ENHANCED HYDROPHOBICITY

SURFACTANT FREE MICROEMULSIONS

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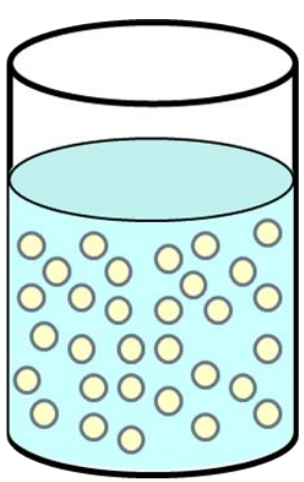
PURE MICHIGAN FURS

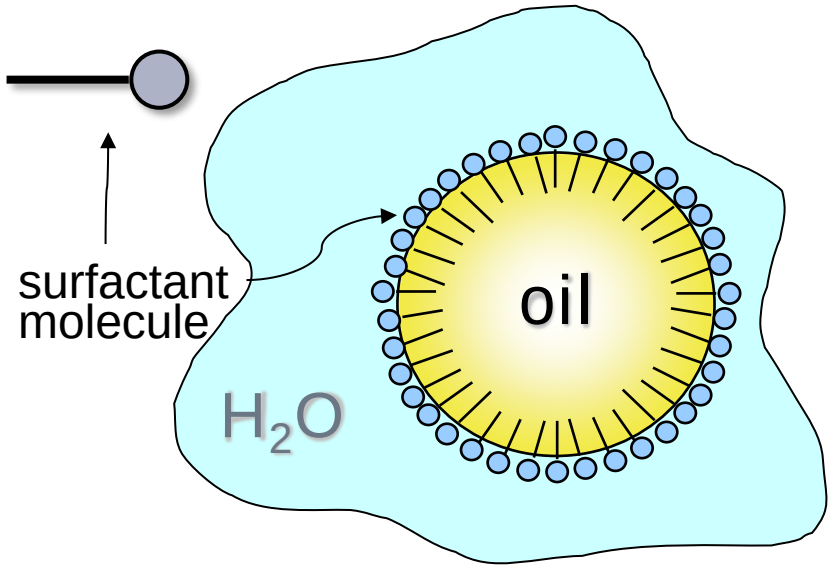
Emulsion Basics

Emulsion: A dispersion of one immiscible liquid in another, usually stabilized by a **surf**ace **act**ive **a**ge**nt.**

Surfactant: A substance which tends to reduce the surface tension of a liquid in which it is dissolved.



Oil in Water Emulsion
(O/W)



Oil-in-Water Emulsion (O/W)

Type of surfactant used imparts certain properties to the emulsion.

In case of multiple surfactant types, the emulsion takes its type from the "**more critical**" surfactant used (i.e., nonionic + anionic = anionic emulsion.)

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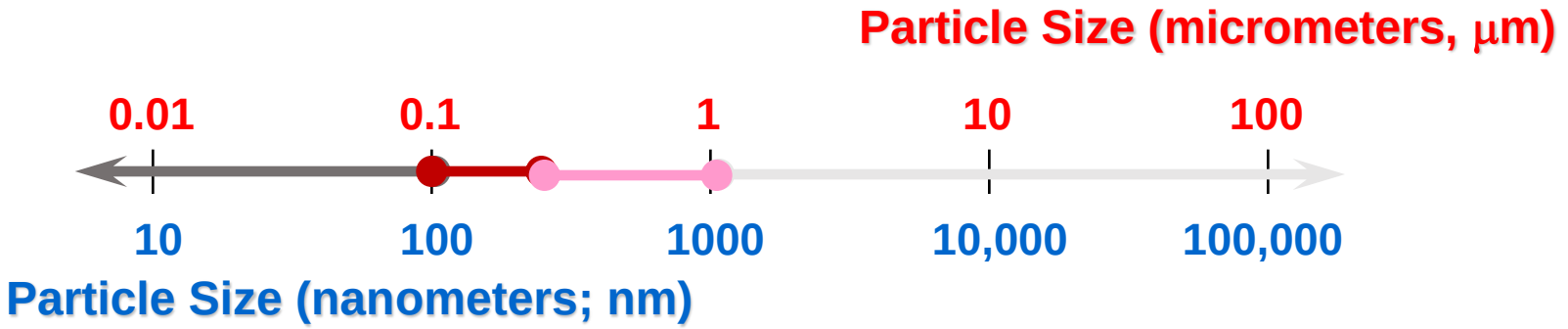
Emulsion Classification by Particle Size



- Microemulsions: <100 nm
- Fine Emulsion: 0.1 µm to 0.3 µm (*Most difficult to manufacture*)
- Coarse Emulsion: 0.3 µm to 1 µm
- Macro Emulsion: >1 µm

100 nm = 0.1 µm

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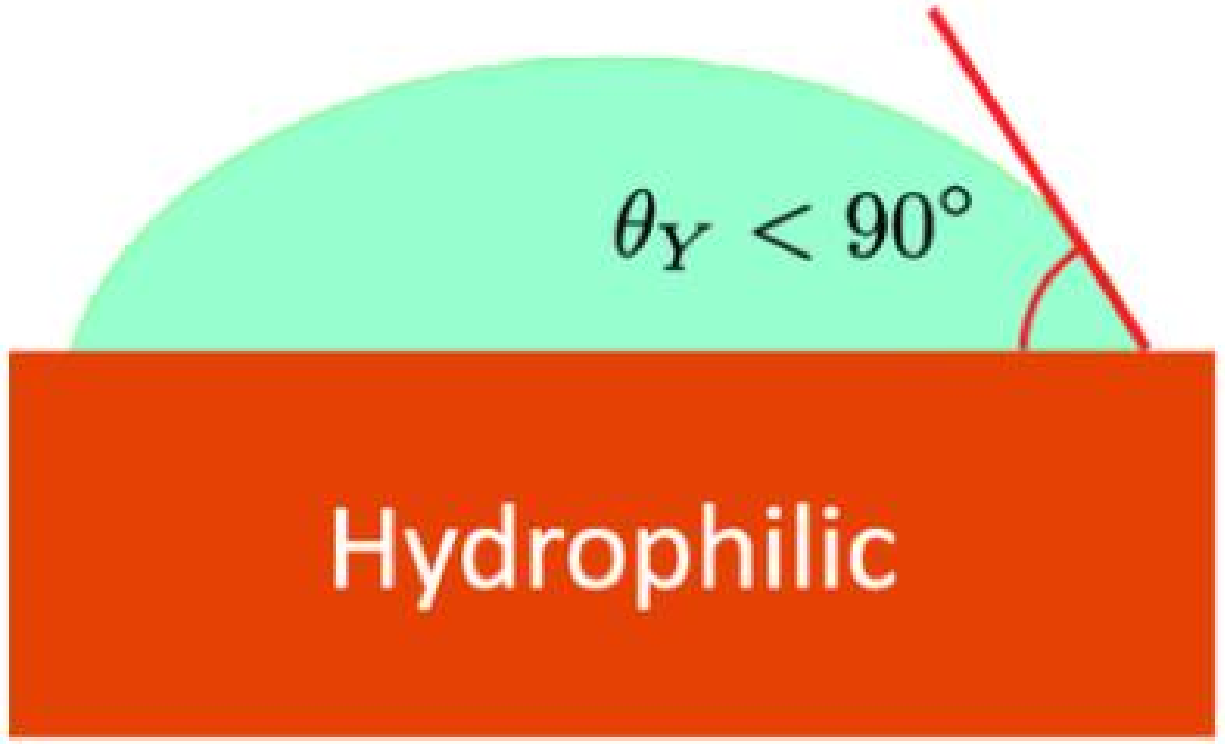
EMULSIONS: HYDROPHILIC CHARACTER



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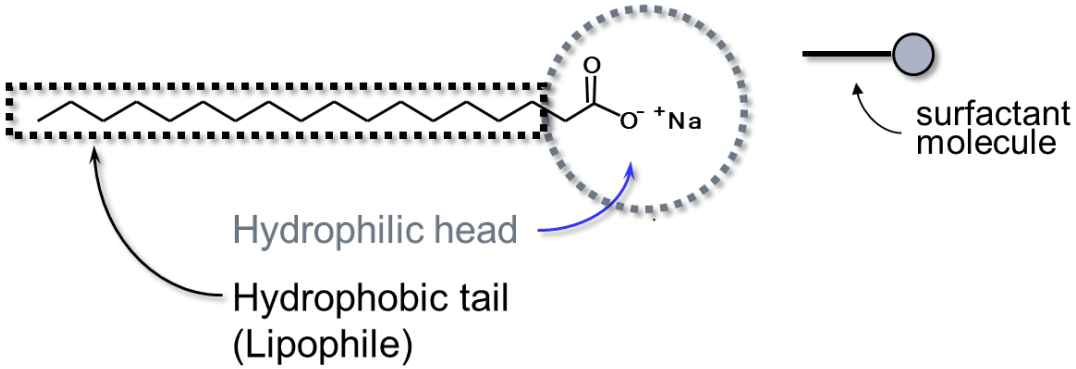
Surfactant Basics

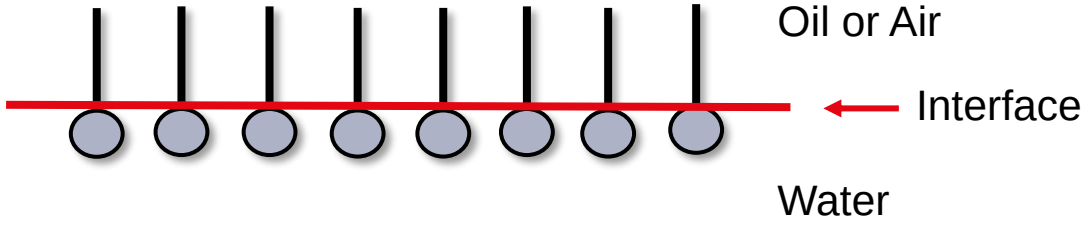
Surfactants are amphipathic compounds. Meaning they have and affinity for both water and oil.

Surfactant molecules have polar “head” groups and nonpolar “tails” chains.

Surfactants accumulate at interfaces (air/water and oil/water interface)

There are three main types of surfactants: Nonionic, Cationic, and Anionic





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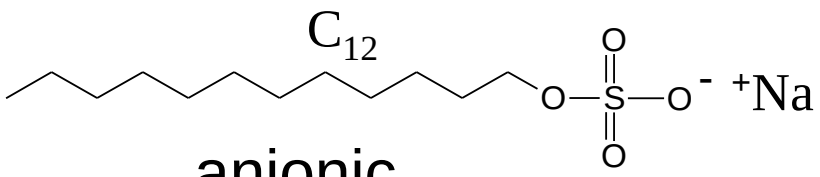
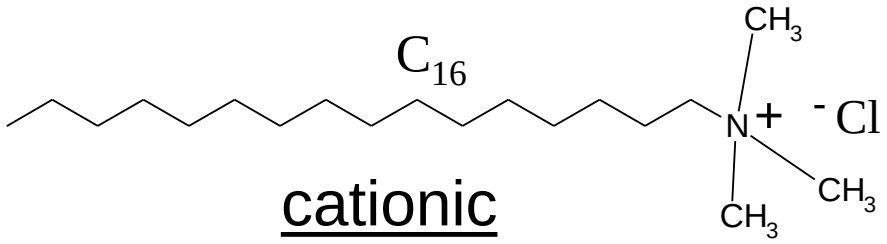
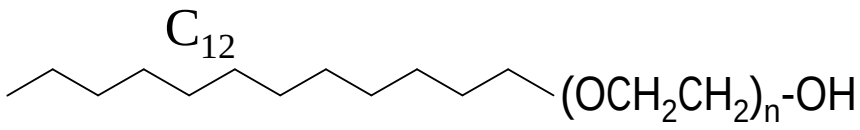
Types of Surfactant



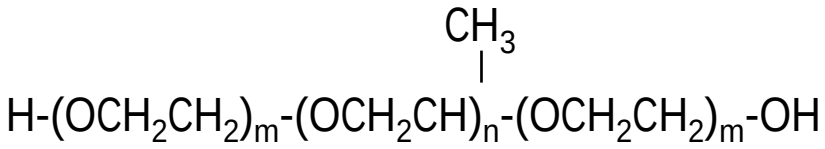
anionic



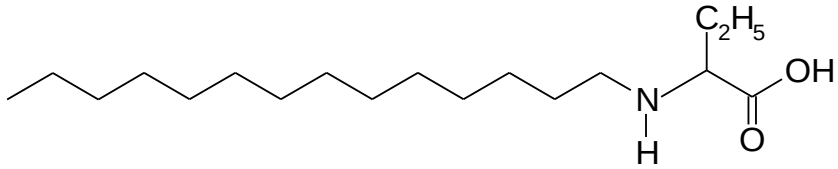
cationic



nonionic



polymeric



amphoteric

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Surfactants – The HLB System

HLB = “**H**ydrophile-**L**ipophile **B**alance”

- Used for identifying emulsifiers for mechanical emulsions
- Numerical scale to describe extent of hydrophilicity
  - oleic acid ~ 1.0
  - potassium oleate = 20.0
  - Most nonionic surfactants fall between 1-20
- Every oil has a “required HLB”

Surfactants – The HLB System

Water Solubility and HLB Relationship

HLB: 0 – 3	No dispersibility in water
HLB: 3 – 6	Poor dispersibility
HLB: 6 – 8	Some dispersibility
HLB: 8 – 10	Good dispersibility
HLB: 10 – 13	Great Dispersibility
HLB: 13 – 20	Soluble - clear solution

Surfactant Application Based on HLB

HLB 3 - 6:	Water in Oil emulsifier (Butter)
HLB 7 - 9:	Wetting agent
HLB 8 - 13:	Oil in water emulsifier (Latex)
HLB 13 - 15:	Detergent (Soap)
HLB 15 - 18:	Solubilizer

Surfactants – The HLB System

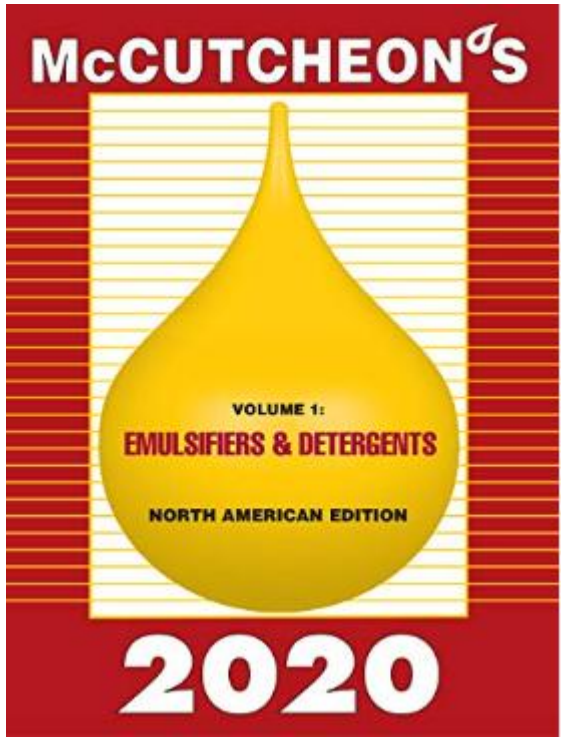
- HLB system will get you into the “ballpark,” when making emulsions.(some of the time)
- HLB does not provide surfactant use level.
- The HLB of a surfactant varies with temperature.
- Ionic surfactants do not have HLBs.
- HLB is a useful tool for communicating general surfactant properties among emulsion chemists.

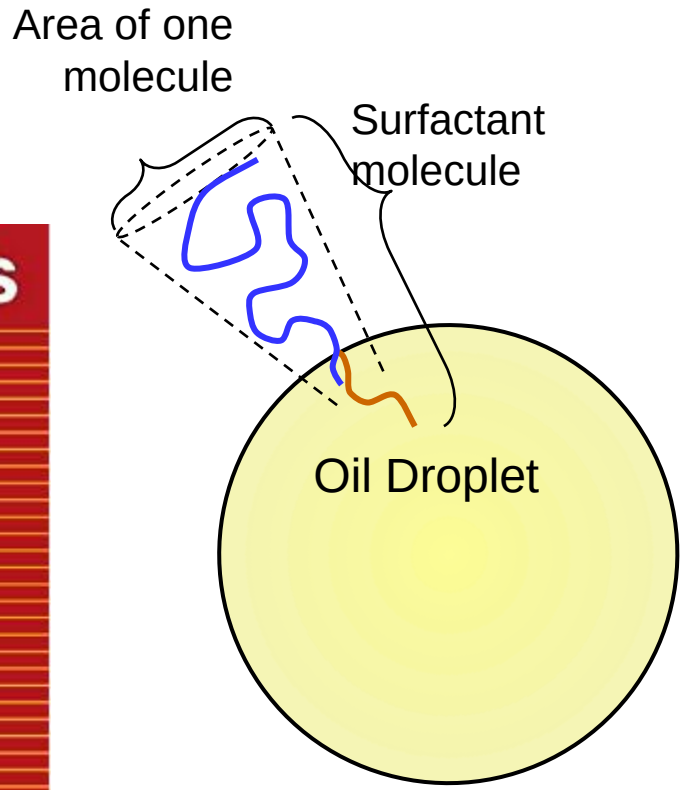
Surfactants – Usage Levels

Minimum required surfactant loading can be calculated.

Considerations:

- Coverage area of one surfactant molecule
- Target particle size of the emulsion
- % solids of emulsion
- Mw of Surfactant
- Density of oil
- Avogadro's #





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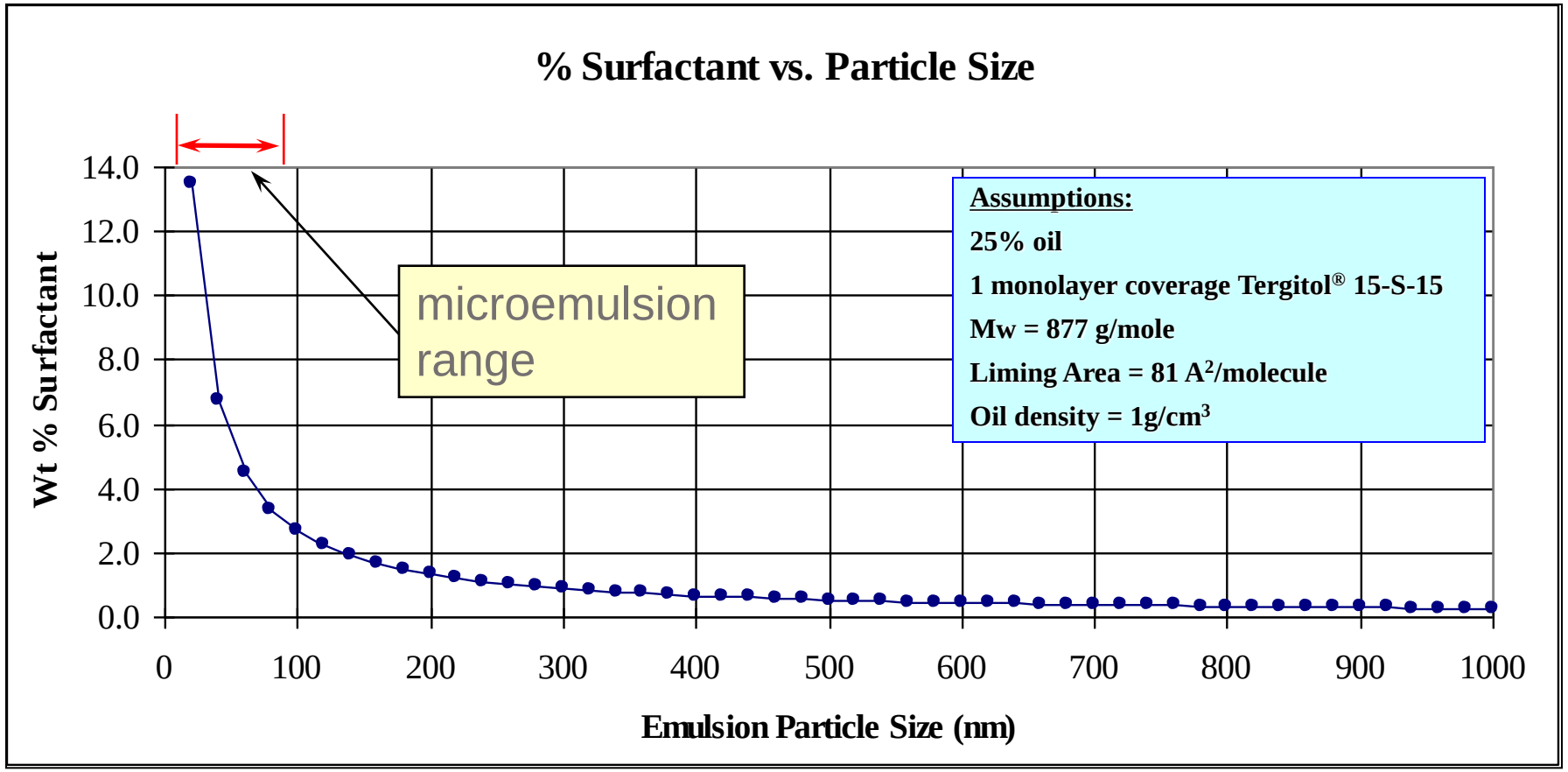
Surfactants – Usage Levels

Surfactant concentration is proportional to 1/Particle Size



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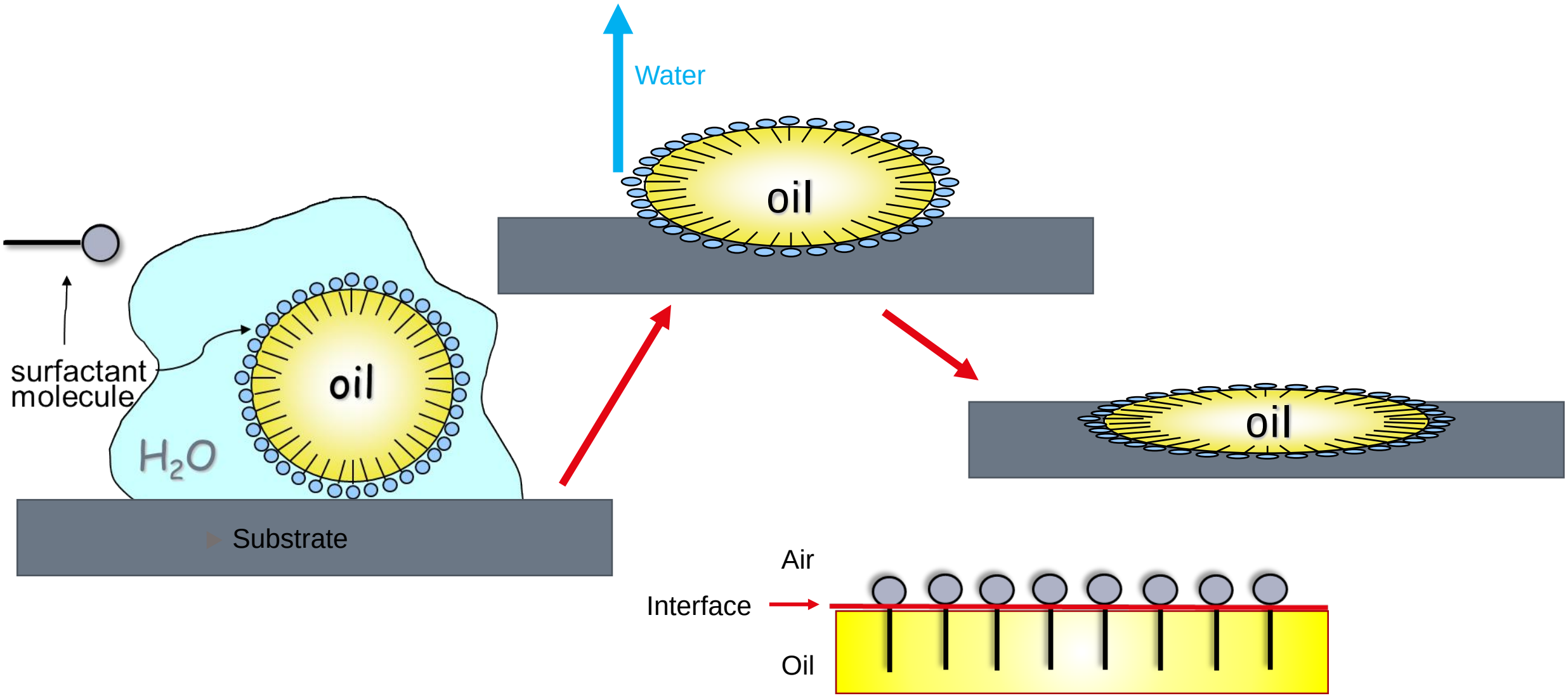

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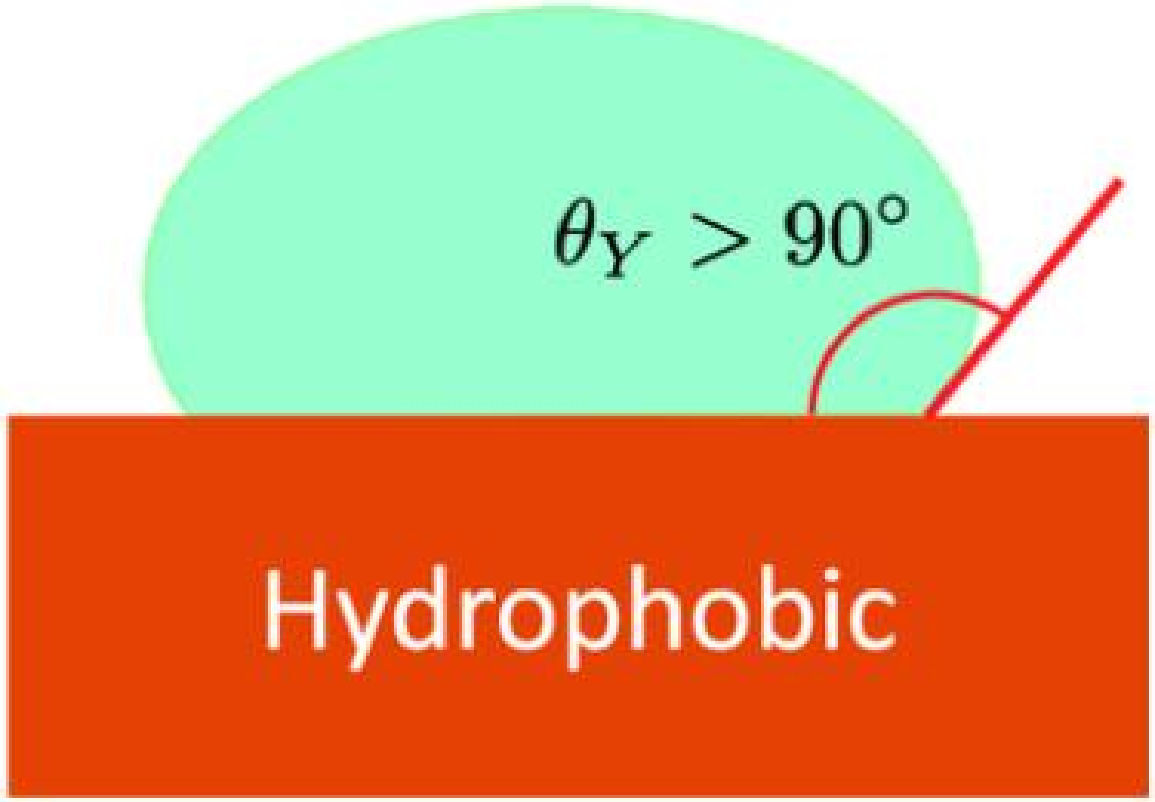
EMULSIONS: HYDROPHOBIC CHARACTER



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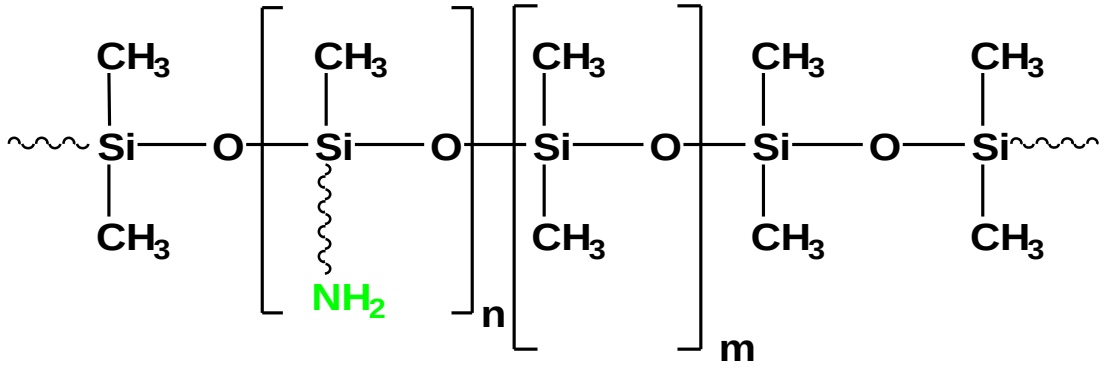
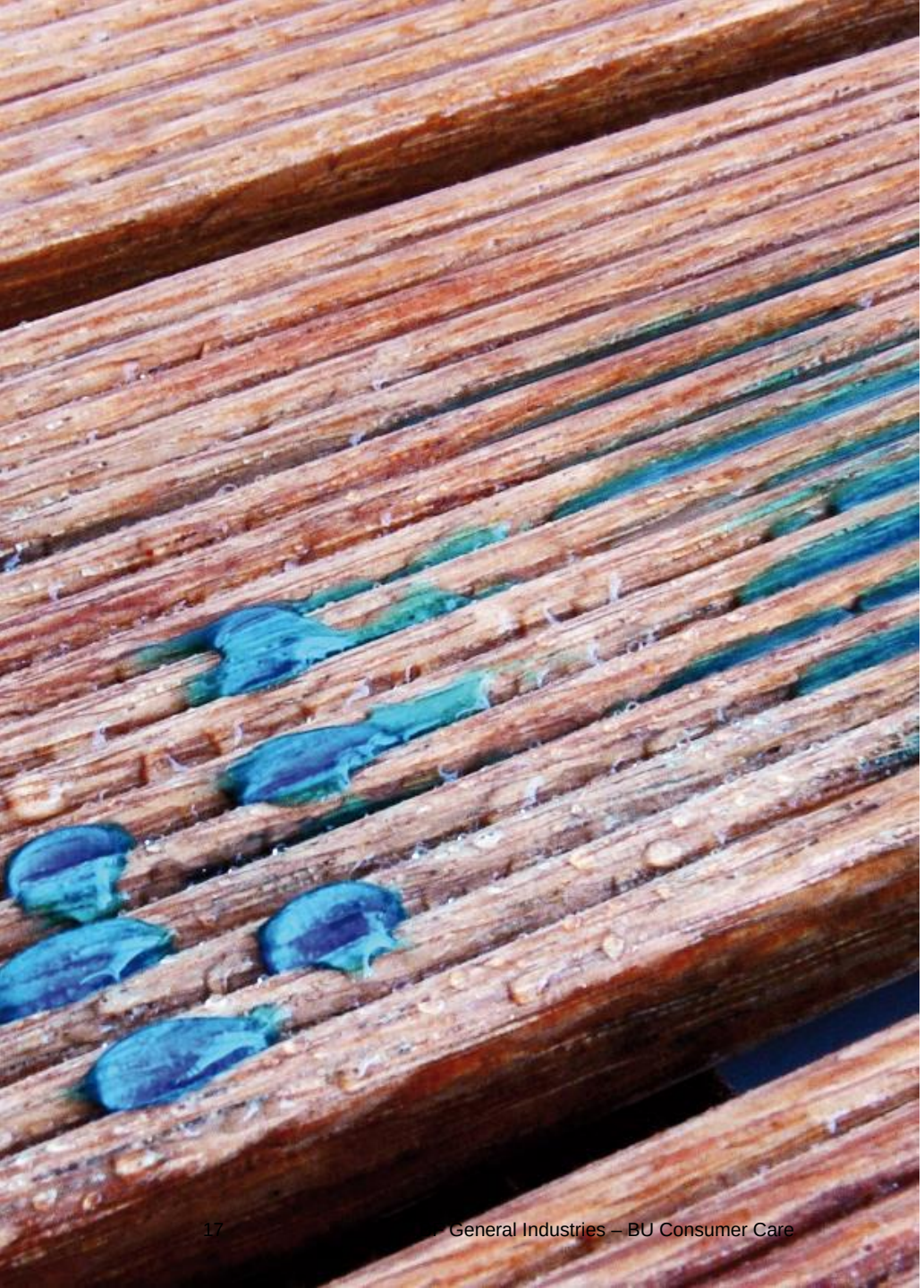
Aminosiloxane – Structure

- The PDMS chain is modified with some amino-alkyl groups
- Manufacturers knowledgeable in siloxane chemistry are able control the length of the silicone chain as well as the amount of the amino groups.
- The length of the silicone chain has an influence on the non-polar character of the molecule as well as the viscosity
- The amount of amino groups has an influence on the polar character as well as the orientation on substrates





AMINOSILOXANE – FUNCTION

- The amino groups have a positive charge and will orientation to the surface, because the most surfaces have a negative potential.
- The effects of aminosiloxanes on surfaces:
  - Strong hydrophobic
  - Good durability
  - Darkening effect
  - Smooth/soft feel

AMINOSILOXANE

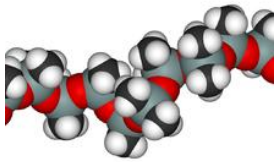
Amino-Siloxanes

- Durable
- Hydrophobic
- Beading
- Water Repellent

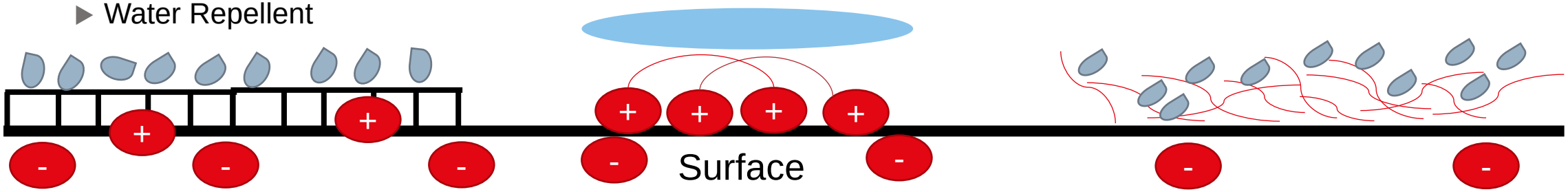
Quaternary Siloxanes

- Low surface tension
- Sheeting effect

PDMS



- Gloss
- Color Depth



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Amino Functional PDMS Microemulsions

- Typical Preparation
  - Start with an aminofunctional PDMS.
  - Form “association complex” with nonionic surfactant & limited amount of H_2O.
  - Dilute rapidly with additional H_2O.

- Characteristics
  - High surfactant content (30-100% based on oil).
  - Small particle size (20-100nm).
  - Low actives concentration (15-25% solids).
  - Clear emulsions possible.
  - **Can be stabilized with acetic acid.**

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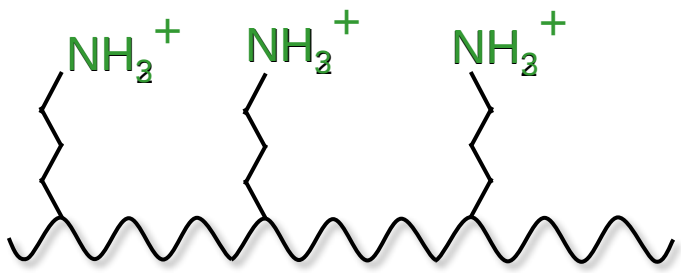
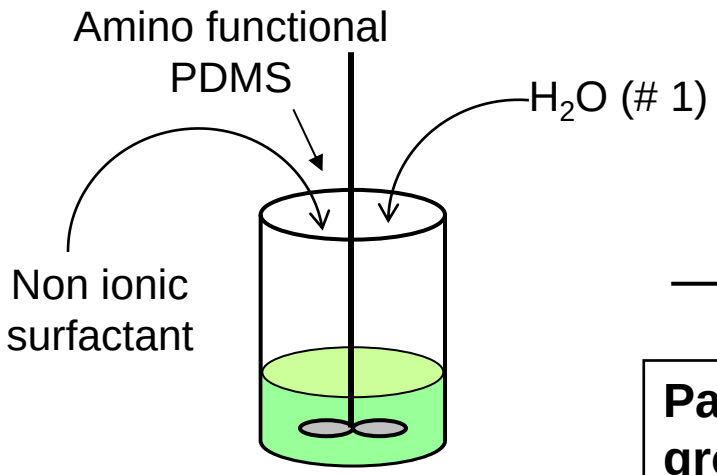
Aminofunctional PDMS Microemulsions



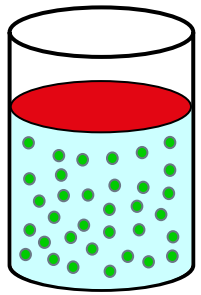
PDMS backbone ~ 2 mole% amine



H_2O Dilution (#2)

Partially neutralizing NH_2 groups results in improved stability and smaller particles

Amino Microemulsion



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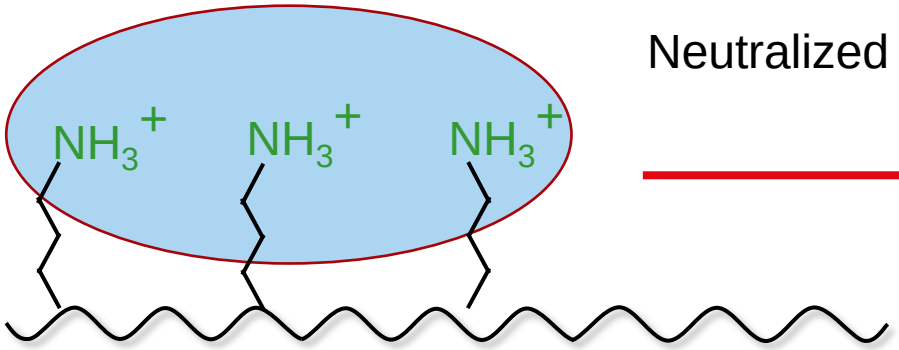
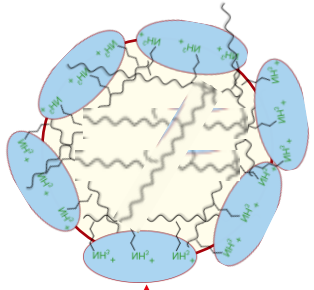
Aminofunctional PDMS Microemulsions – Surfactant Free



Neutralized amine acts as hydrophilic “head”



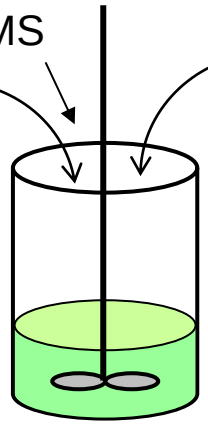
PDMS backbone acts as hydrophobic “Tail”

Amino Microemulsion forms without traditional surfactant

Amino functional PDMS

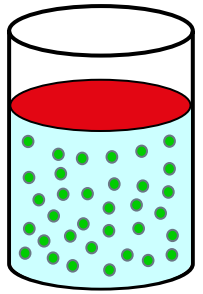
H_2O (# 1)

Acid



Protonated amine groups allows polymer to act as its own surfactant

H_2O Dilution (#2)



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APPLICATION TESTING – HYDROPHOBICITY

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APPLICATION TESTING – KARSTEN TUBE

Max permissible values

Type of building material	Water penetration value	Type of building material	Water penetration value
1. Facade surfaces in clinker or red brick outside the joint area. Mean from 10 individual tests, half of which are detemined over fire cracks single values not above	 0.5 ml/min 2.0 ml/min	5. Hydrophobed waterproofing or sealing concrete acc. to DIN 4117, Nov. 1960 edition on outside surface on fresh surfaces of fractures (Note: compliance with the maximum values is not a fully valid substitute for the test of the barrier effect, see also No.7)	 0.1 ml/min 0.1 ml/min
2. Mortar joints on facade surfaces from all building stones Mean from 10 individual tests Single values not above	 0.5 ml/min 2.0 ml/min	6. Hydrophobed waterproofing or sealing mortar or plaster acc. to DIN 4117. Nov. 1960 edition, as above according to No.5	
3. Exterior rendering resistant to pelting rain as No.2		7. "Waterproof concrete" acc. to DIN 1048 (not hydrophobed) on outside surfaces on fresh surfaces of fractures (Note: compliance with the maximum values is an aid to assessment for the expert but not a substitute for the standard test acc. to DIN 1048	 0.3 ml/min 0.5 ml/min
4. Facade surfaces after hydophobic silicone or siloxane impregnation in stone and joint area (Precondition: cracks sealed beforehand with permanent plastic sealing material)	0.0 ml/min		

APPLICATION TESTING – KARSTEN TUBE

Procedure

- Prepare 1, 2, 3, 5, 7 and 10% dilutions of each hydrophobic agent in water and apply a total amount of 190 - 200 g / m2 to fiber cement in each case.
- Let it dry at room temperature for 24 hours and to characterize according to the mentioned laboratory tests.

Product	Actives Content (as supplied)
Comp 1 - Siliconate	53.2%
Comp 2 - Siliconate	52.8%
Comp 3 - Siliconate	53.3%
Surfactant Free Microemulsion	15.3%

1% dilution = 0.532% actives (5,320 ppm)

1% dilution = 0.153% actives (1,530 ppm)

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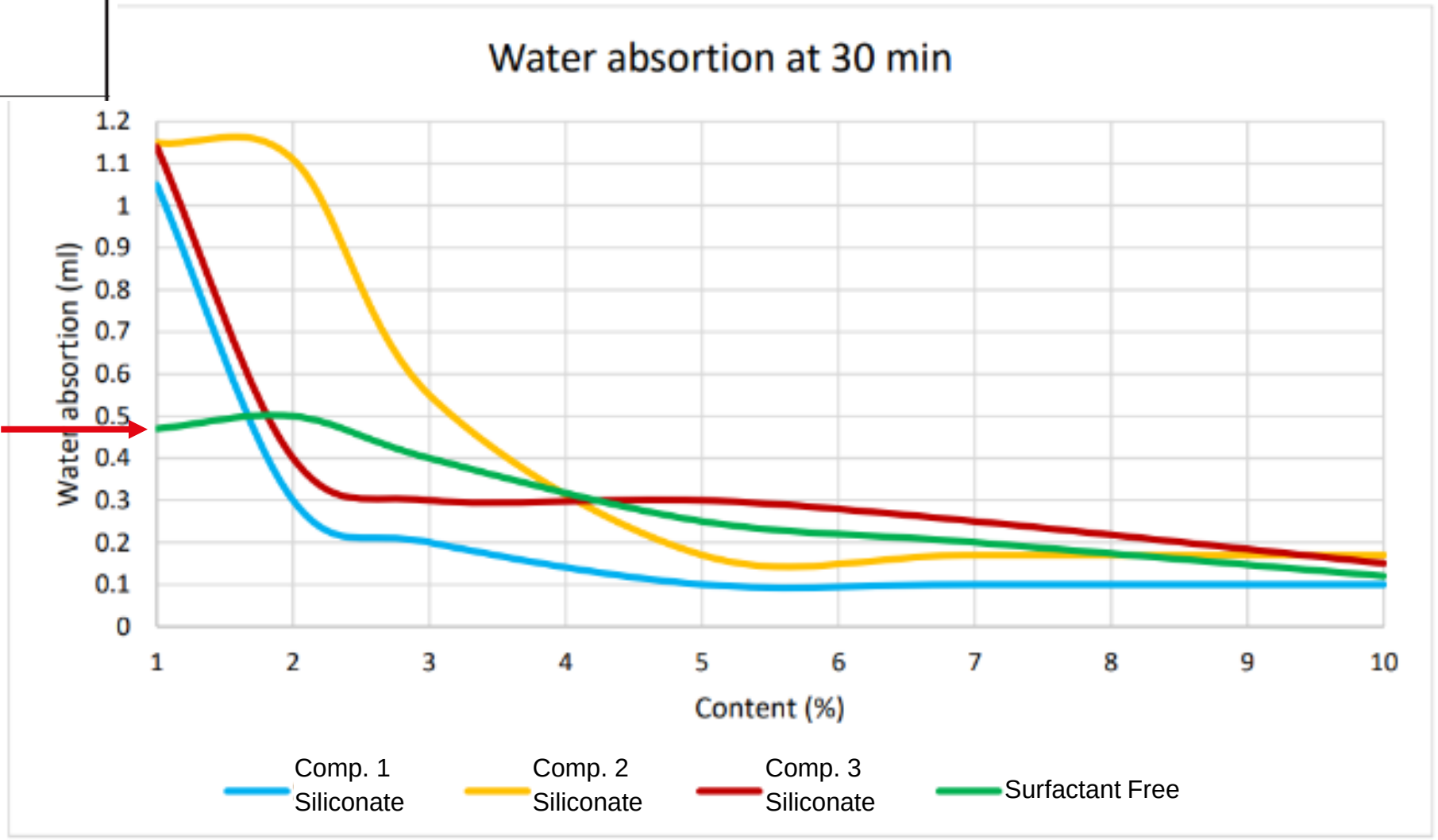
Type of building material	Water penetration value
5. Hydrophobed waterproofing or sealing concrete acc. to DIN 4117, Nov. 1960 edition on outside surface on fresh surfaces of fractures (Note: compliance with the maximum values is not a fully valid substitute for the test of the barrier effect, see also No.7)	 0.1 ml/min 0.1 ml/min

0.5 mL absorbed over 30 minutes

- **0.016 ml/min**



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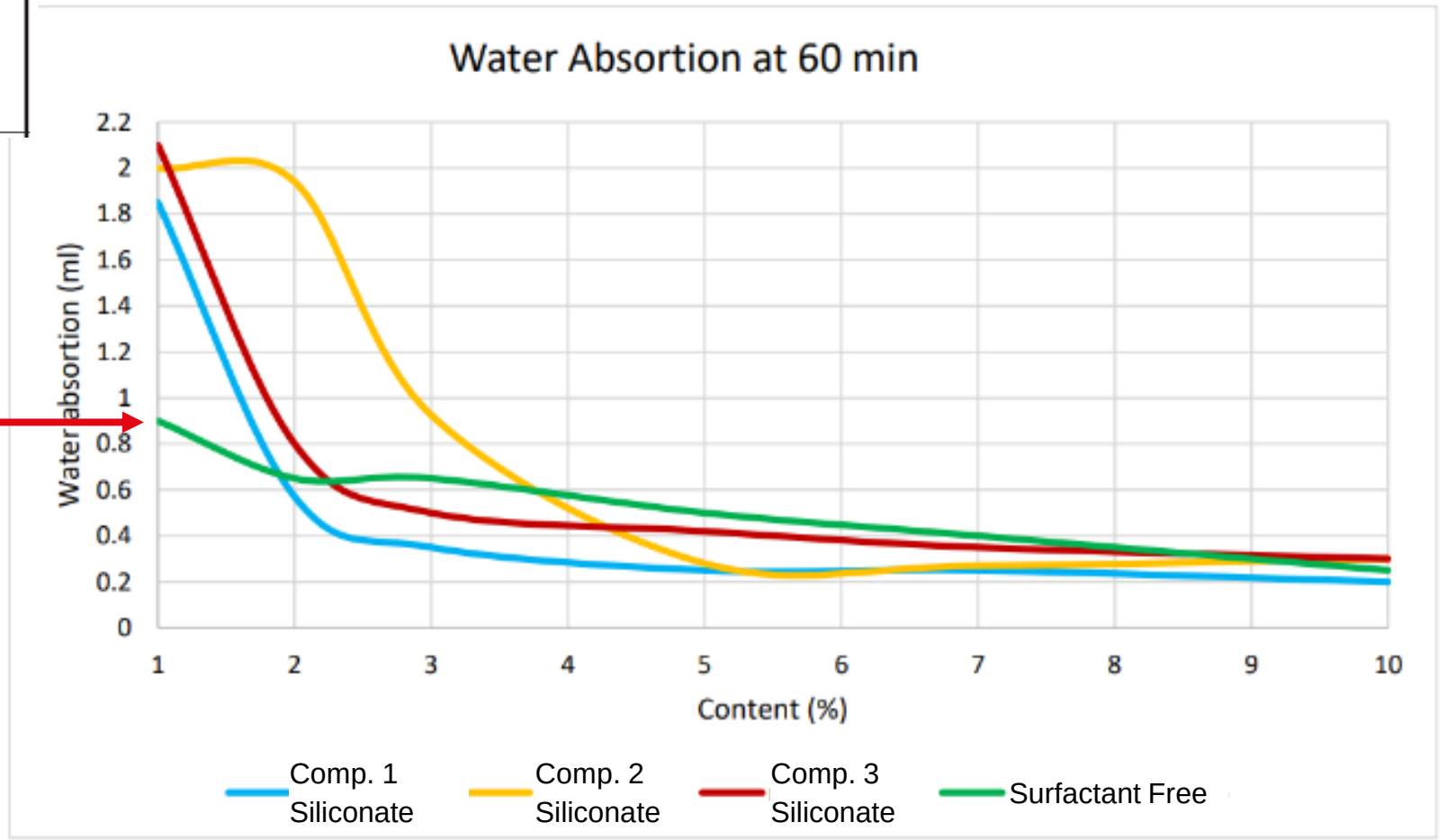
Type of building material	Water penetration value
5. Hydrophobed waterproofing or sealing concrete acc. to DIN 4117, Nov. 1960 edition on outside surface on fresh surfaces of fractures (Note: compliance with the maximum values is not a fully valid substitute for the test of the barrier effect, see also No.7)	 0.1 ml/min 0.1 ml/min

0.9 mL absorbed over 60 minutes

- **0.015 ml/min**



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APPLICATION TESTING – EFFLORESCENCE

Application Product is applied on the substrate by brush and stored 7 days in a climate chamber 20°C / 65% air humidity. After drying the samples set upended in a 14% sodium chloride solution. The samples stay for 21 days in the salt solution.

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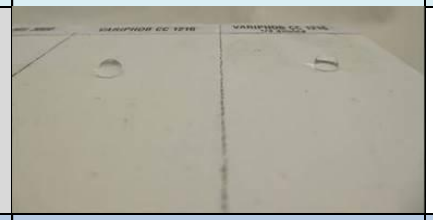
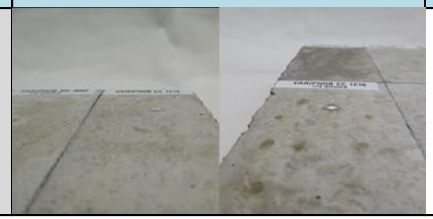
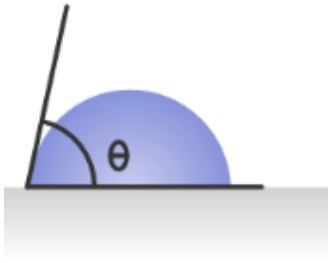
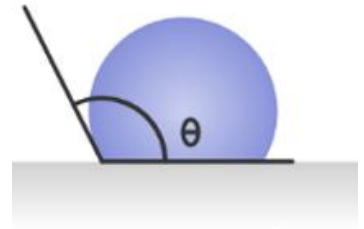
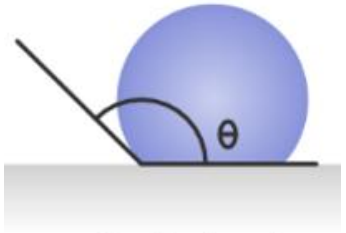
Description		Standard Siliconate	Standard Siliconate diluted 1/3 dest. water	Surfactant Free Microemulsion	Surfactant Free Microemulsion diluted 1/3 dest. water
Contact angle after 1h[°]	natural stone	0	0	46	101
Contact angle after 4h[°]		52	84	67	105
Contact angle after 24h[°]		97	75	118	105
Observation during testing process		1h = wet 4h = slightly wet 24h = slightly wet / Film	1h = slightly damp 4h = shiny surface 24h = OK	1h = slightly damp 4h = shiny surface 24h = OK	1h = slightly damp 4h = shiny surface 24h = OK
Contact angle after 1h[°]	limesandbrick, painted	22	84	67	103
Contact angle after 4h[°]		53	87	108	110
Contact angle after 24h[°]		78	97	105	118
Observation during testing process		1h = wet 4h = slightly wet 24h = slightly wet / Film	1h = slightly damp 4h = shiny surface 24h = OK	1h = wet 4h = shiny surface 24h = shiny surface / Film	1h = slightly damp 4h = shiny surface 24h = OK
Contact angle after 1h[°]	wood	0	94	106	124
Contact angle after 4h[°]		0	89	127	127
Contact angle after 24h[°]		79	103	124	127
Observation during testing process		1h = wet 4h = slightly wet 24h = slightly wet / Film	1h = OK 4h = OK 24h = OK	1h = OK 4h = OK 24h = OK	1h = OK 4h = OK 24h = OK
Contact angle after 1h[°]	concrete	0	> 140	139	139
Contact angle after 4h[°]		29	145	135	135
Contact angle after 24h[°]		87	136	140	140
Observation during testing process		1h = wet 4h = slightly wet 24h = slightly wet / Film	1h = OK 4h = OK 24h = OK	1h = OK 4h = OK 24h = OK	1h = OK 4h = OK 24h = OK



Contact angle
< 90°
Hydrophilic
material



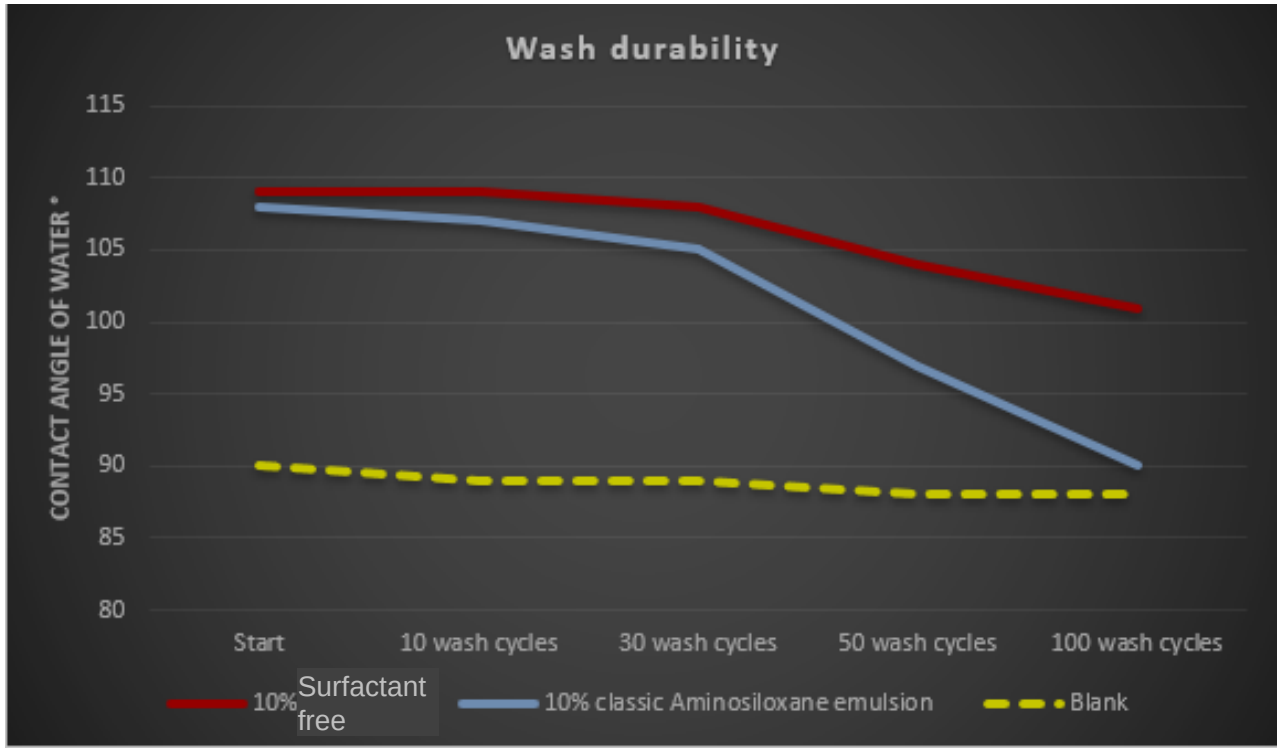
Contact angle
> 90°
Hydrophobic
material



Contact angle
> 150°
Superhydrophobic
material.

APPLICATION TESTING - CAR CARE APPLICATION

Application:	By trigger spray or as liquid on vehicle surface
Method:	Spread even on a clean surface and rub off immediately with a soft microfiber cloth.
Drying time:	10 min after rub off.



Benefits :

- Super hydrophobic effect
- High durability up to 6 – 12 month
- Easy to apply
- Water based formulation
- Strong smoothness
- Low roll down angle of water drops

Appearance: Clear to opaque liquid

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APPLICATION TESTING

DIRT PICKUP

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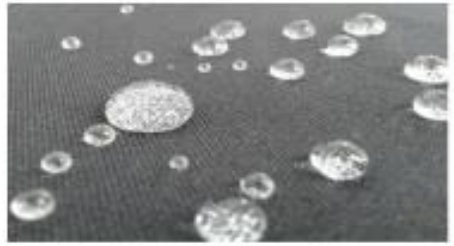
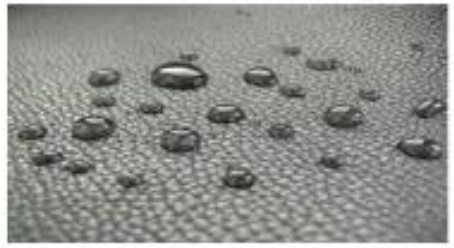
APPLICATION TESTING / GUIDE FORMULATIONS

Wash-in impregnation for outdoor or functional clothes		
Water, dem.	78.0	%
Glycolic acid	2.0	%
Surf. Free Microemulsion	20.0	%
	100.0	%



Paint or glass sealant		
Water, dem.	69.9	%
Isopropanol	20.0	%
Glycolic acid	0.1	%
Surf. Free Microemulsion	10.0	%
	100.0	%

Impregnation for leather, textile and soft-top		
Water, dem.	89.7	%
Glycolic acid	0.3	%
Surf. Free Microemulsion	10.0	%
	100.0	%



Impregnation for wood		
Water, dem.	77.7	%
Glycolic acid	0.3	%
Butylglycole	7.5	%
Ethanol	5.0	%
Surf. Free Microemulsion	10.0	%
	100.0	%

Impregnation for mineral surfaces		
Water, dem.	89.7	%
Glycolic acid	0.3	%
Surf. Free Microemulsion	10.0	%
	100.0	%

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