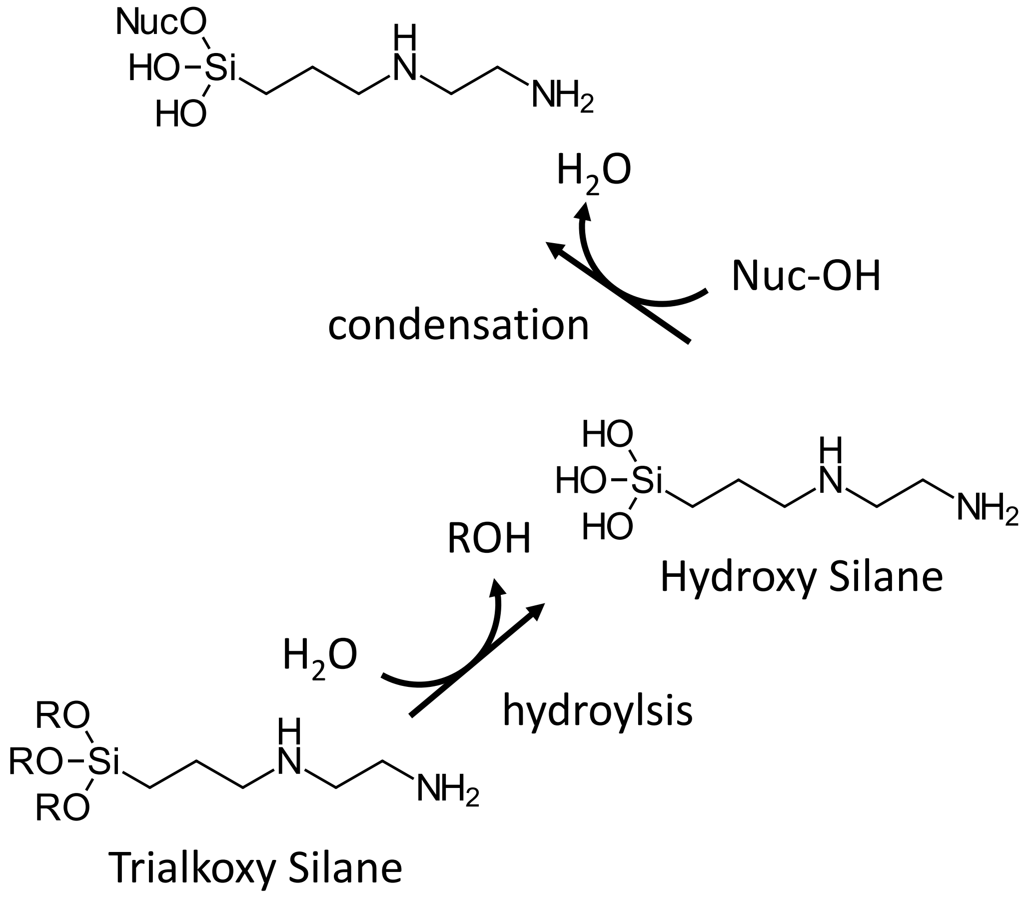
Siltech Corporation
Toronto, ON Canada

[1]robert@siltech.com, [2]tom2@siltech.com, [3]mike.gunther@siltech.com

Introduction

- Trialkoxysilanes are used as adhesion promoters, surface treatments or resin modifiers.
- They can be used 100% active, pre-hydrolyzed or condensed into alkoxyfunctional oligomers
- In the final products, the siloxane network formed has a complex architecture. This is either formed randomly or it can be formed in a more directed fashion by beginning with reactive siloxane oligomers
- In this talk, we will show some trialkoxy silicon products that are different from traditional silane monomers
- Examples include reactive oligomers, reactive silicone emulsions, and silane modified silicones.

Simplified Silane Mechanism



In aqueous solution the hydrolyzed silane is often stable, (Le Chatelier's Principle).

If **NucOH** is another silane then this results in a condensate or oligomer that is easily further reacted.

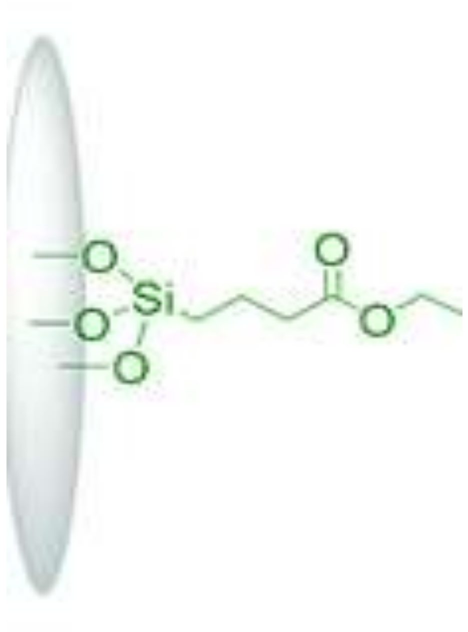
If **NucOH** is a surface then the silane becomes part a surface treatment.

Resins can react as **NucOH** or with organic chain (**NH** in this case)

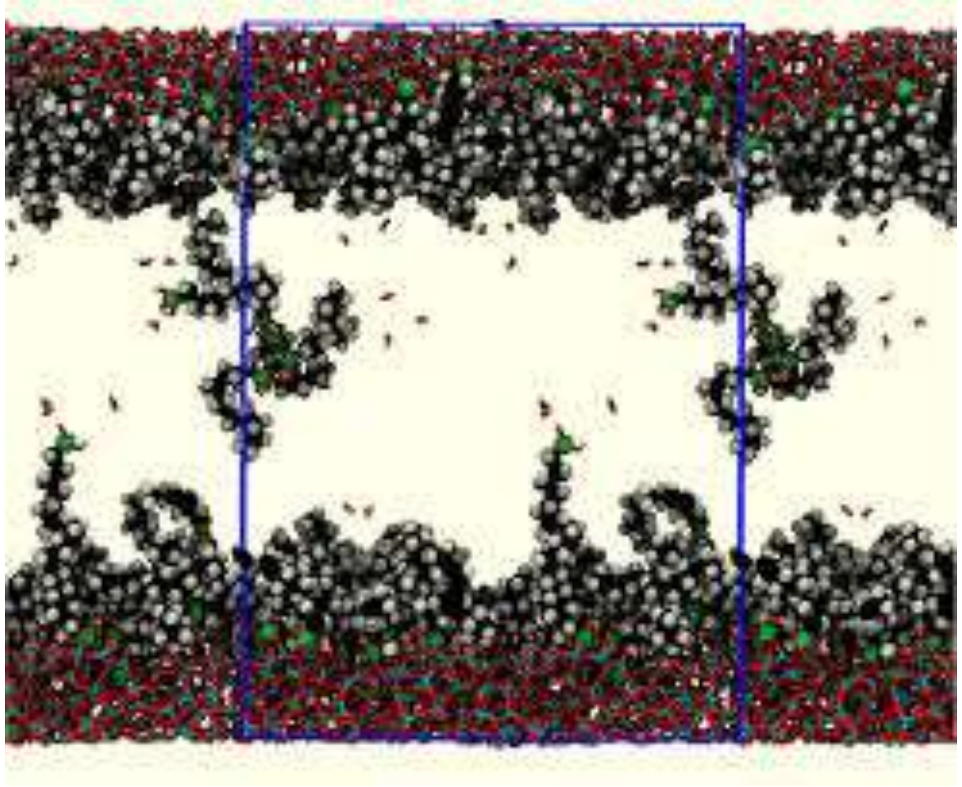
In practice all of these reactions and others occur.

A picture is worth…

The simplistic model



It’s never this…

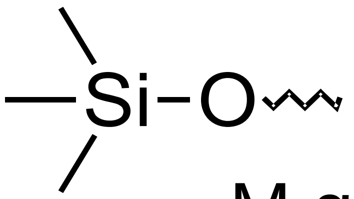


It’s THIS!

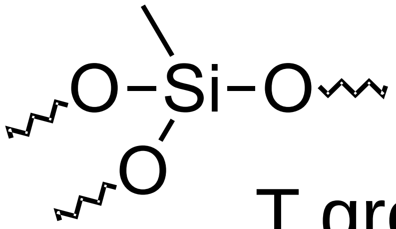
Org. Biomol. Chem., 2013,**11**, 6397-6406

Faller, et al. Langmuir 2016, 32, 7045−7055

Silicon Jargon

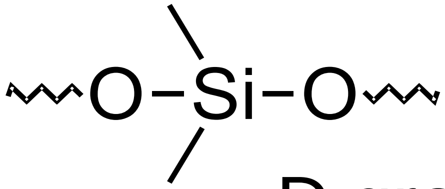


M group

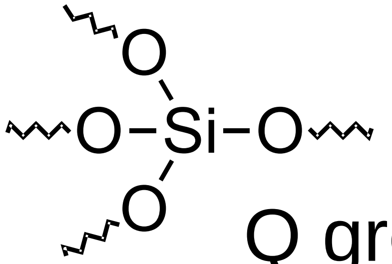


T group

Trialkoxy silanes are T groups



D group



Q group

MD_xM is the standard formula for silicone

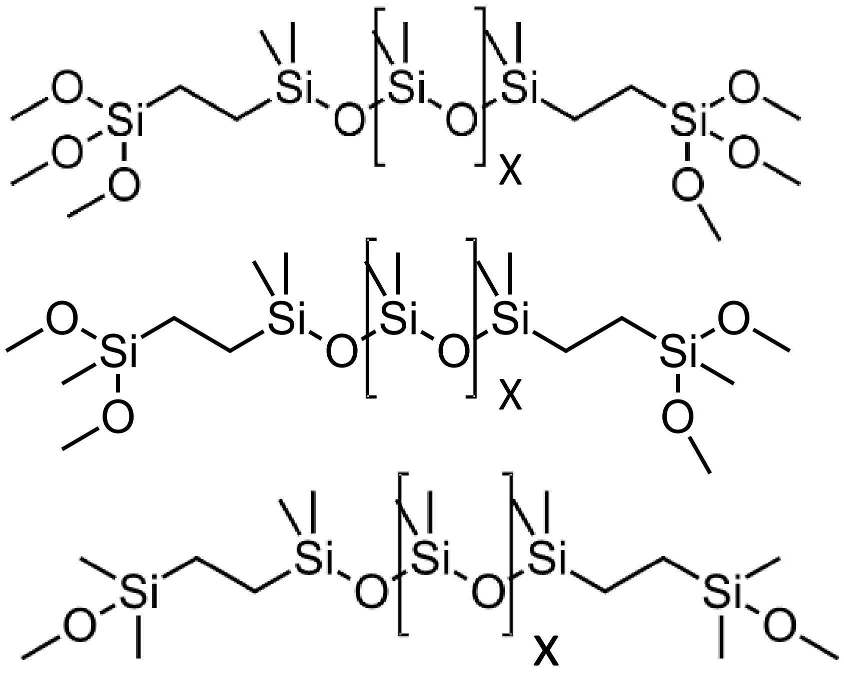
Film Forming Emulsions of Condensates

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

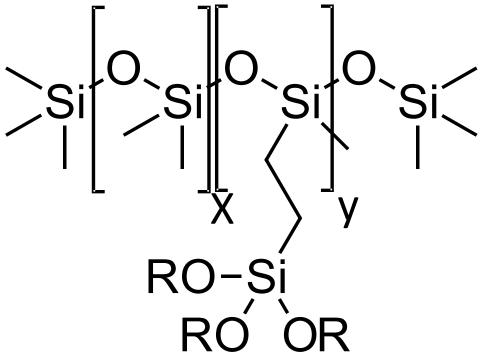
- Many variants are possible with alkyl, aryl, or reactive silanes
- We explore many in this talk without details of the differences.
  - Labeled Emulsions A-W

Reactive Alkoxy Silicones: TMS and DMS Types

- 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 one to dial in the amount of silicone character needed
- Functionality on silicon, mono, di- or tri-, provides control over siloxane network density

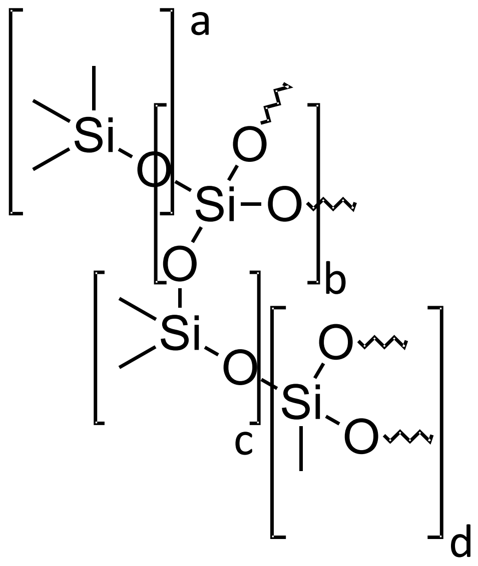


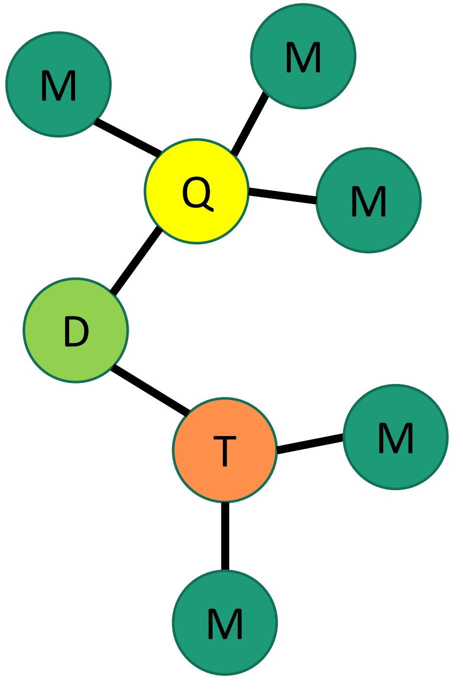
Linear:
X= 0, 10, 50, 100, 400



Pendant:
X,Y:various

DTQ Resins





Reactive Alkoxy DTQ Type Resins

Type	DT			DTQ					TQ	T	Phenyl DT
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
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
Kinetic CoF	2.598	2.643	1.097	0.660	1.264	0.394	2.093	0.343	0.287	0.652	0.682
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**

Hardness ranges from 5B to over 9H!

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

Too Soft To Measure

Hard

9H 8H 7H 6H 5H 4H 3H 2H H HB B 2B 3B 4B 5B 6B 7B 8B 9B

Soft

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Adhesion

TMS types can improve adhesion

Improved Adhesion of Alkoxy Cured Silicone Sealants – acid cat.

Sealant	Additive A (2.5%)	Additive B (2.5%)	0-10
A			0
A	TMS type X=10		1
A	TMS type X=10	Phenol mod silicone	1
A	alkyl silane condensate		1
A	Eugenol modified silicone		2
A	TMS type X=8		2
A	NCO type X-10		2
B	X=10	Eugenol mod silicone	3
B	X=10	Silicone alkyl polyether	3
A	Eugenol		3
A	Silicone alkyl polyether		3
A	TMS type X=0		3
A	Amino silicone A		4
B	TMS type X=0	Amino silicone D	5
A	Amino silicone D		5

Aminosilicones are the most effective here.

Cured with an alkyl acid phosphate catalyst

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

Improved Adhesion of Alkoxy Cured Silicone Sealants – Sn cat.

Sealant	Additive A (2.5%)	Additive B (2.5%)	0-10
B			0
A	NCO type X-10		2
B	TMS type X=10	Eugenol	3
A	Eugenol		3
A	Silicone alkyl polyether		3
A	TMS type X=8		3
A	Amino silicone A		3
A	TMS type X=10	Eugenol mod silicone	4
A	Phenol mod silicone		4
B	TMS type X=10	Silicone alkyl polyether	5
A	Amino silicone D		6
A	TMS type X=10		7
A	TMS type X=0		7
B	TMS type X=10	Amino silicone D	7.5
A	alkyl silane condensate		8

Amino-silicones are again effective but TMS types look good as well.

Improved Adhesion of Alkoxy Cured Silicone Sealants with Aminosilane and TMS type

Sealant	TMS type	Silane type Additive B	A/B	0-10
B	X=10	aminopropyltrimethoxysilane (no cat)	1:1	7
B			1:2	7
B			**2:1**	**10**
B		aminopropyltriethoxysilane (K-Kat A)	1:1	9
B		aminopropyltriethoxysilane (K-Kat B)	1:1	10
B		aminopropyltriethoxysilane (K-Kat B)	1:1	10
B		aminopropyltriethoxysilane (K-Kat D)	1:1	10

TMS type x-10 with amino silane far out performed all others in this study

The preps rated 10 had excellent improved adhesion to PVC

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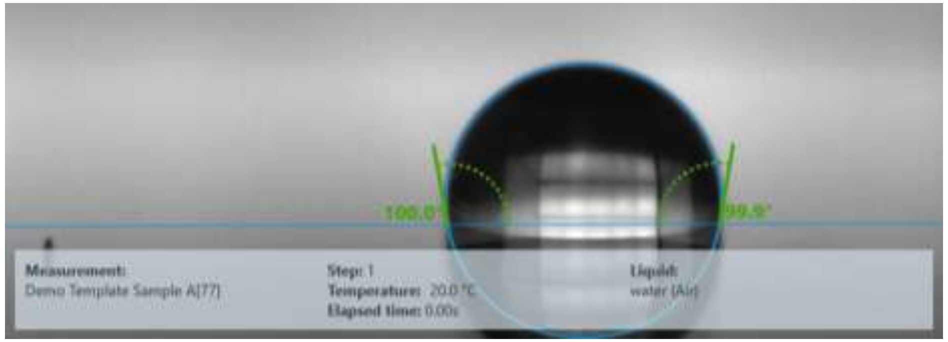
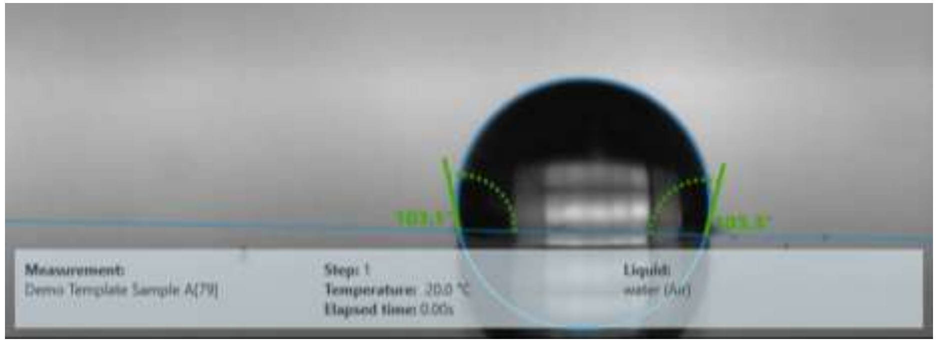
Hydrophobicity/ Surface Treatments

Emulsions and TMS type are effective

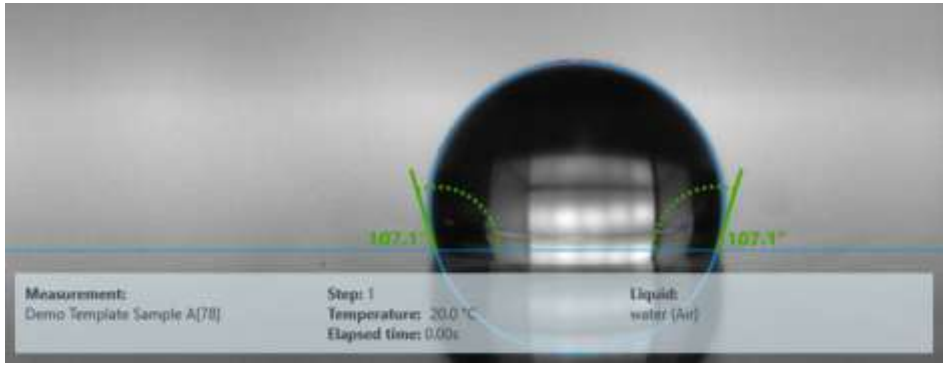
Contact angle increase



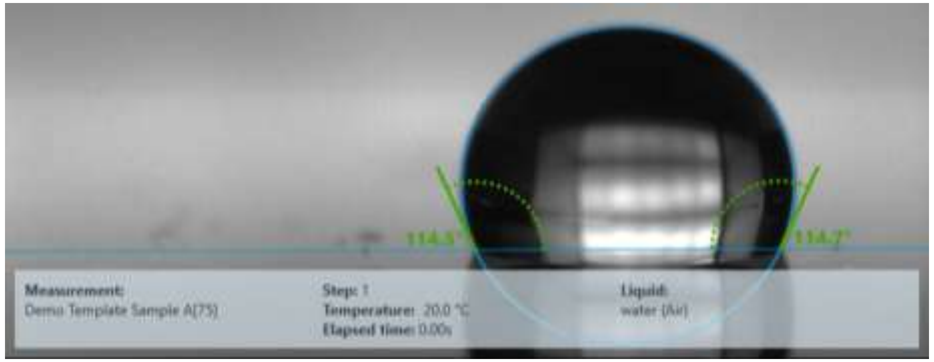
TMS, X=0 angle 100° on glass



TMS, X=10 angle 103°



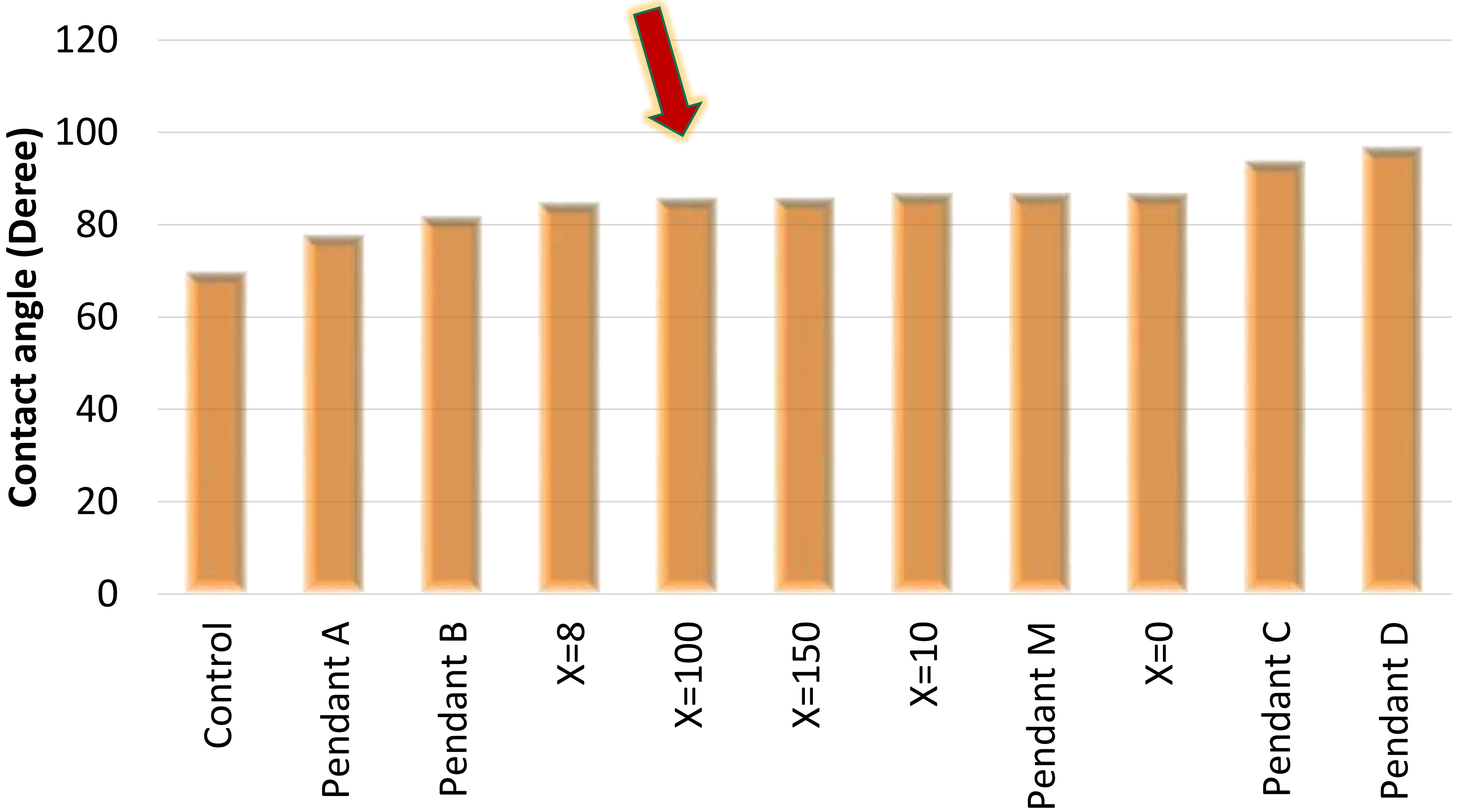
TMS, X=50 angle 107°



TMS, X=400 angle 115°

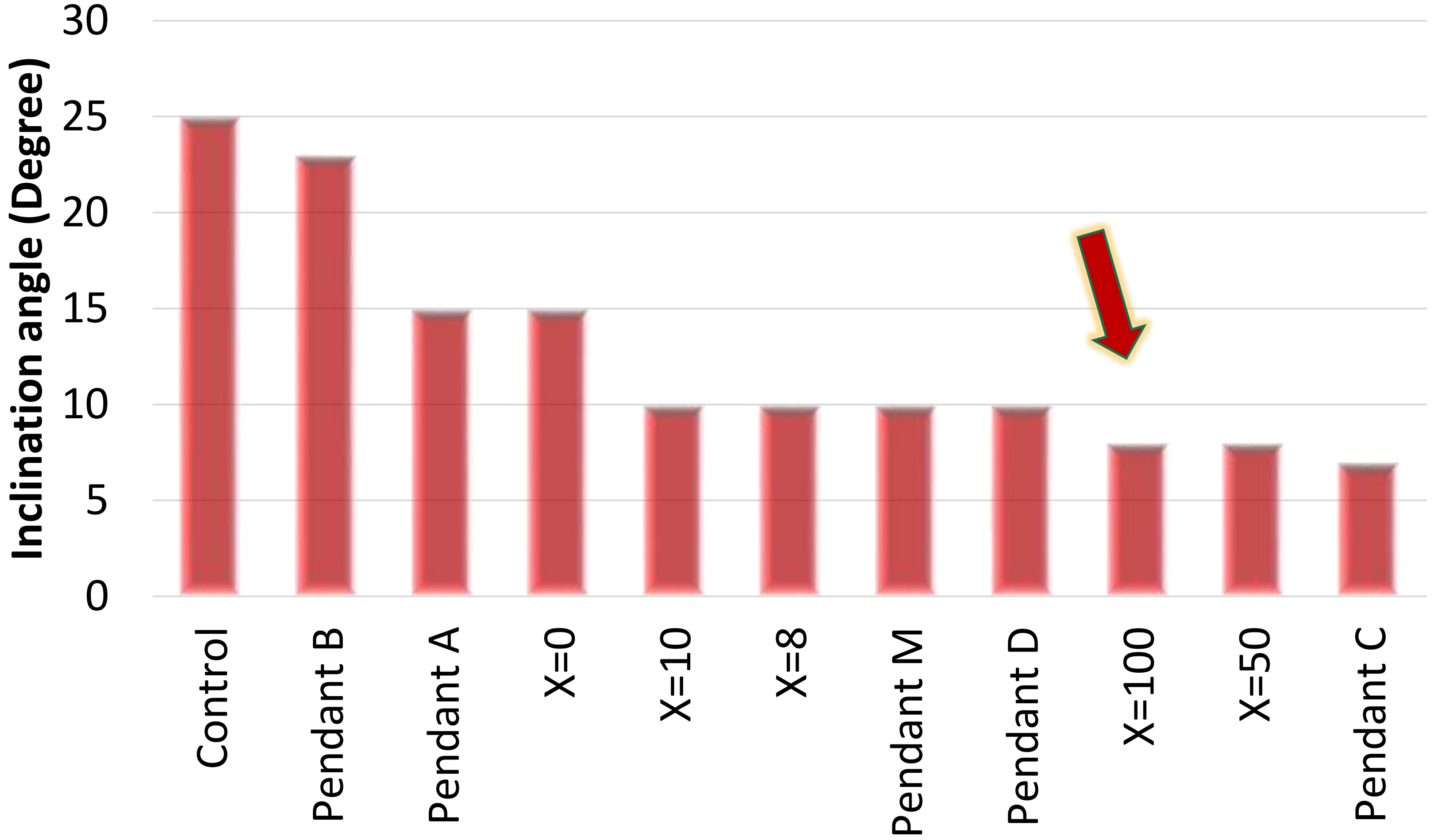
Contact Angle of TMS Type Polymers on Glass

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. High MW and functional C,D are better.

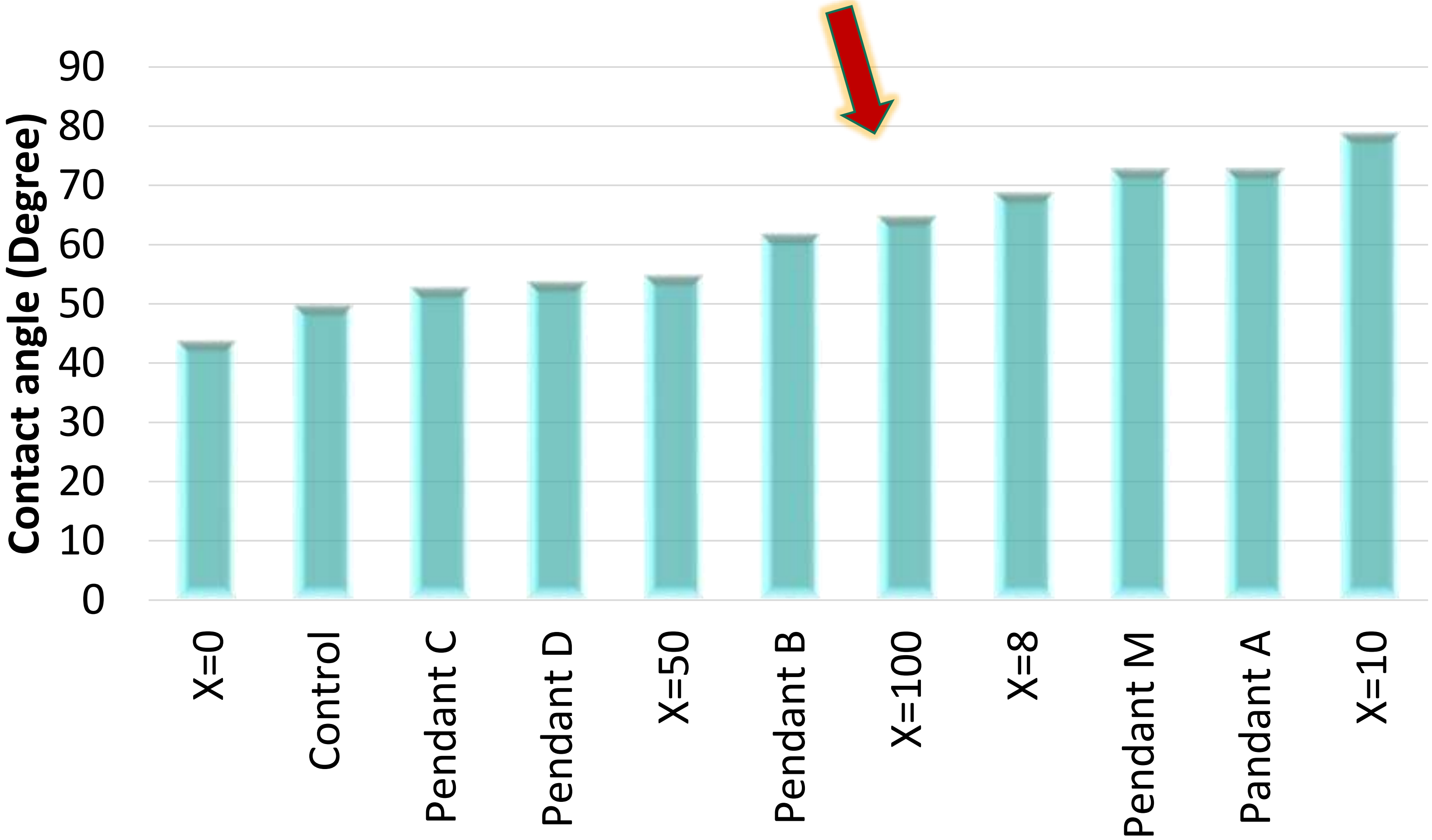
Inclination Angles of Water on Al Panels Coated with TMS Types



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

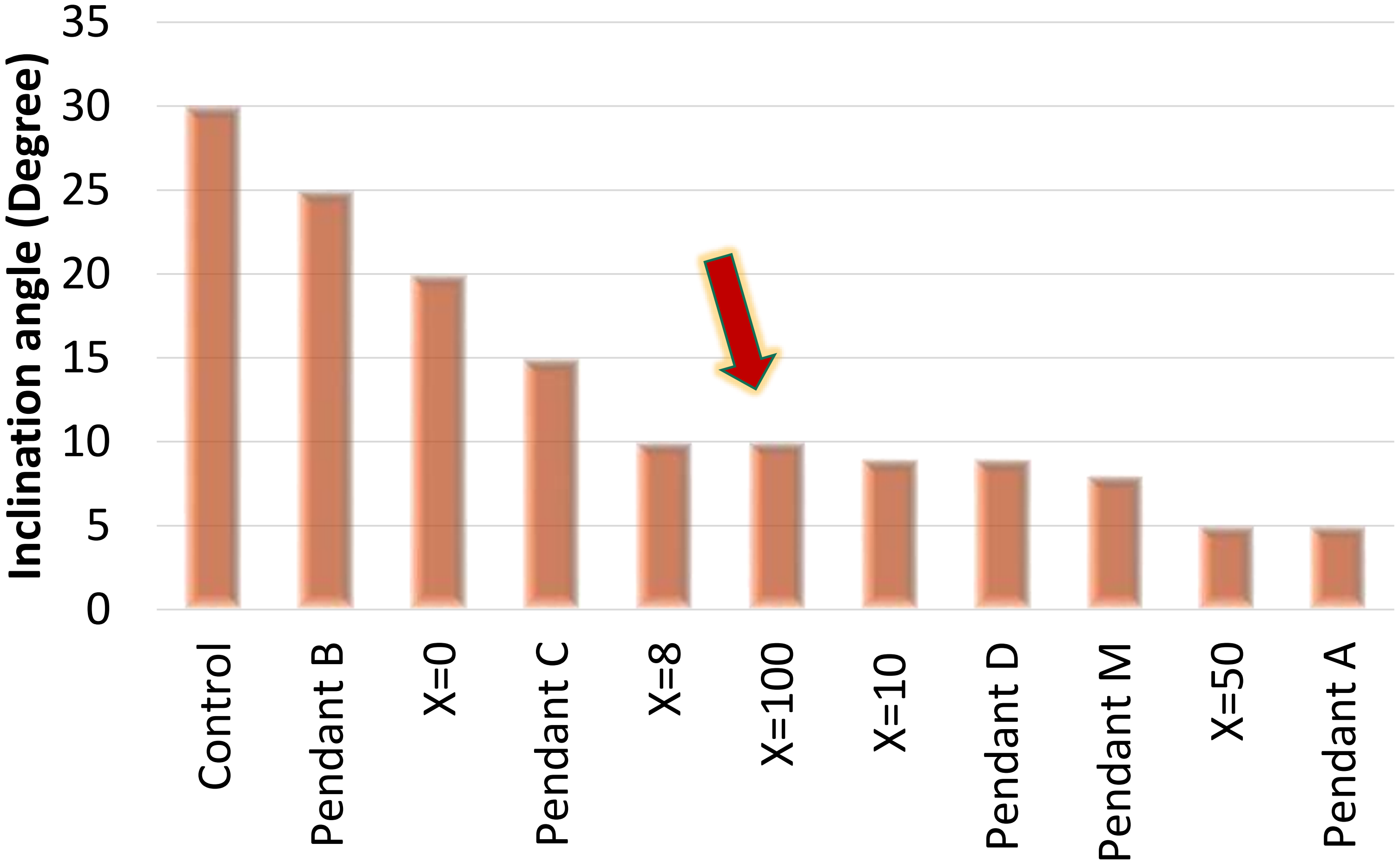
Contact Angles of Water on Leneta Paper Coated with TMS Types



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

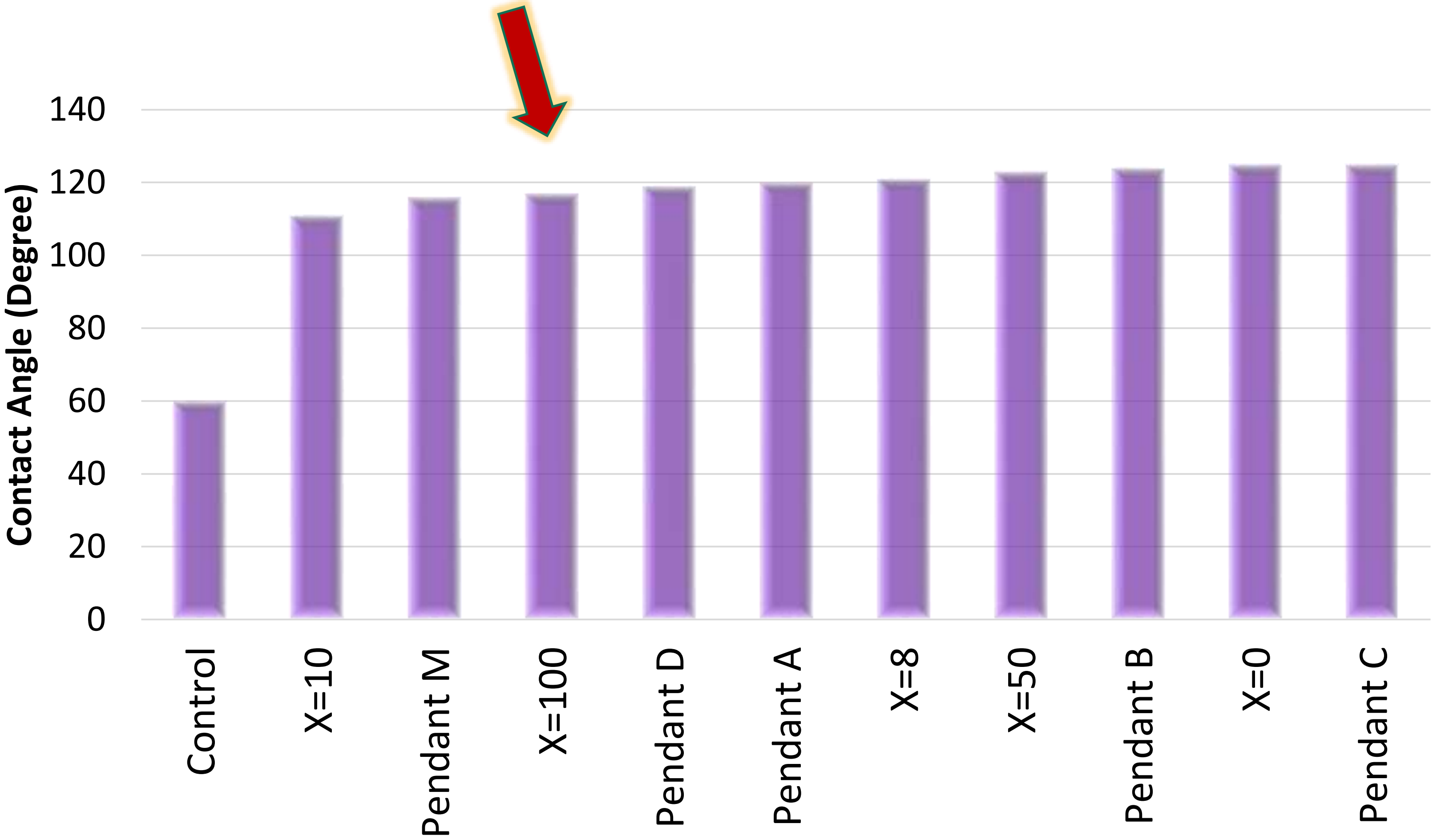
The paper coated by X=10 has the largest contact angle at 79 degree and X=0 has the smallest at 44 degree

Inclination Angles of Water on Leneta Paper Coated with TMS Types



The paper coated by Pendant B has the largest inclination angle at 25 degree and X=50 and Pendant A share the smallest at 5 degree

Contact Angle 5% TMS Types on Cotton



All fabric samples coated with TMS type samples had high contact angles with excellent water repellency

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Waterproofing Glass Beads

1% additive	Dry Wt.	Wet Wt.	Water Pick Up (gm)	(%)	Rating
Emulsion F	20.4	21.6	1.2	5.9%	9.0
Emulsion E	20.3	22.2	1.9	9.5%	8.1
Octyl Trimethoxy Silane	20.2	23.1	2.9	14.5%	7.5
TMS X=50	20.9	24.0	3.1	14.6%	7.5
Exp Emulsion	20.0	23.4	3.4	16.8%	7.0
Emulsion D	20.4	24.0	3.6	17.5%	6.8
Silicone Quat	20.0	23.7	3.7	18.4%	6.7
TMS Pendant A	20.5	24.4	3.9	19.1%	6.6
alkyl silane condensate	19.9	24.2	4.3	21.7%	5.7
Silane Quat	20.1	24.9	4.8	23.8%	5.3
Emulsion B	20.0	25.6	5.6	27.9%	3.9
Control (no additive)	20.0	28.6	8.6	42.9%	0

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

The TMS types are moderately effective

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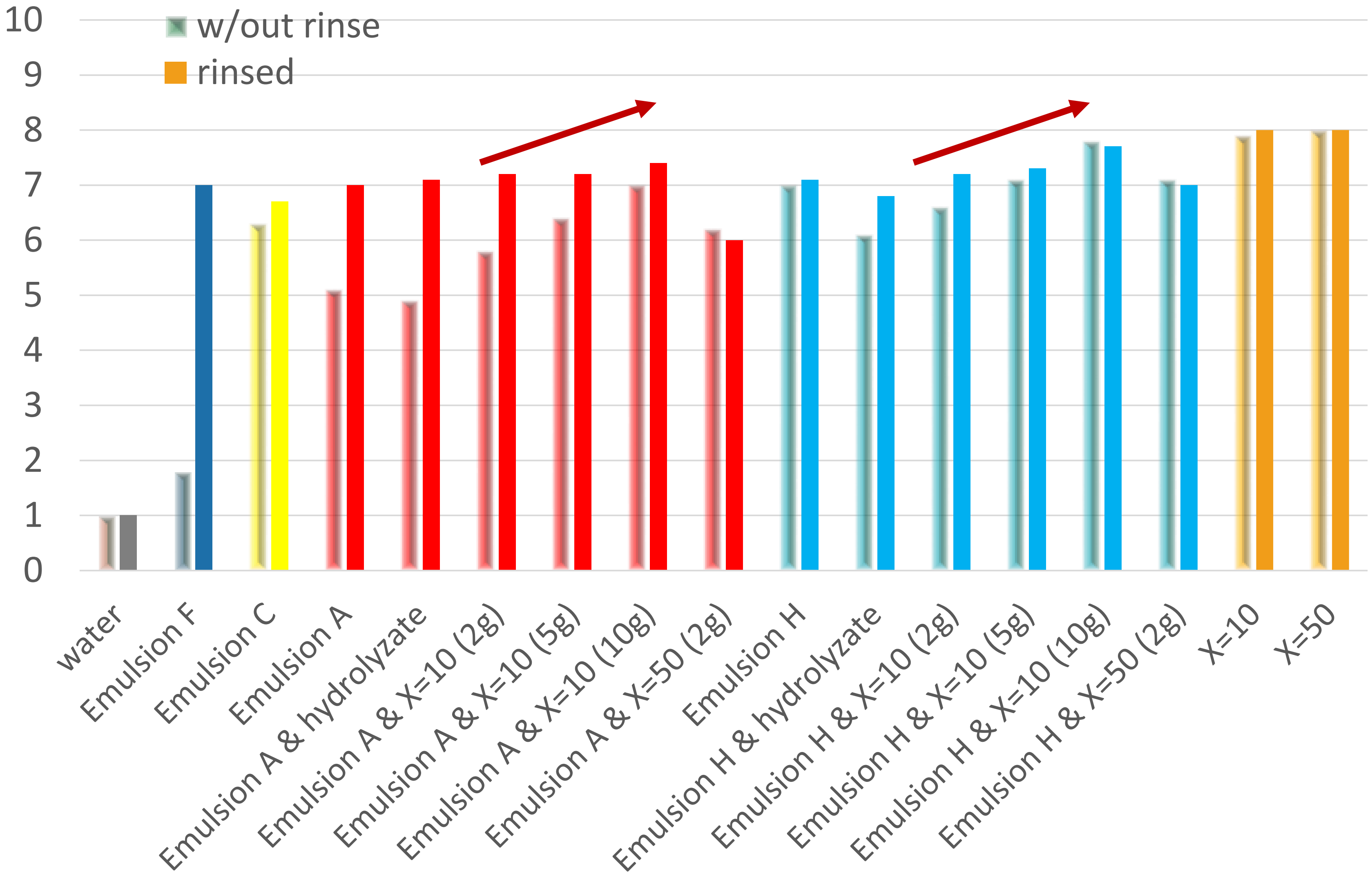
Hydrophobic Coatings on Al Panels

charge (g)	A	C	D	B	E	F	G	H
SiO_2	0.2			0.2				
Nano SiO_2		0.2	0.2		0.2	0.2	0.2	
Aminoethylaminopropyltrimethoxysilane	20	20	20					
alkyl silane condensate						20		
Dabco T-12						0.02		
Toluene (g)	50	50	50	50	50	50	50	50
Cure temperature		Ambient for 1 hour				110°C for 1 hour/R.T. Overnight		
Appearance	particles coalesced	Unstable		particles too large		Unstable		Clear
# of coatings	0	1	2	0	1	2	3	1
Hydrophobicity	ND	1	1	ND	6	9	8	5

Super-hydrophobicity was achieved by spraying nano SiO_2 particles with hydrolysate

Fabric Water Repellency: Film Forming Emulsions and TMS type

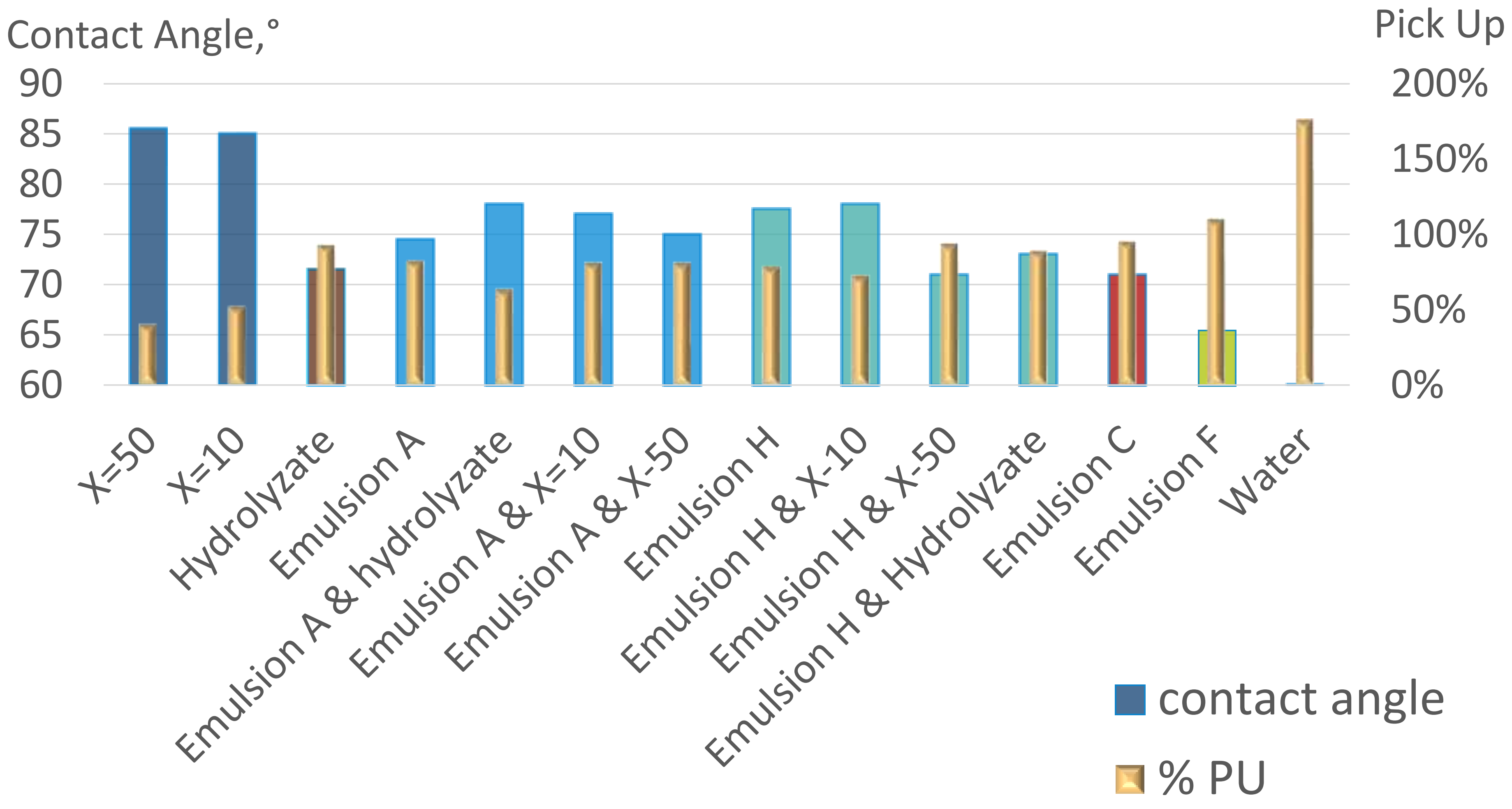


The film forming emulsions gave good water repellency over the control

The addition of TMS types with catalyst gave a slight improvement

The TMS types alone gave the best performance

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

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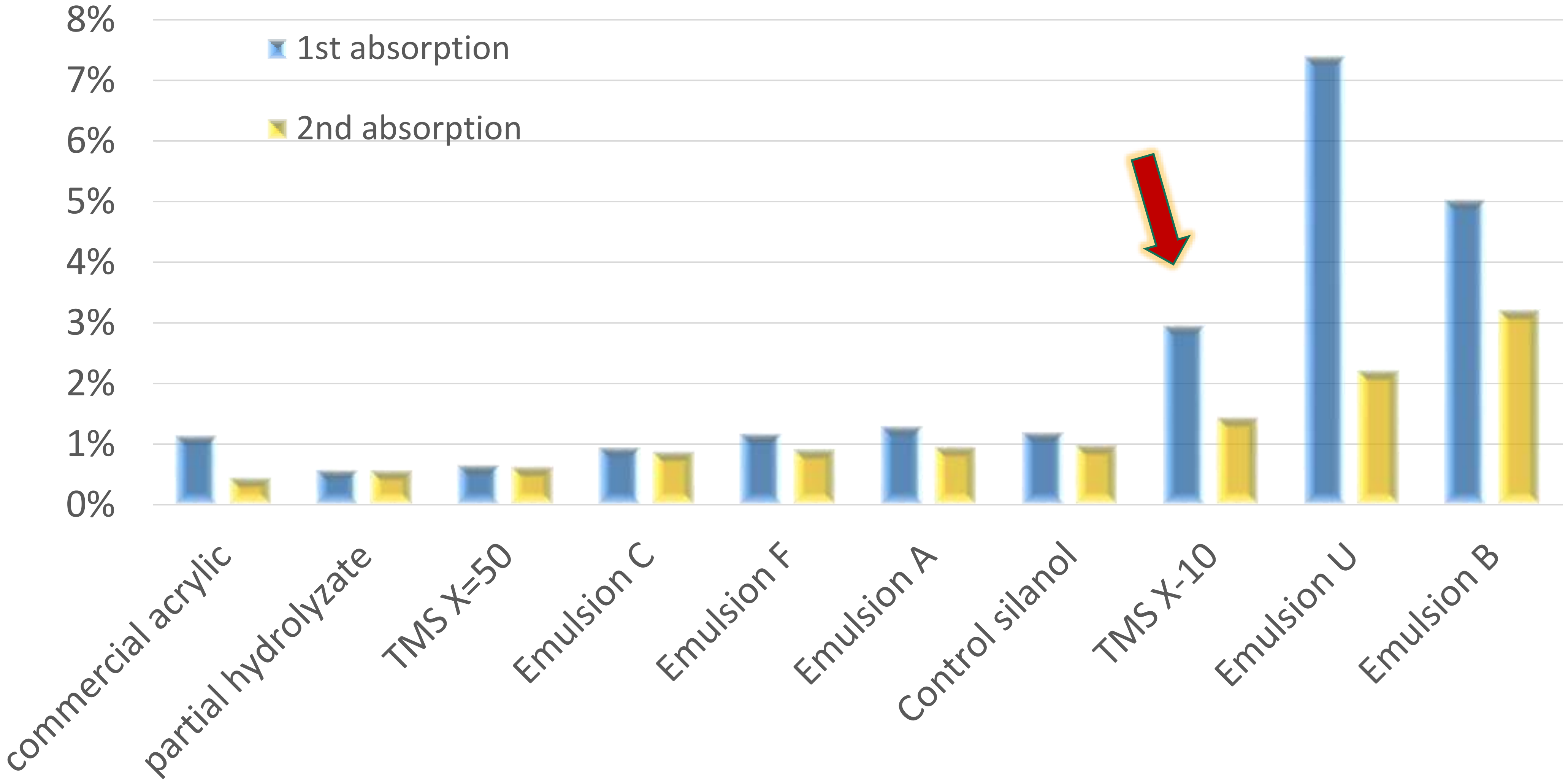
Water Pickup: Concrete Tiles



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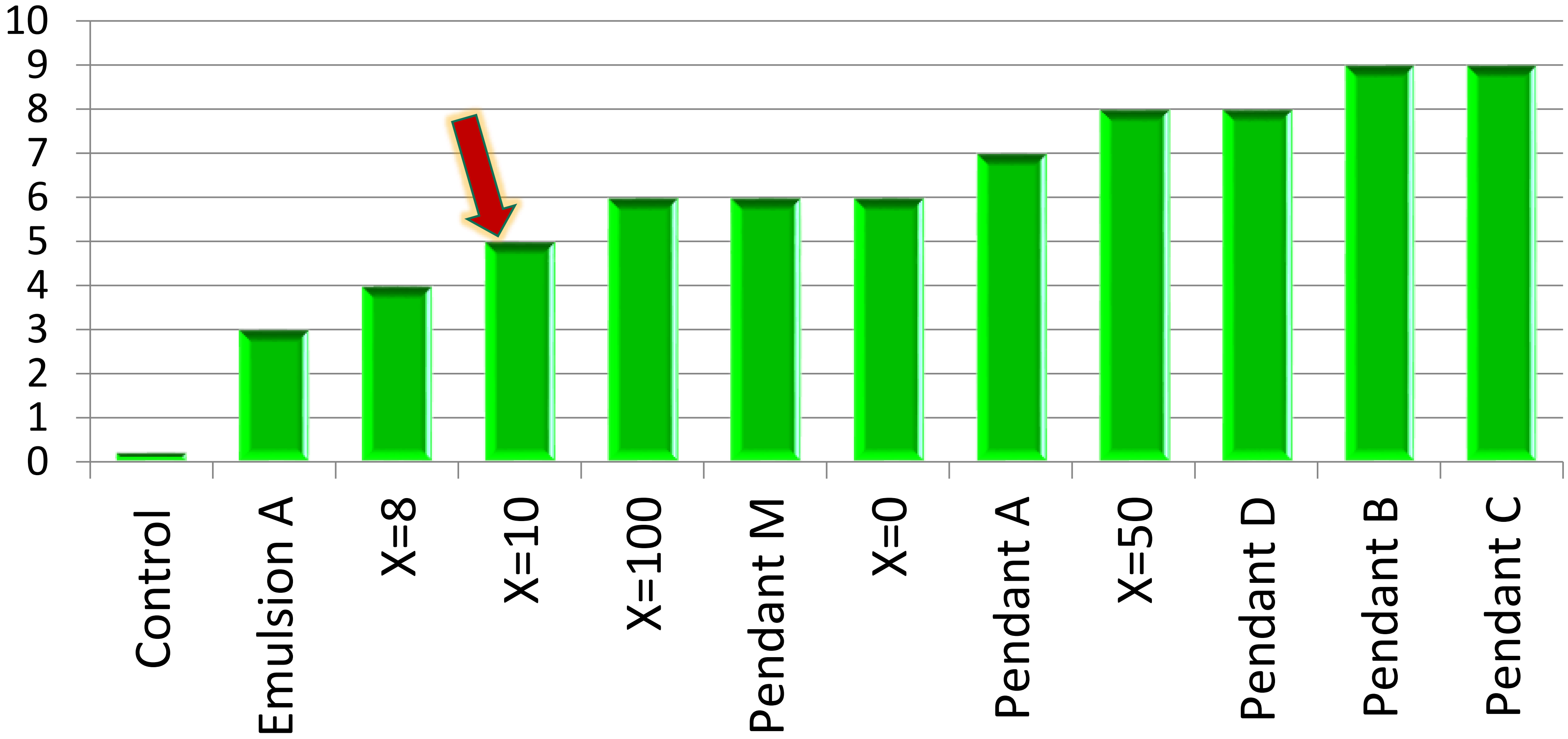
Waterproofing Concrete: TMS Types



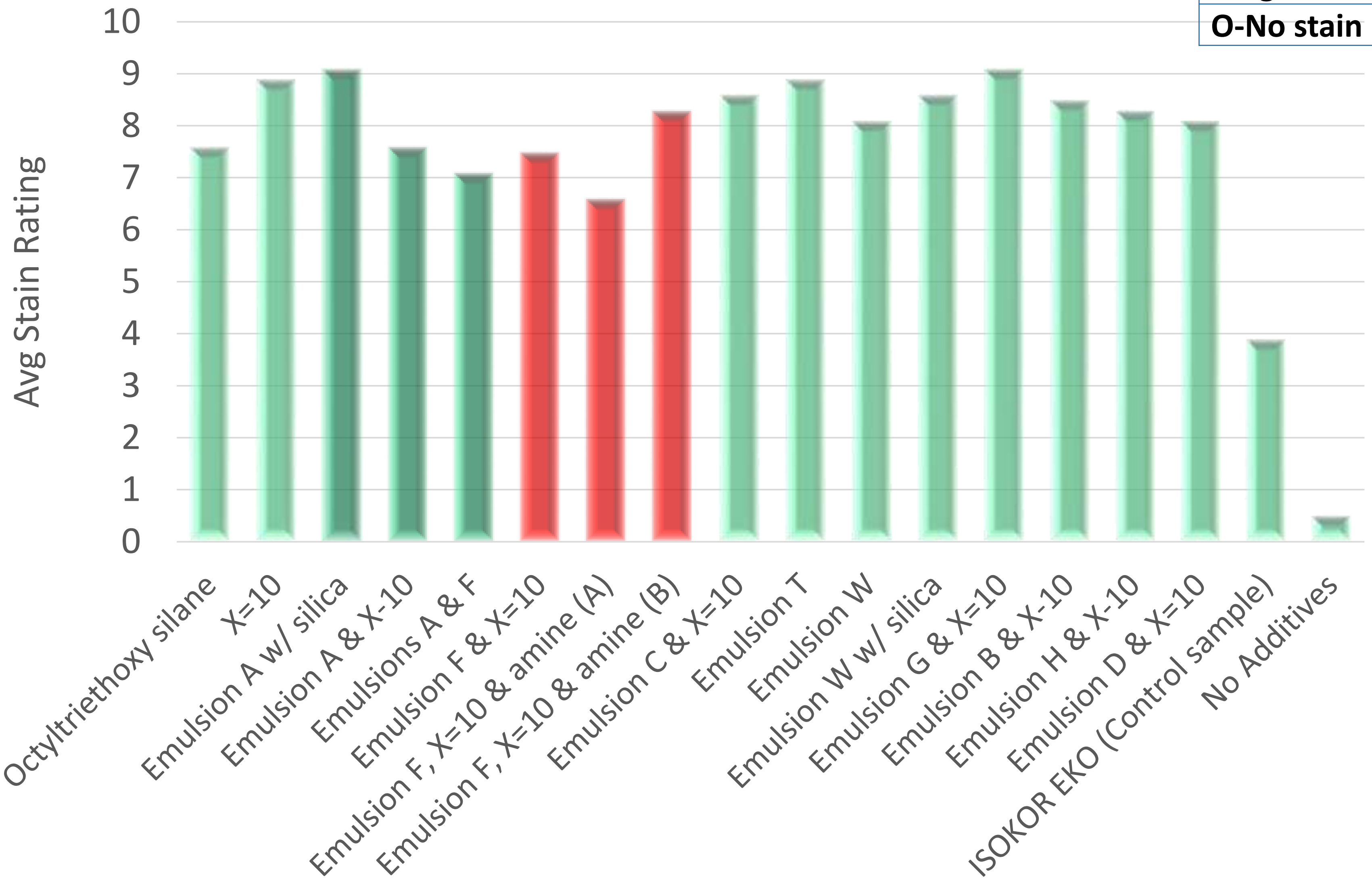
All samples treated with TMS types are much better than control

Stain Resistance/ Surface Treatments

Emulsions and TMS type are effective

Improved Stain Resistance of Commercial Tile Sealant

Stain rating scale (0 STAIN -10 NO STAIN)	
N=No improvement	0
H-Heavy stain	3
M-Medium stain	5
L-Light stain	7
O-No stain	10



TMS type X=10 is excellent alone

Many of the combinations are better than OTS treatment

The addition of silica helps in some cases

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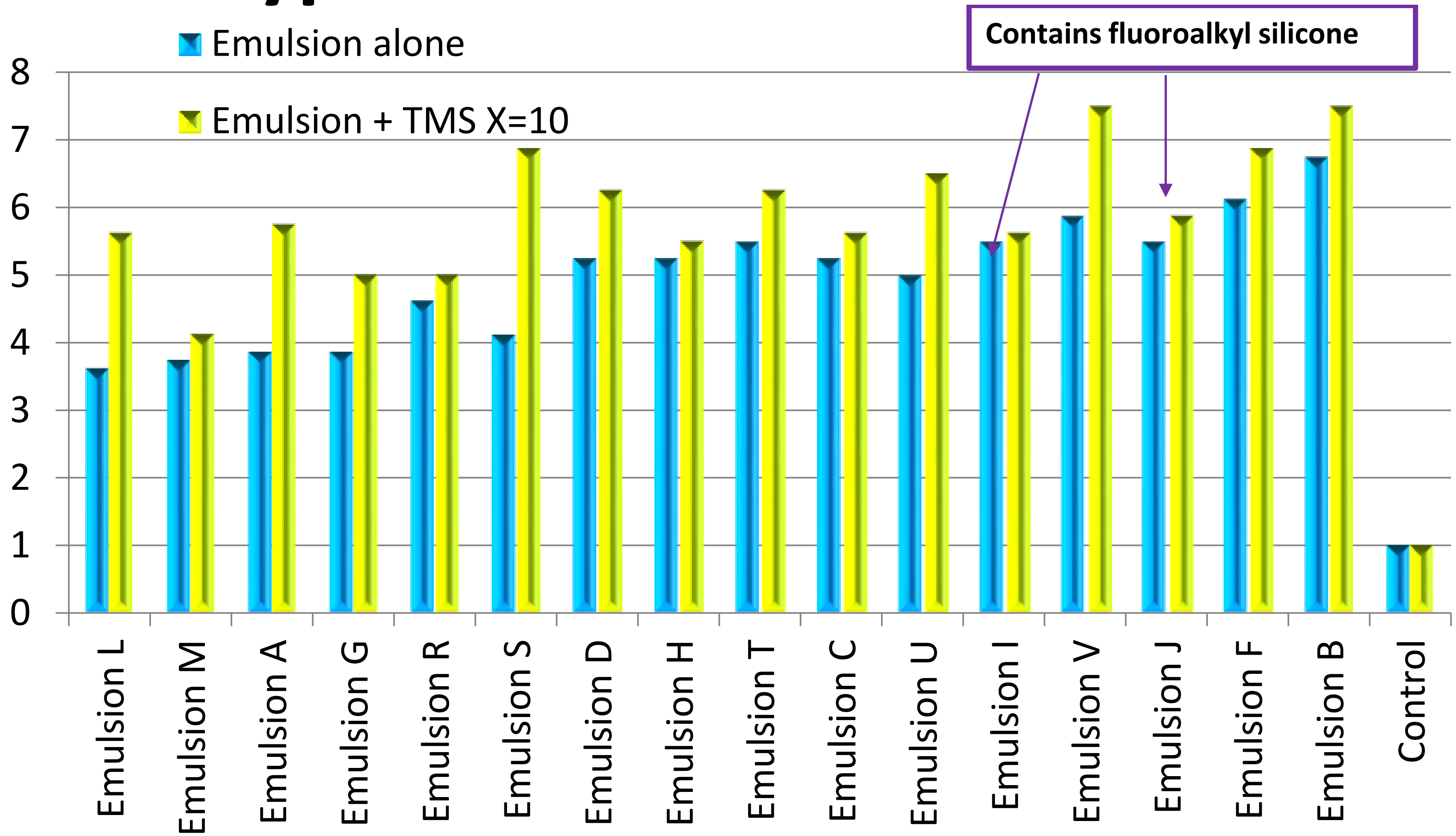
Stain Resistance Of Fabric: Emulsions W & W/O TMS Type X=10



All samples with 7% added TMS type x=10 show improved stain resistance

Marker Resistance On Al Panel: Various TMS Types with Epoxy Silane

	Part A	Part B
Xylene	61.7%	98.3%
TMS type	34. 8%	0.0%
3-Glycidoxypropyl methyldimethoxysilane adhesion promoter	3.5%	0.0%
Titanium Diisopropoxide Bis(ethylacetoacetate)	0.0%	1.74%

Part A: Part B = 1:1

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

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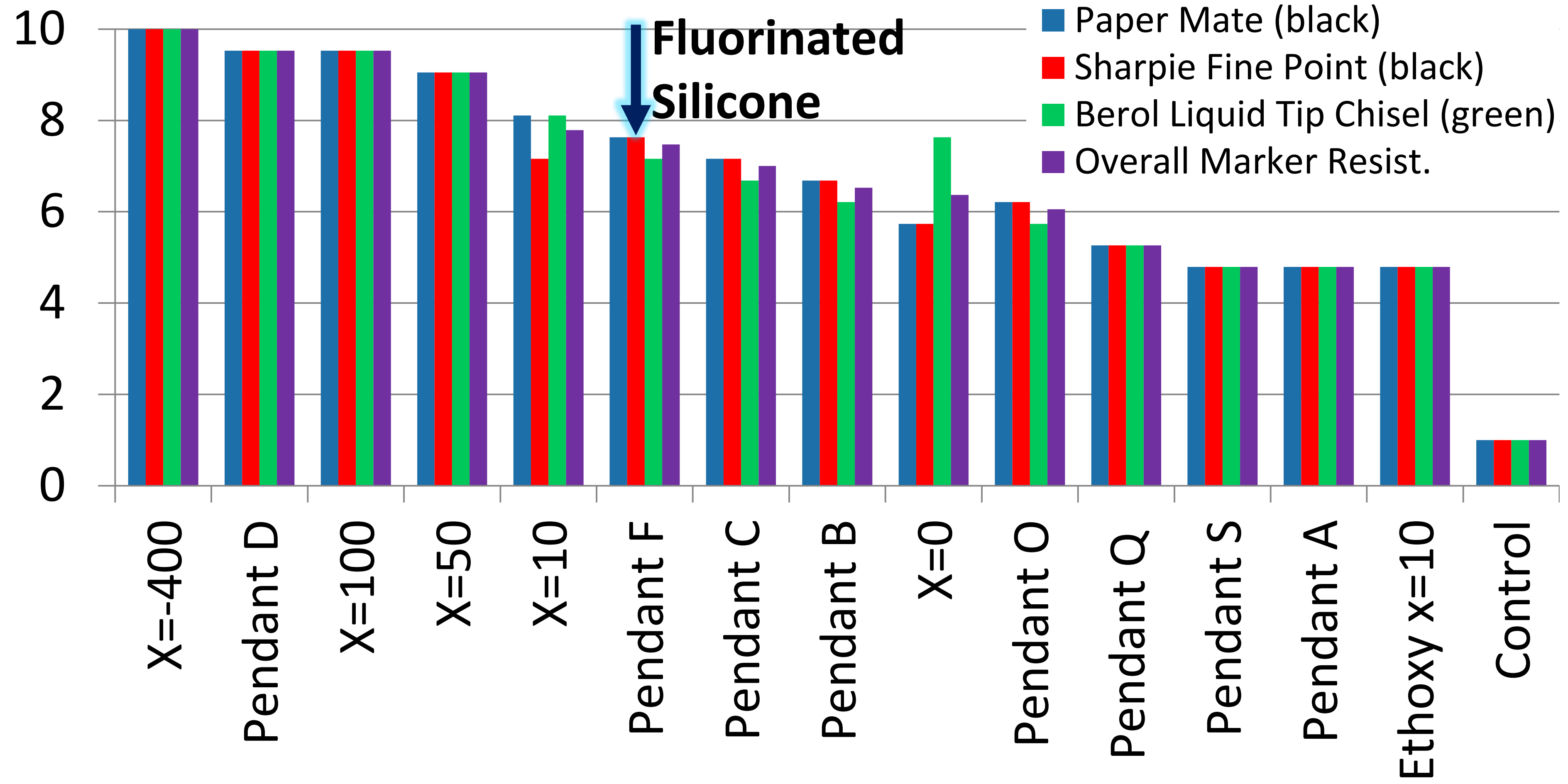
Marker Resistance: Al Panels W/ TMS types



Marker resistance improved with higher MW

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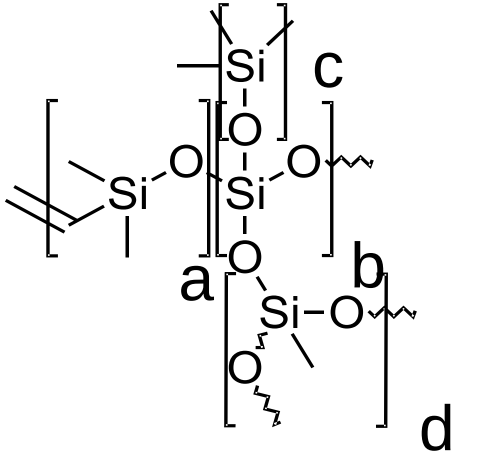
2° Cure/ Resin Modification

TMS type are effective

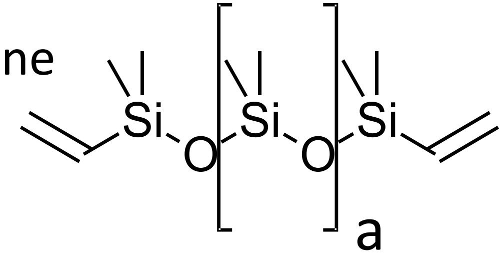
2° Cure: Water Repellency Of Fabric Treated With 2K VIN/SiH, TMS Type And Vinyl Silane

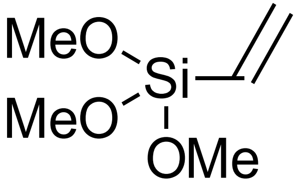
	Formulation
10,000 cps vinyl silicone	14.2%
VQ resin/ 10,000 vinyl (1:1)	41.11%
Karstedt's Catalyst	0.01%
HQ resin	3.43%
VTMO (vinyl silane)	0.10%
TMS type X=10	40.9%
Ti-(II)-Ethylhexoxide	0.21%



VQ resin (d=0)

10,000 vinyl silicone
a~150





VTMO

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

TMS (41%)	TMS Di-10	TMS Di-50	TMS Di-100	TMS Di-400	No TMS
Comments	Clear liquid				
Water Repellency Rating	8	7	6.5	6.5	2

All were close to each other and much better than control.

2K system sprayed from 5% solution in IDD

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

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UV Cured Acrylate Formulation w/ Added Reactive Silicones

	TMS x=10	TMS x=50	NCO x=10	NCO x=50
G' (Pa) first cure	$8.58*10^4$	$3.64*10^4$	$2,21*10^5$	$5.62*10^3$
G' (Pa) seven days	$2.02*10^6$	$2.76*10^6$	$7.22*10^7$	$6.84*10^6$
G' change (%)	**2,254%**	**7,482%**	**32,570%**	**121,608%**
G'' (Pa) first cure	$1.08*10^3$	$5.26*10^2$	$5.54*10^3$	$7.29*10^2$
G'' (Pa) seven days	$6.10*10^4$	$1.79*10^5$	$2.64*10^7$	$5.01*10^5$
G'' change (%)	**5,548%**	**33,930%**	**476,434%**	**68,624%**
Tan delta first cure	0.013	0.014	0.025	0.13
Tan delta seven day	0.03	0.065	0.365	0.073
Tan delta change (%)	**131%**	**364%**	**1,360%**	**-44%**

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Q-Panels

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Appearance	smooth			
Pencil Hardness first cure	<6B	6B	<6B	<6B
Pencil Hardness seven day	**4H**	**6H**	<6B	<6B
Contact Angle (°) first cure	99.6	101.7	107.7	115.3
Contact Angle (°) seven day	101.1	100.9	102.5	103.4
Change contact angle (%)	**1.7%**	**-0.8%**	-4.9%	-10.4%
Gloss first cure	151	163.3	68.9	72
Gloss seven day	147	165	70	59
Change in gloss (%)	**-2.6%**	**1.1%**	2.3%	-18.3%

Improvement in hardness for TMS

NCO too soft to measure

Surface Properties

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Tesa release (N/m) first cure	0.624	0.624	0.936	0.624
Tesa release (N/m) seven day	0.78	0.546	0.858	0.858
Change in tesa release (%)	**25%**	**-13%**	**-8%**	**38%**
BRB release (N/m) first cure	0.429	0.507	0.936	0.312
BRB release (N/m) seven day	0.468	0.234	0.546	0.507
Change in BRB release (%)	**9%**	**-54%**	**-42%**	**63%**
Slip (Static CoF) first cure	3.614	3.625	4.855	3.896
Slip (Static CoF) seven day	2.865	3.168	4.903	4.434
Change in Static CoF (%)	**-21%**	**-13%**	1%	14%
Slip (Kinetic CoF) first cure	3.422	3.289	3.141	2.873
Slip (Kinetic CoF) seven day	2.852	3.164	3.465	3.585
Change in Kinetic CoF(%)	**-17%**	**-4%**	10%	25%

Better results on surface energy

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Transfer and Resist

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Silicone transfer first cure	8	8	2	2
Silicone transfer seven day	**2**	**2**	2	2
Stain resistance first cure	10	10	4	4
Stain resistance seven day	10	6	6	10
Mar resistance first cure	6	6	4	6
Mar resistance seven day	**8**	6	4	4
Rub resistance first cure	>100	>100	>100	>100
Rub resistance seven day	>100	>100	>100	>100

Conclusions

- In some cases, condensed or reacted polymers can improve performance over or with trialkoxysilanes
- Film Forming, cured silanol condensate emulsions, often offer superior water repellency and stain resistance.
- Reaction of TMS types with resins has been demonstrated with secondary cure.
- Super hydrophobicity can be achieved with TMS products and nano-silica.

Conclusions

- 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.

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