CHT
SMART CHEMISTRY WITH CHARACTER.

Emulsion Principles and Hydrophobic Additives in Architectural Paints

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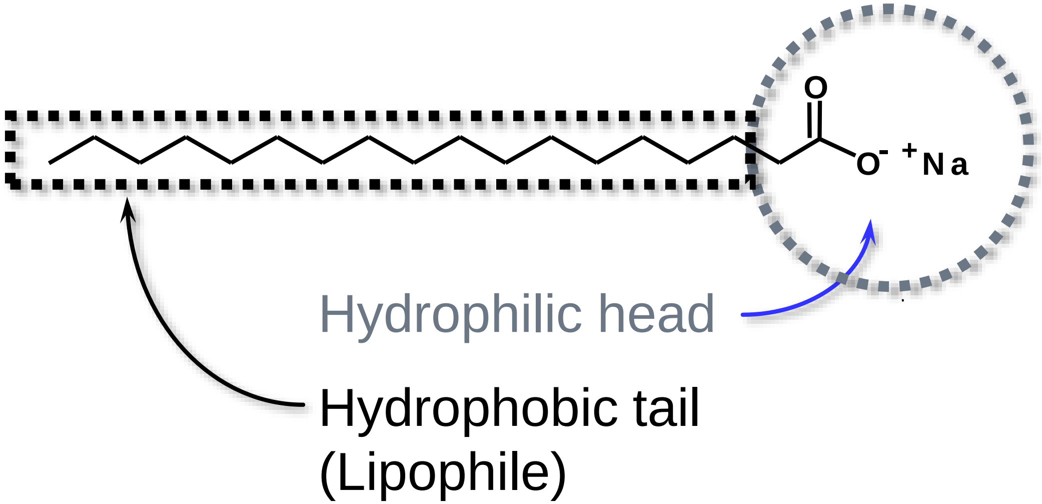
Emulsion Basics

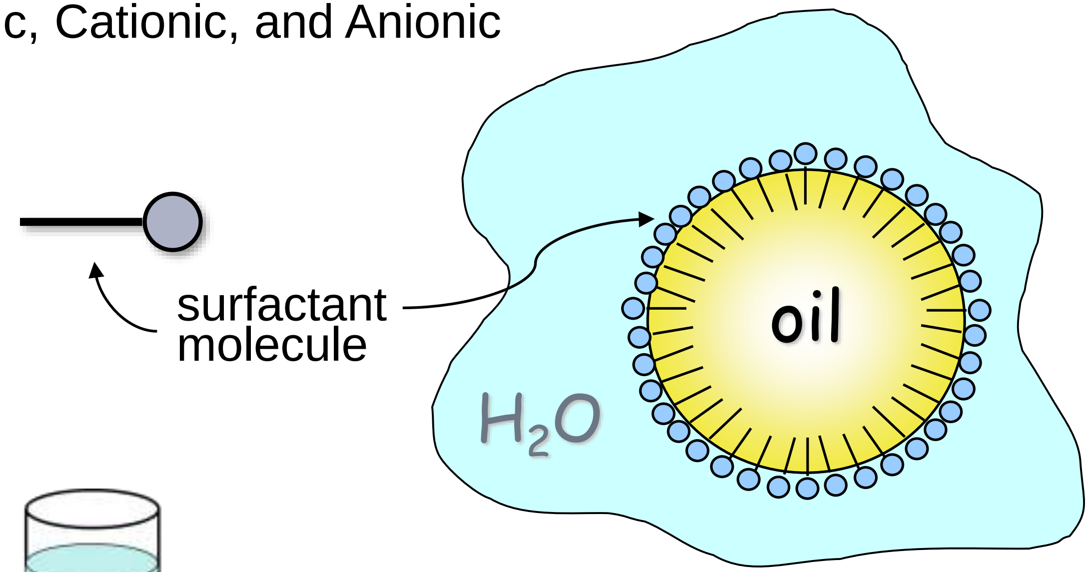
Emulsion: A dispersion of one immiscible liquid in another, usually stabilized by a **surf**ace **act**ive **agent.**

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

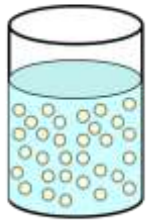
Surfactants are amphipathic compounds. Meaning they have and affinity for both water and oil:

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



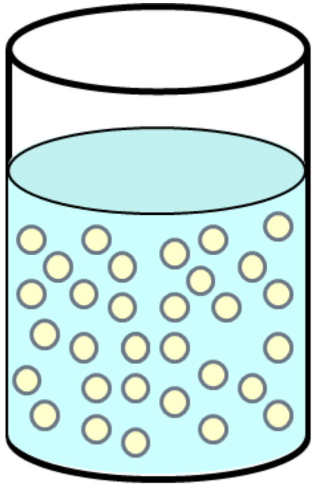


Oil-in-Water Emulsion (O/W)

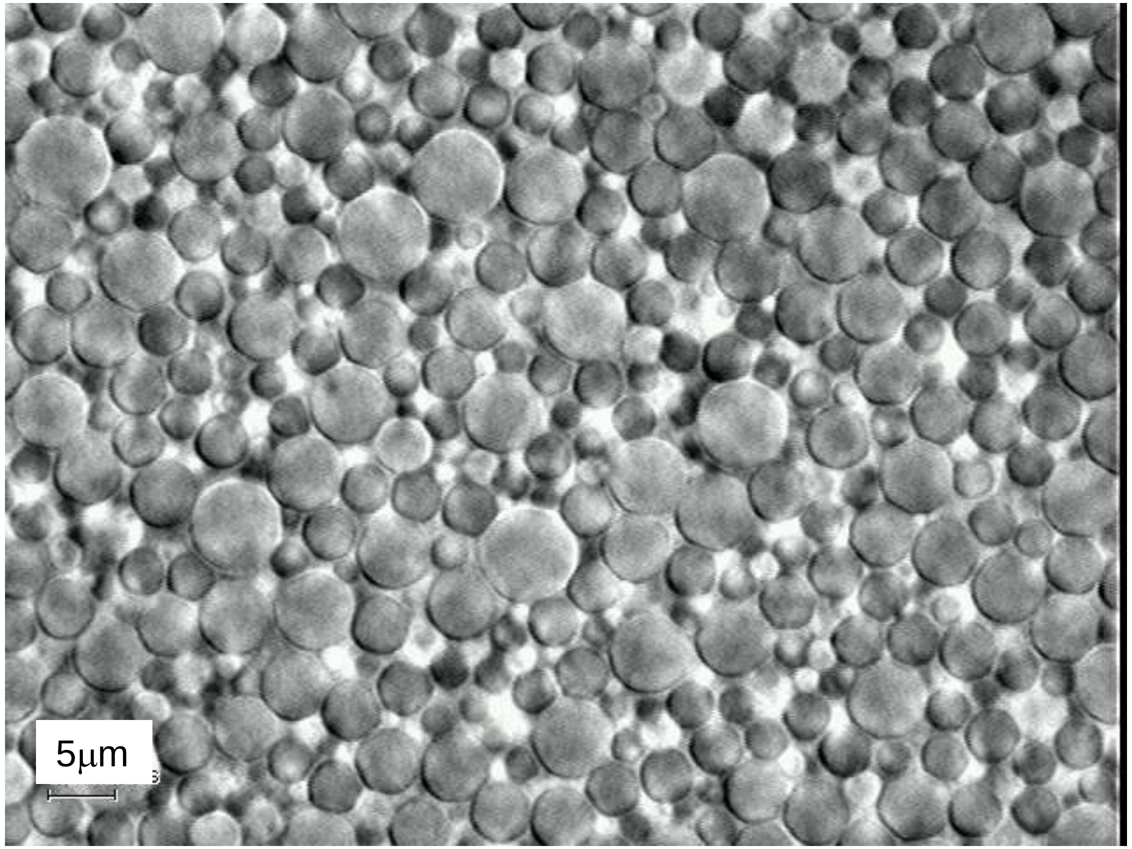


Oil in Water Emulsion (O/W)

Oil in Water Emulsion



Oil in Water Emulsion
(O/W)



Optical micrograph by Jennifer Stasser

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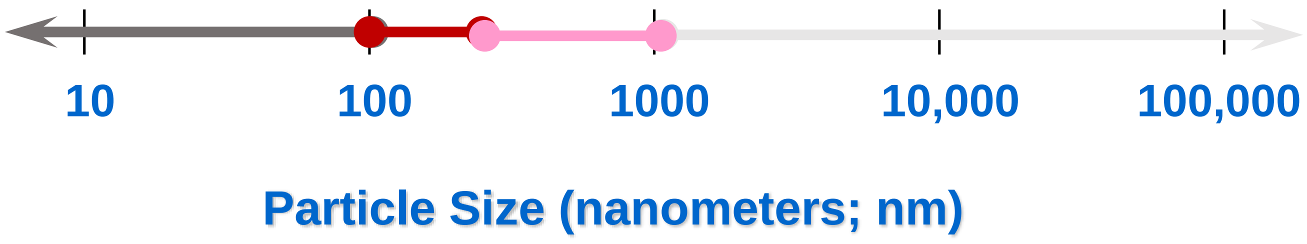
Emulsion Classification by Particle Size



- Microemulsions: <100 nm
- Fine Emulsion: 100 nm to 300 nm (*Most difficult to manufacture*)
- Coarse Emulsion: 300nm to 1000 nm
- Macro Emulsion: > 1000 nm

100 nm = 0.1 µm

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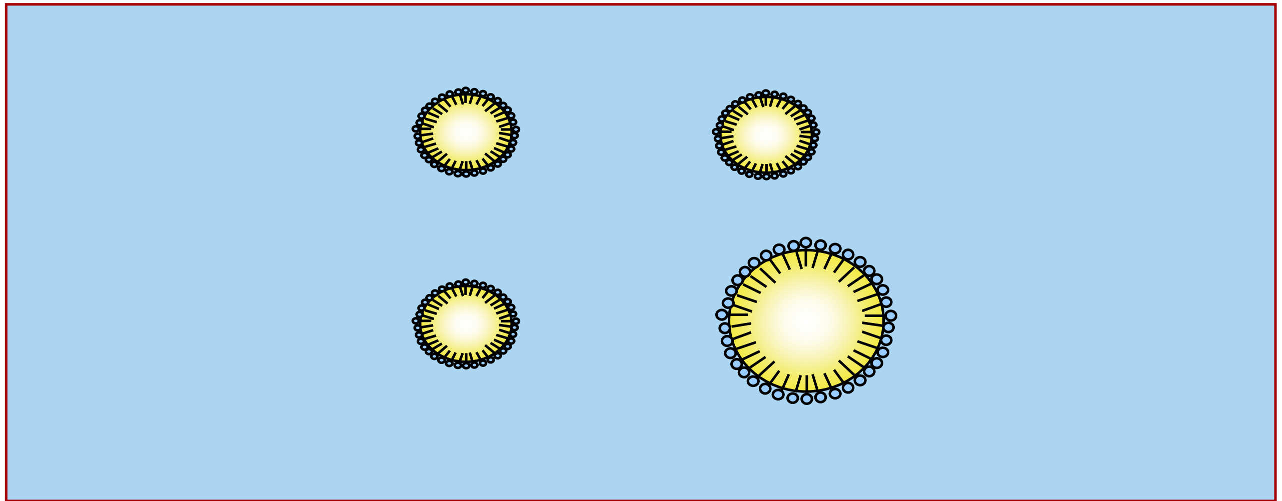
Particle Size Affects Emulsion Stability

- Emulsion particles are in constant motion thank to Brownian Motion! These particles carry energy and constantly collide with one another.
- Each particle has a barrier, in the form of surfactant (ionic stabilization and steric stabilization), to prevent particles from coalescing as they collide.
- Larger particles carry more energy (momentum) than smaller particles. If sufficient momentum is achieved, it can penetrate the particles “barrier” thus beginning the process of flocculation/coalescence.
- Don’t forget gravitational force also affects emulsions as the particles tend to segregate in emulsions this can be observed by creaming or settling.



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Particle Size Affects Optical Properties

Rayleigh Scattering

–intensity proportional to 1/(wavelength)^4

–sky is blue, since 1/400nm^4 > 1/700nm^4

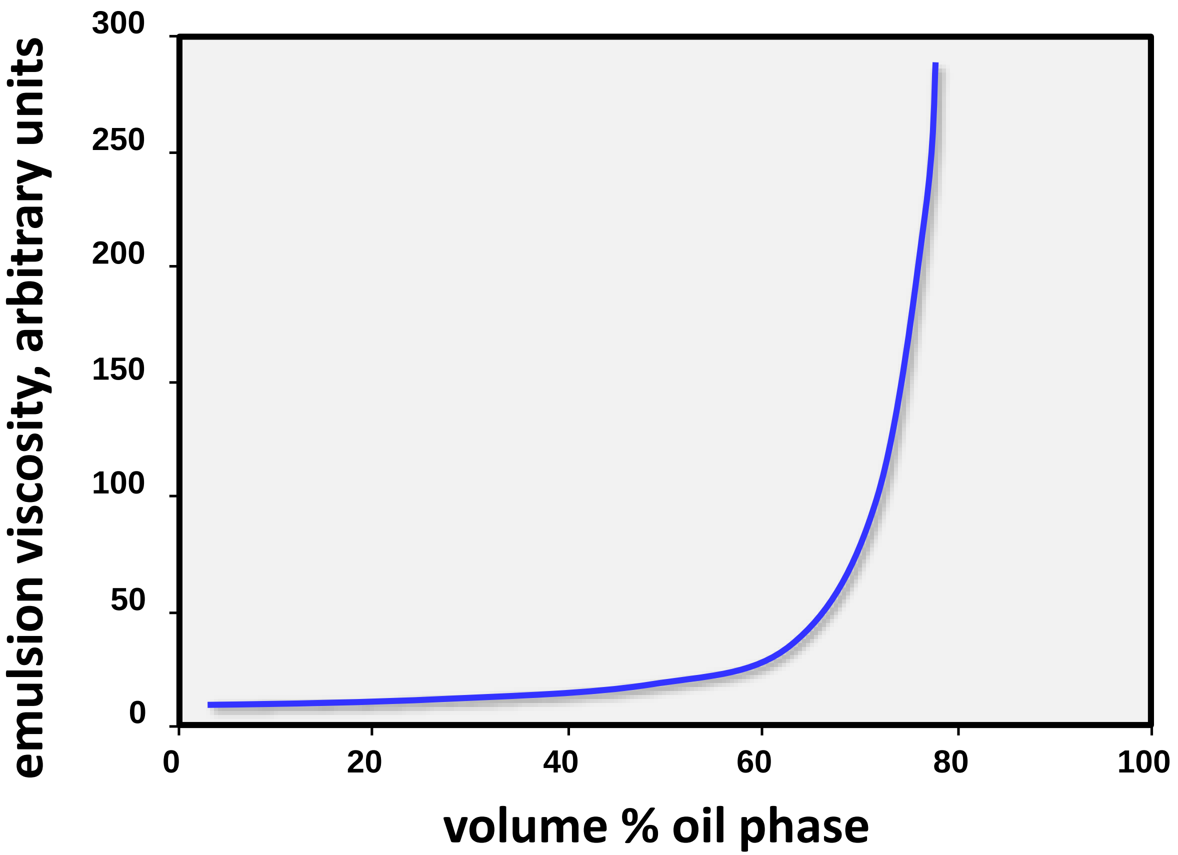
Emulsion Particle Size (mm)	**Appearance**
> ~50	gray
0.5-10	white
0.1-0.2	blue-white
0.05- 0.1	semitransparent
< 0.05	transparent

Particle Size Affects Rheology Profiles

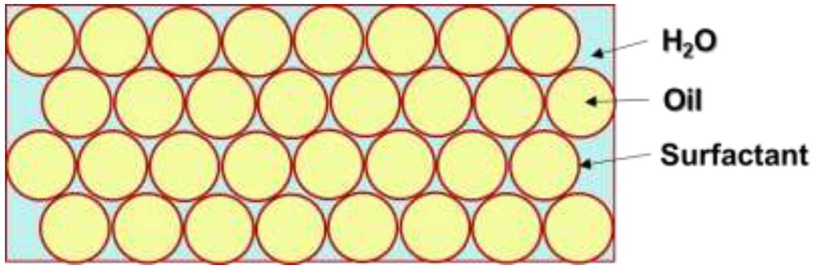
- Viscosity of dispersed phase has no influence of emulsion viscosity.
- Emulsion rheology depends upon how particles interact with each other.
- Higher solids content leads to higher viscosity emulsions. More particles are interacting with each other
- Smaller particle sizes lead to higher viscosity emulsions.
- Viscosity of emulsions does not change appreciably below 50% by volume.
- Not only does the particle size dictate the rheology profile, but the particle size distribution also plays a large role.

Rheological Properties of Emulsions

Viscosity of emulsions are governed by how particles interact with each other.
<u>Not</u> by viscosity of internal phase (oil)



Maximum volume for close packed spheres is ~74%…



Below ~50% volume, viscosity of emulsions. do not change appreciably.

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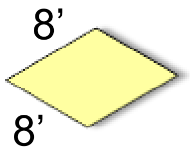
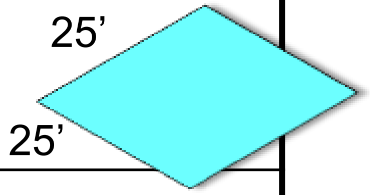
Relationship of Sizes in Emulsions

2g of a 50% solids emulsion w/oil density of 1 has the following:

$V = 4/3\pi r^3$

$A = 4\pi r^2$

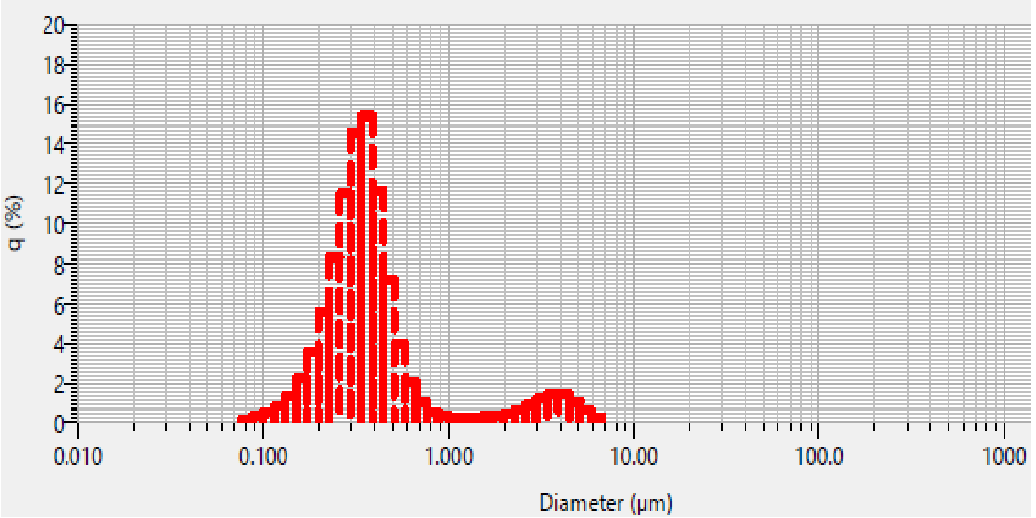
$\rho = 1\ g/cm^3$

Particle Diameter	# of Particles	Total Surface Area
1000 μm (1mm)	1.91×10^3 (~2 thousand)	$0.003 m^2/g$ ($3 mm^2/g$)
100 μm (0.1mm)	1.91×10^6 (~2 million)	$0.06 m^2/g$ ($60 cm^2/g$)
1 μm (.001mm)	1.91×10^{12} (~2 trillion)	$6 m^2/g$ 
0.1 μm (100nm)	1.91×10^{15} (~2 quadrillion)	$60 m^2/g$ 
0.01μm (10nm)	1.91×10^{18} (~2 quintillion)	$600 m^2/g$

Significance of Particle Size Distribution

<u>Bimodal Emulsion Example:</u>

	1 μm	3 μm
Percent droplets	97	3
Percent Surface Area	78	22
Percent Total Volume	54.5	45.5



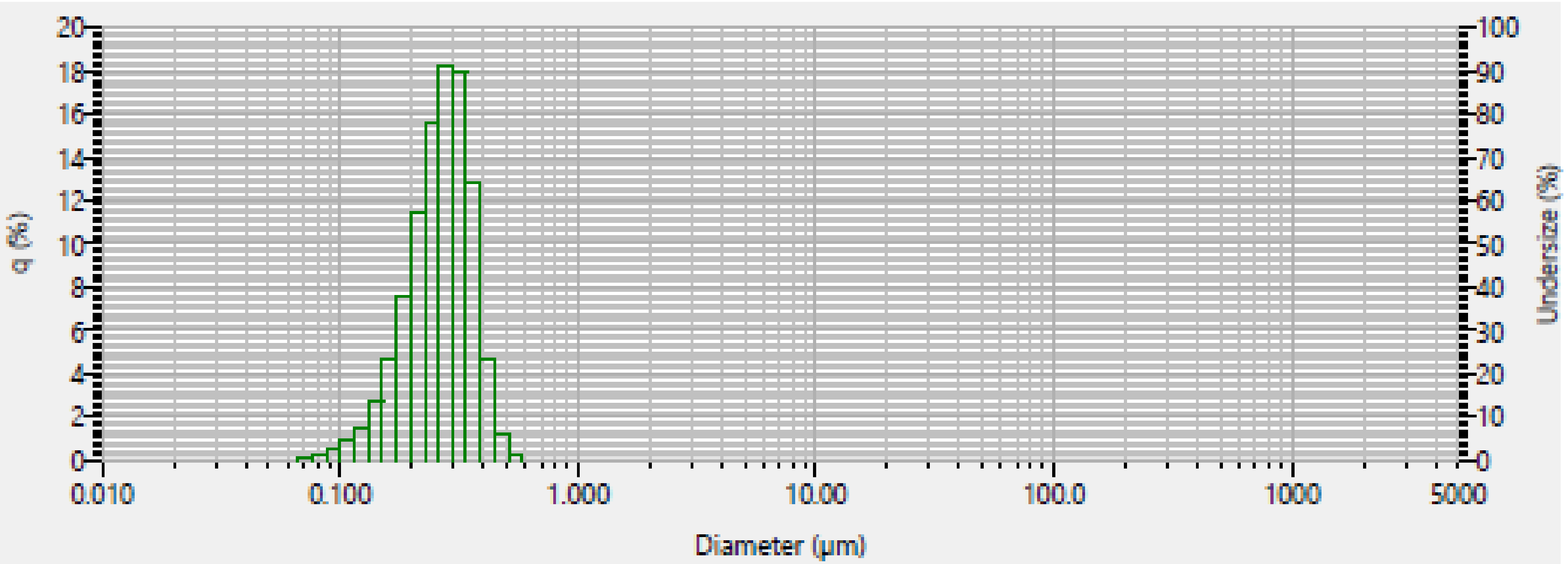
HORIBA Laser Scattering Particle Size Distribution Analyzer LA-960

Sample name : I-EM-100-55
ID# : 202302080612193
Data name : BPM2
Transmittance (R) : 97.2 (%)
Transmittance (B) : 85.4 (%)
Circulation speed : 5
Agitation speed : 3
Ultrasound : Off
Iteration mode : Auto
Distribution base : Volume
Refractive index (R) : Silane
[Silane(1.410 - 0.000i),water(1.333)]
Refractive index (B) : Silane
[Silane(1.410 - 0.000i),water(1.333)]
Material :
Source :

Test or assay number
Median size : 0.26838 (µm)
Mean size : 0.27023 (µm)
St. Dev. : 0.0778 (µm)
Geo. mean size : 0.2582 (µm)
Geo. St. Dev. : 1.3670 (µm)
Mode size : 0.2791 (µm)
Span : 0.7540
Diameter on cumulative % : (2)10.00 (%)- 0.1703 (µm)
: (5)50.00 (%)- 0.2684 (µm)
: (9)90.00 (%)- 0.3726 (µm)
: (10)99.00 (%)- 0.4652 (µm)

nt

ns.



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Controlling Emulsion Stability

Emulsions are thermodynamically unstable. They will eventually separate.

Factors which influence emulsion stability

- Type and level of emulsifier/surfactant/dispersant
- Particle size and distribution
- External destabilizing conditions (shear, freeze/thaw, temp.)
- Density difference and interfacial tension between the two phases
- Viscosity of external phase

Stokes' Law (Rate of Sedimentation)

$$v = \frac{2a^2 (p_2 - p_1)\, g}{9\,\eta}$$

v	=	rate of settling
a	=	particle radius
η	=	viscosity of medium (external phase)
p_1, p_2	=	densities of medium(external) & particle (internal)
g	=	gravitational constant

Viscosity and rheology profiles of the media can be adjusted by using thickeners

How Various Types of Emulsions are Made

High Shear Processing aka “Mechanical Emulsions”

Mix oil, H_2O, surfactant; subject mixture to high shear.

Mechanical emulsions is a broad term which captures various methods of high shear processing….. More to come!!

Emulsion Polymerization (EP):

Subject polymerizable monomer, H_2O, & surfactant to high shear; carry out polymerization of monomer. Useful with hydrophobic polymerizable monomers.

Think of each particle in this emulsion of being a micro-reactor

Microemulsion:

Emulsions < 100nm; spontaneously formed emulsions. Don’t require shear forces.

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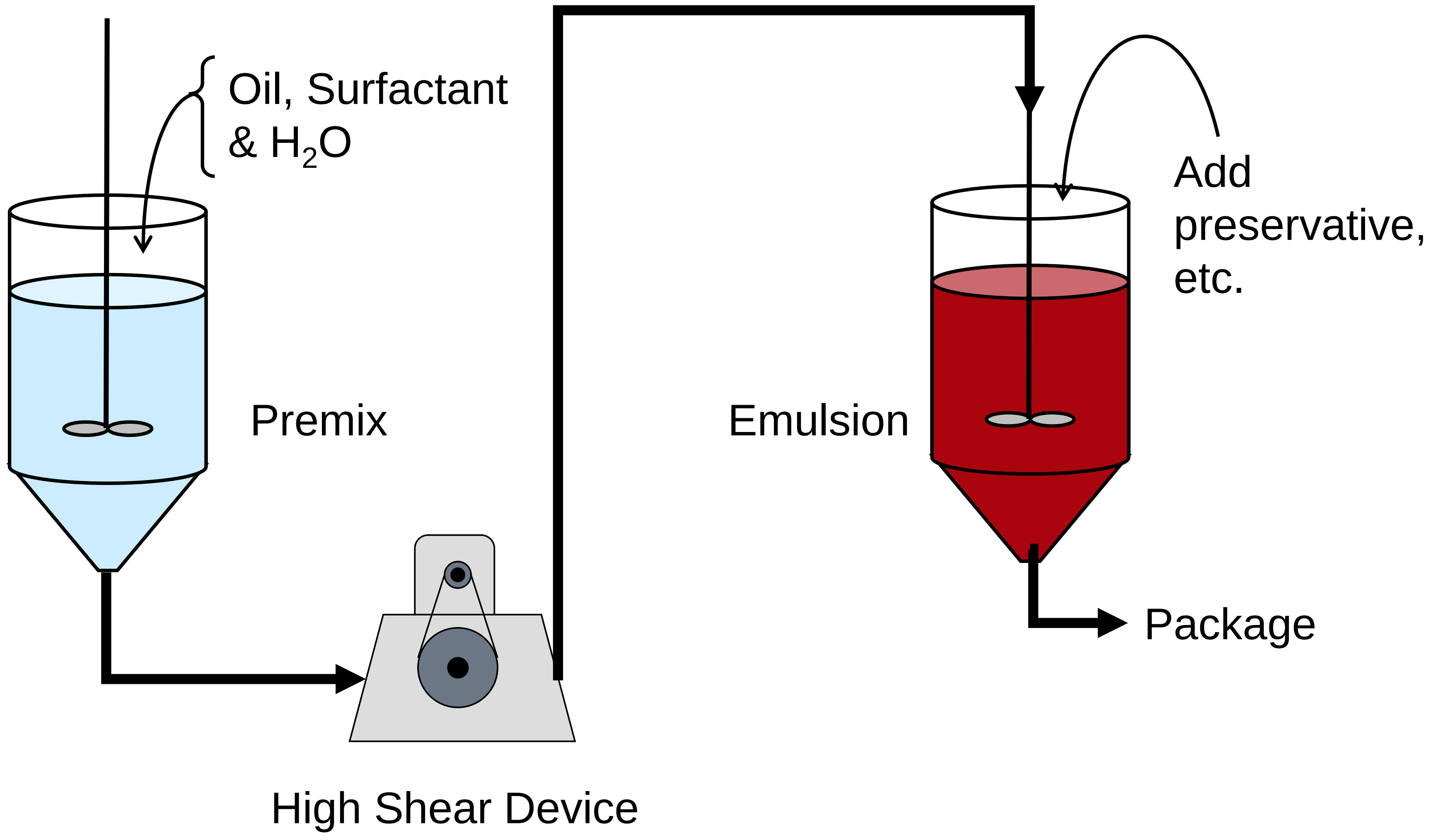
Basic High Shear Mechanical Emulsification Process Example



Colloid Mill, Homogenizer, Sonolator®, Homogenizer, Rotor Stator, Change Can(Cowles Blade)

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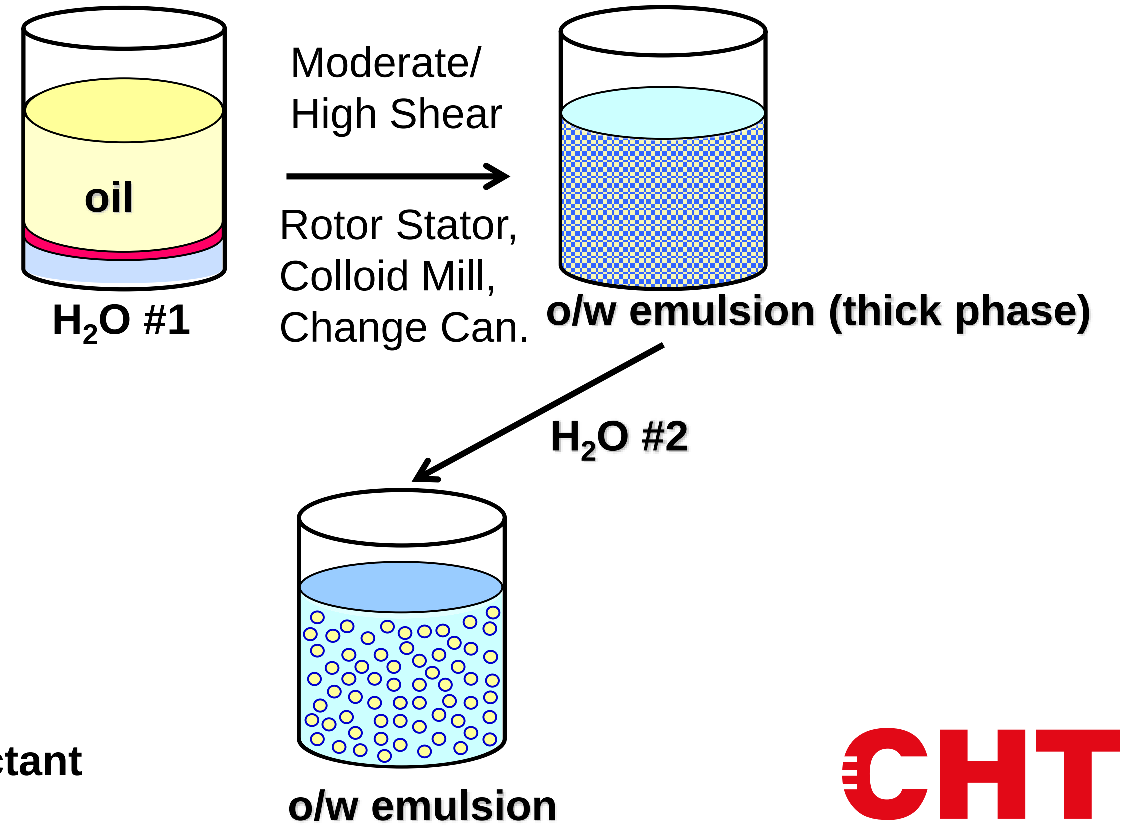
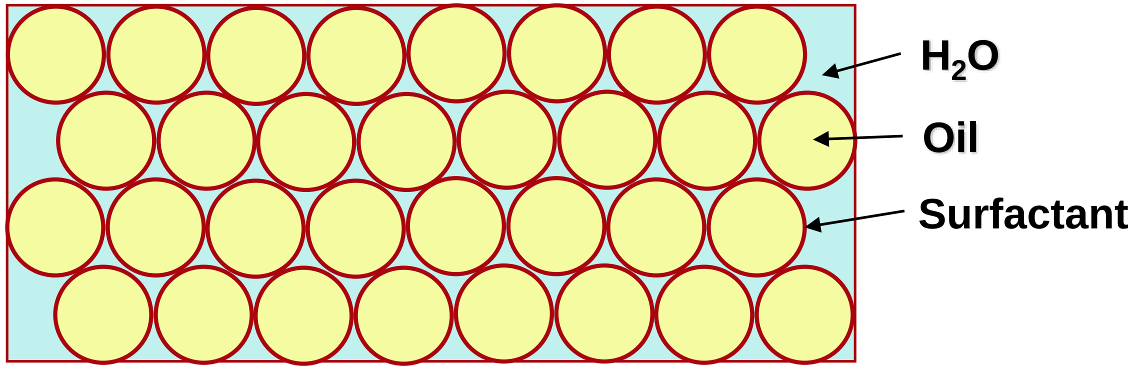
cal Emulsions

Phase Inversion Method





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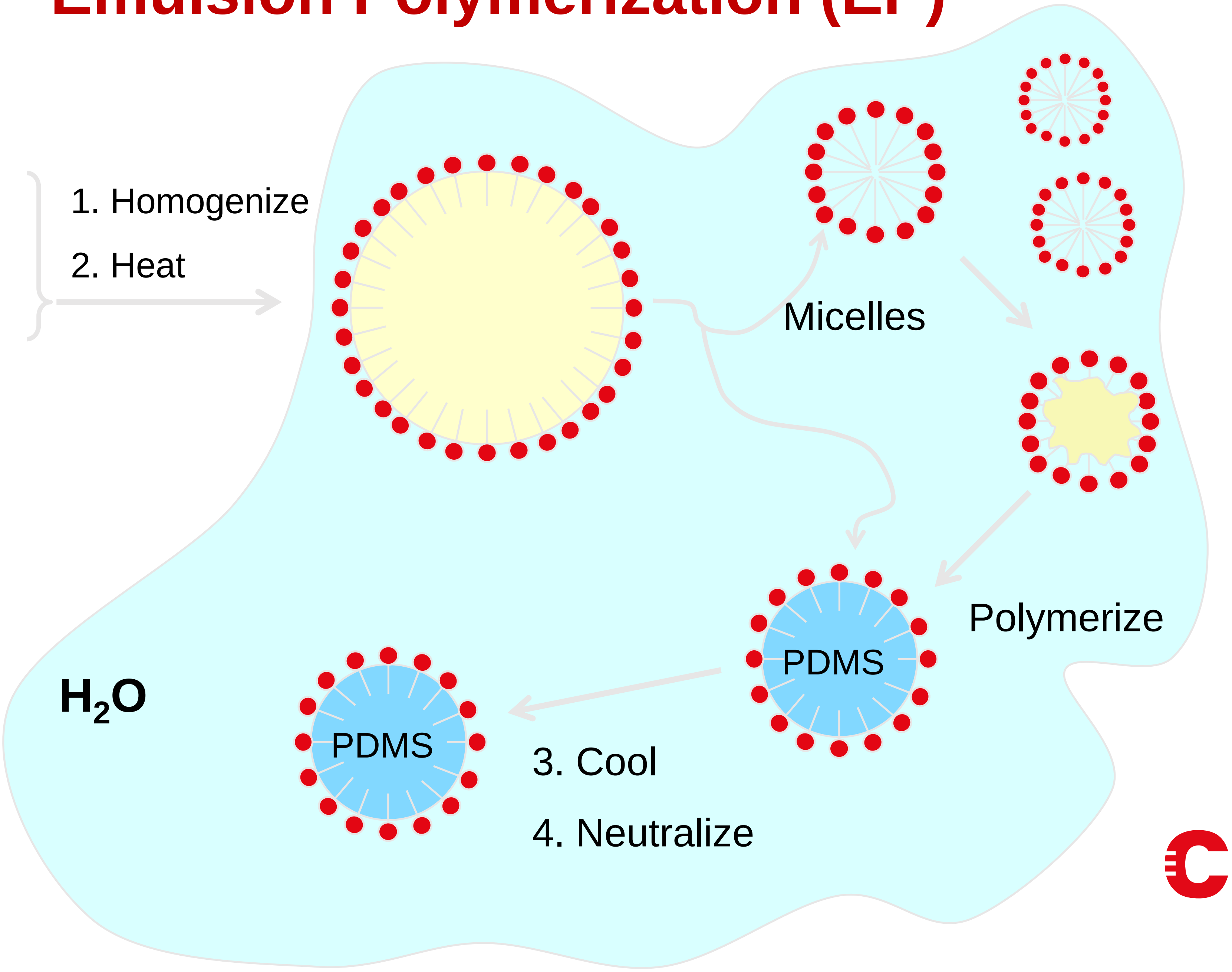
Emulsion Polymerization (EP)

Siloxane Monomer
+ H_2O +Surfactant

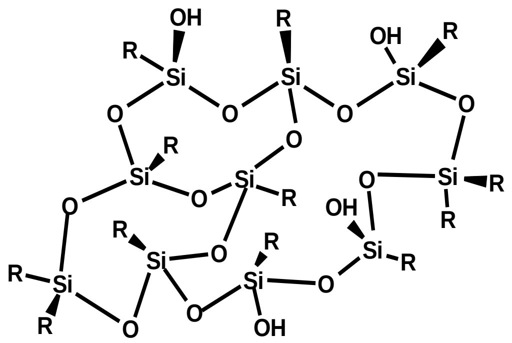
Can be anionic or cationic surfactant

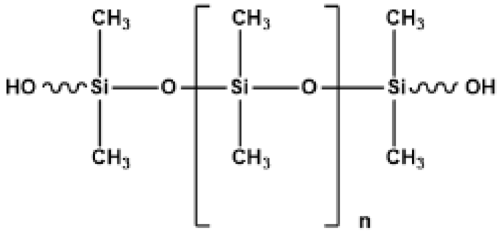


Silicone Additives in H_2O-Based Coatings

Silicone additives are used in H_2O-based coatings primarily to:

• Improve adhesion	Silanes
• Improve wetting	Silicone Polyethers(silicone surfactants)
• Improve flow & leveling	Silicone Polyethers(silicone surfactants)
• Control foam	Silicone Antifoam Compounds
• Obtain slip, abrasion, & mar resistance	Silicone Polymers (fluid, resin,, etc)
• Obtain waterproofing	Silicone Polymers (fluid, resin,, etc)
• Effect crosslinking	Silanes and Reactive Silicone Polymers





Silicones are generally not used for dirt pickup resistance, however they can help improve stain resistance

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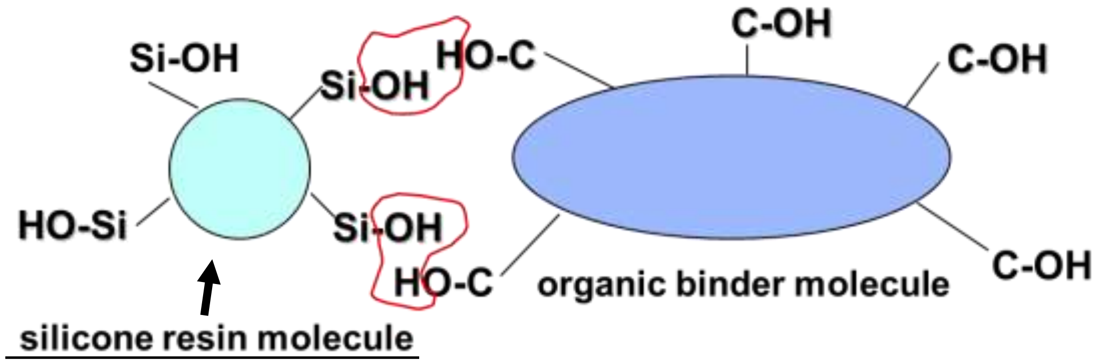
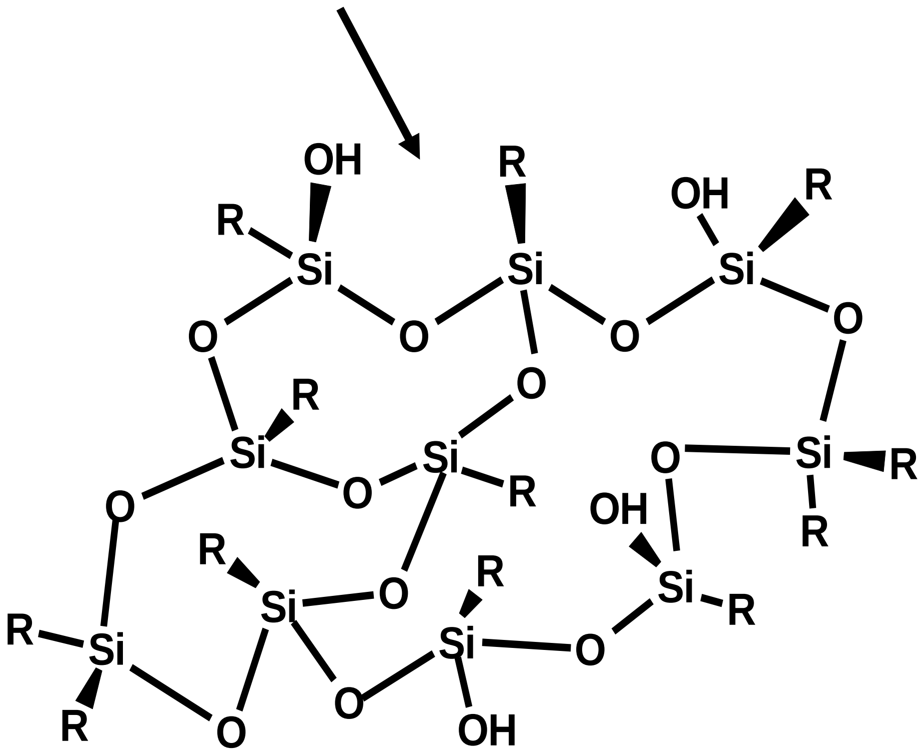
Silicone Resins in H_2O-Based Coatings





- $RSiO_{3/2}$
- R: Me, Ph, n-Pr
- OH can be substituted with reactive groups such as OMe to produce more reactive resins.

Silicone resins are added to coatings primarily for improved weatherability, hydrophobicity, and increased breathability.

Silicone resins are extremely stable to the effects of weather, their presence prolongs the life of coating binders.

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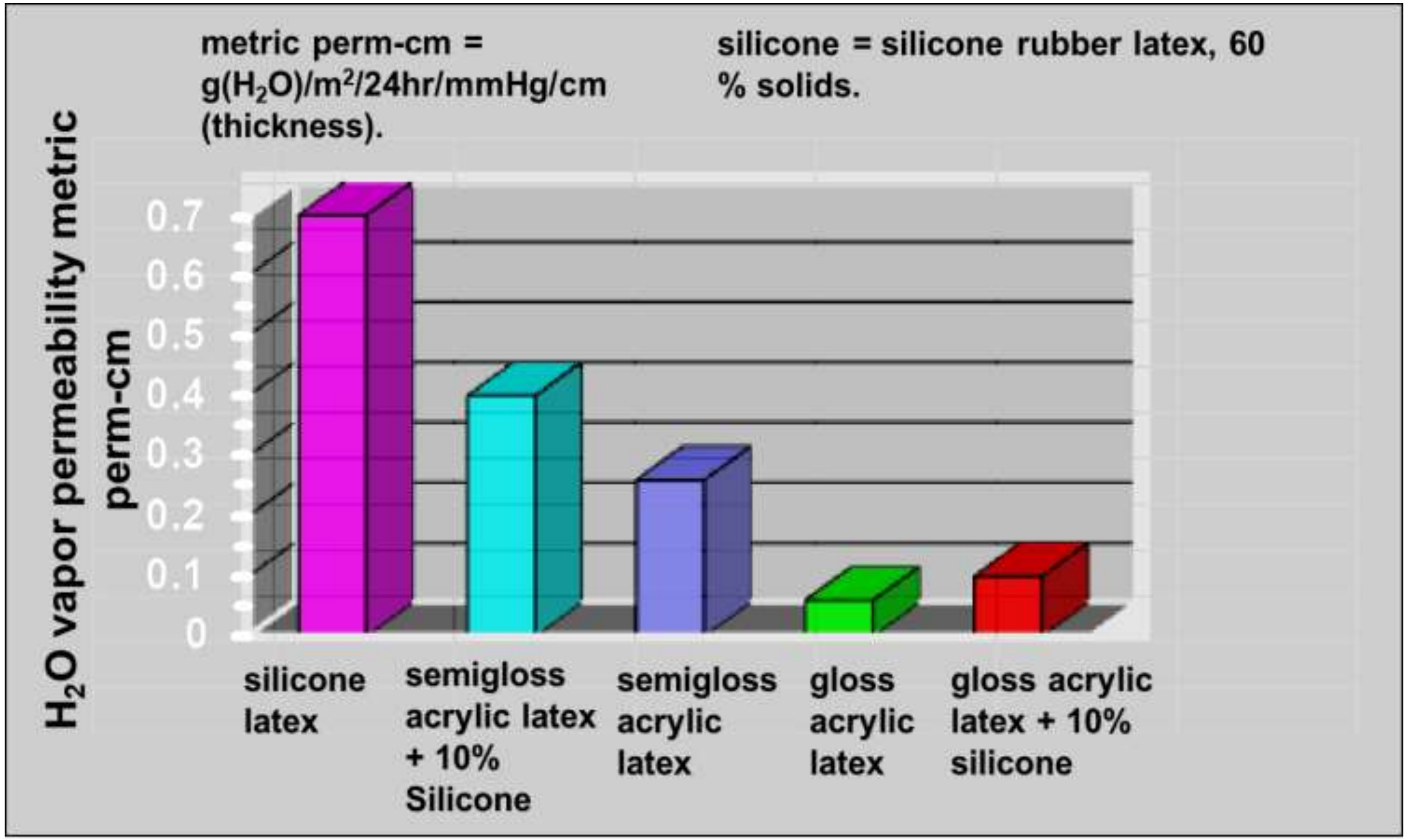
Silicones in Exterior Architectural Coatings



In exterior facade coatings, it is desirable to have both low resistance to H_2O vapor diffusion and low liquid H_2O permeability.

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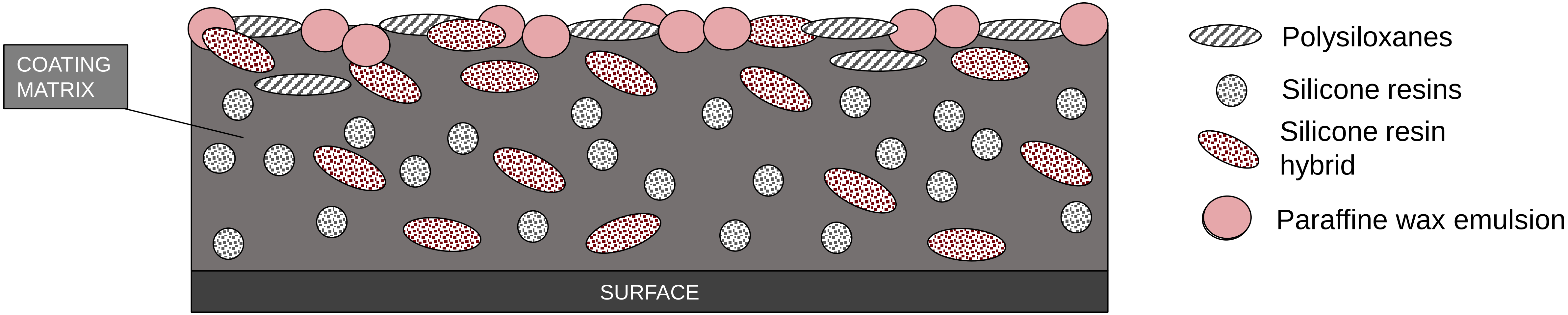
Hydrophobic Additive Visual in Coating Matrix



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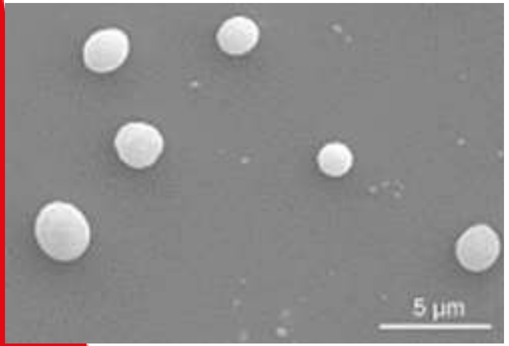
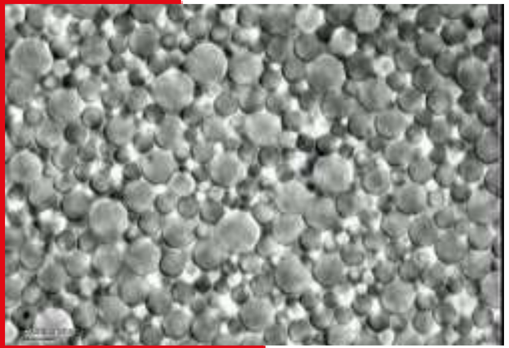


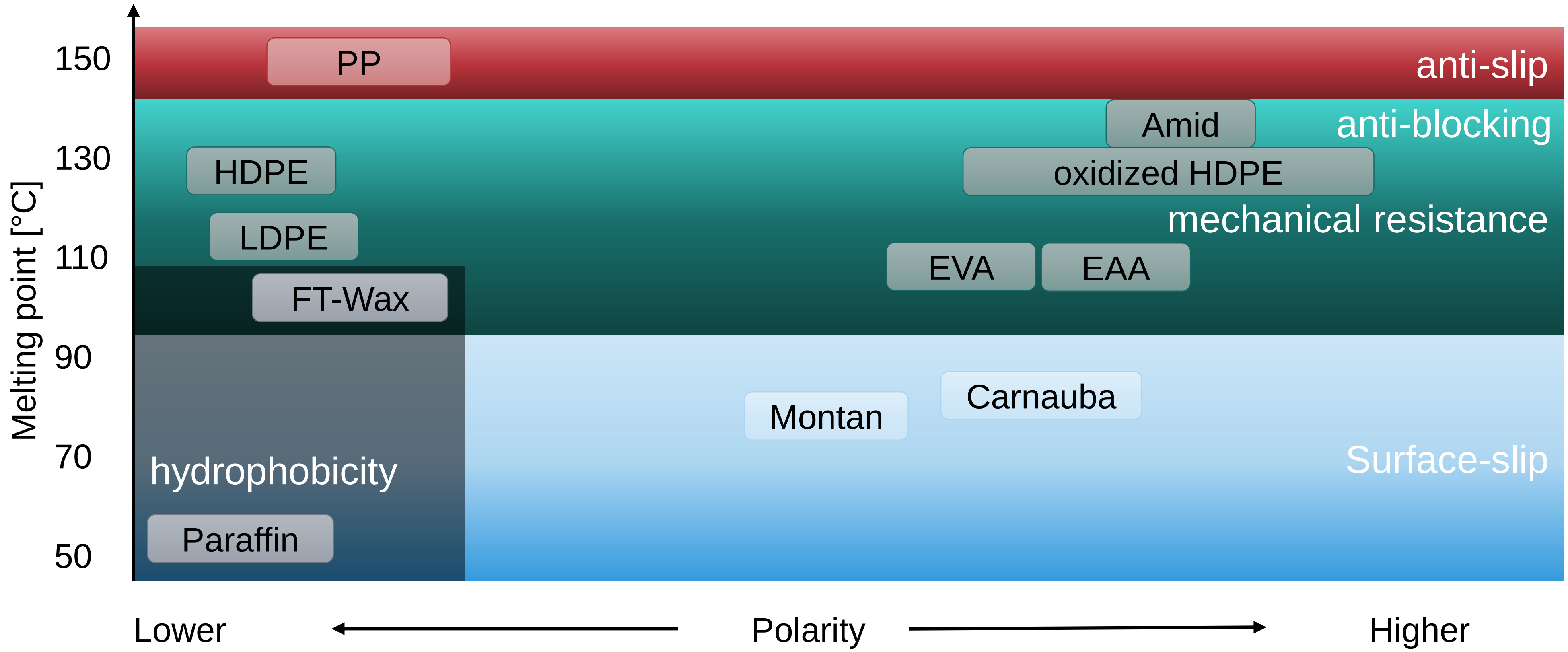


EMULSION VS DISPERSION

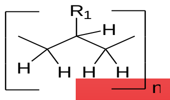
Emulsion - Homogenous mixture of a **liquid** finely dispersed in another liquid which are not soluble in one another

Dispersion - A system were fine, water insoluble **particles** are mixed in a liquid

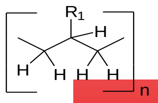
WAX CHARACTERISTICS



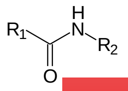
WAX PROPERTIES



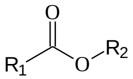
HDPE
- Abrasion resistance
- Antiblocking
- Slip



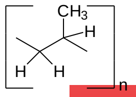
Paraffine
- hydrophoby
- Antiblocking
- Slip



Amid
- Antiblocking
- Slip
- Soft touch



Carnauba Montan
- Scratch resistance
- polishable



PP
- Antislip

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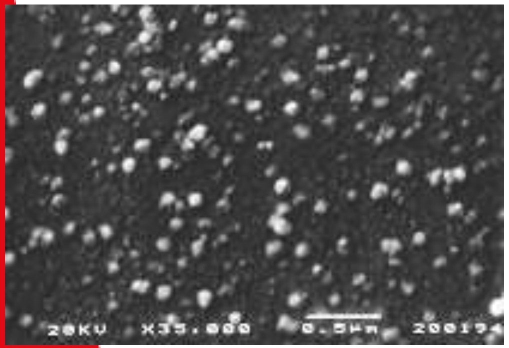
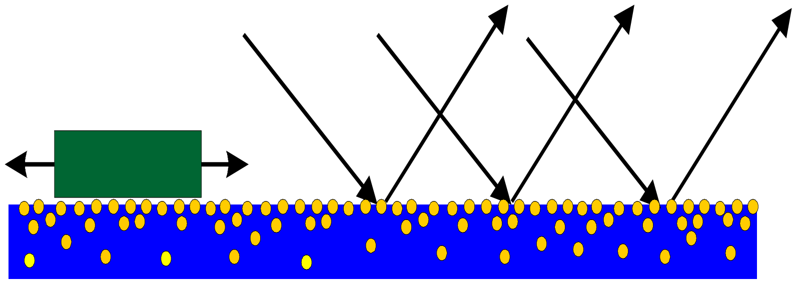
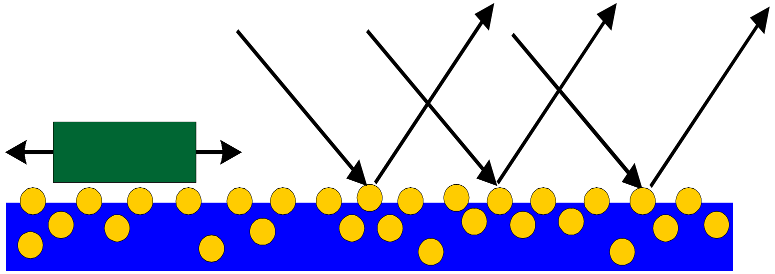
PARTICLE SIZE AND SHAPE

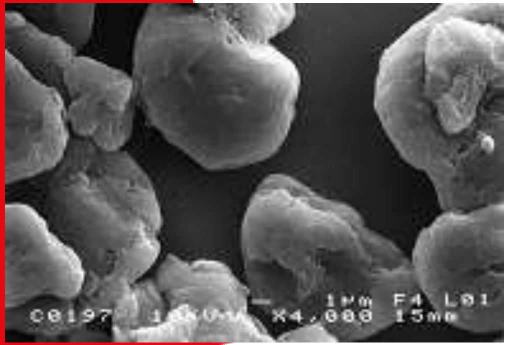


- Wax Emulsion
  - Ø 35nm
  - High gloss
  - Mechanical resistance

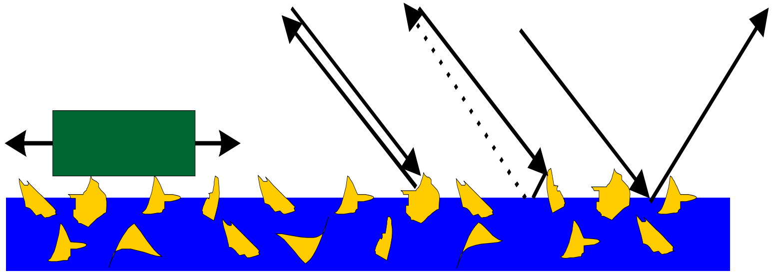


- Wax-microdisperion
  - Ø 0,2 – 2µm
  - Gloss
  - Very good mechanical resistance





- Wax-dispersion
  - Ø <15µm
  - Matting effect
  - Best mechanical resistance



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Paraffin Wax in Hydrophobic Architectural Paint

Silicones are notorious for their ability to pick up dirt, however when used with paraffin wax additives, superior dirt pickup resistance can be achieved.

PAINT
WITH TEST DIRT

Standard | + 1% VARIPHOB Paraffine Wax

PAINT
AFTER WATER APPLICATION

Standard | + 1% VARIPHOB Paraffine Wax

PAINT
AFTER RINSING

Standard | + 1% VARIPHOB Paraffine Wax

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Hydrophobic Additives

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