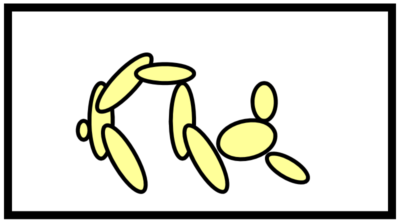
Dispersing Powders in Liquid

Mark Bumiller
mark.bumiller@horiba.com

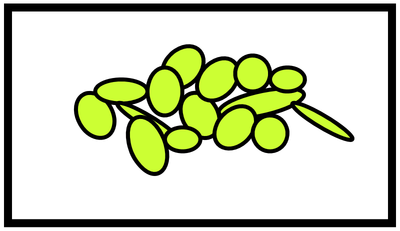
Definitions

- Typical powder: individual particles and “clumps” stuck together by weak or strong forces

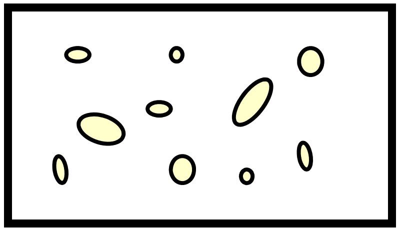
- Agglomerates: assemblage of particles which are loosely coherent



- Aggregates: assemblage of particles rigidly joined together



- Well dispersed: individual particle state



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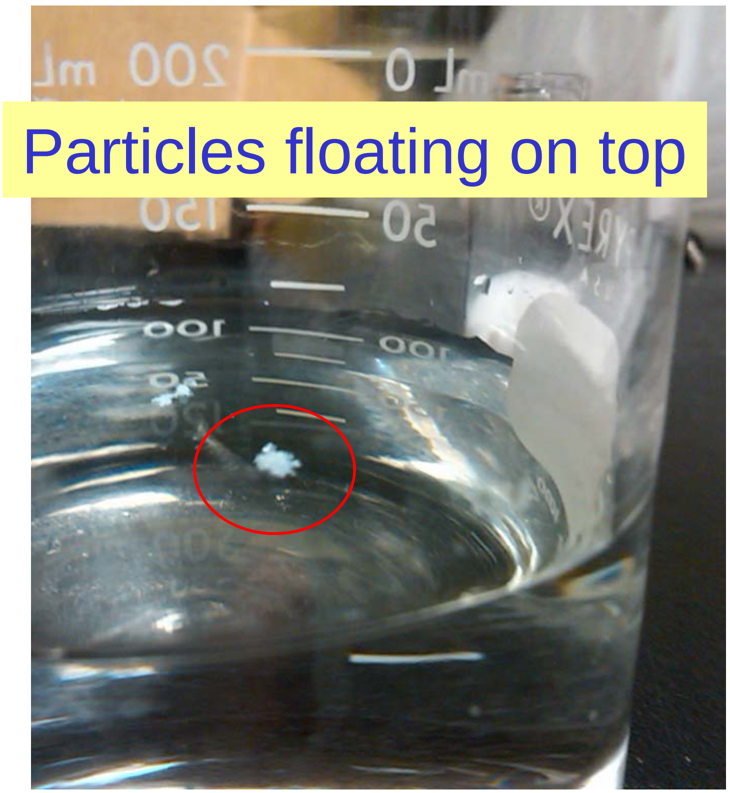
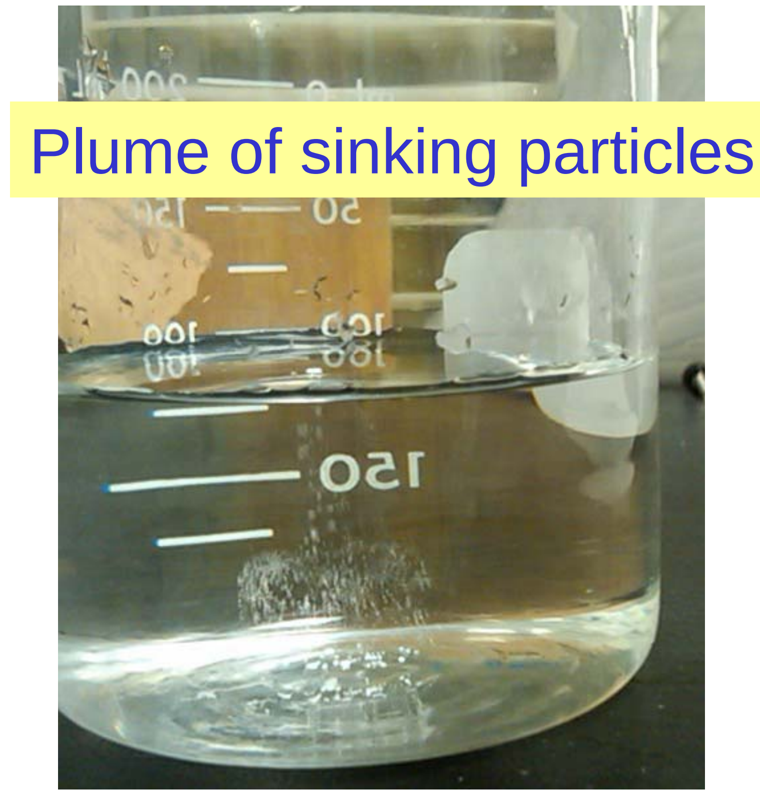
Dispersion Strategies

- Powders
  - When measuring powder as suspension
  - Choose solvent (avoid dissolution)
  - Wet powder (surfactant)
  - Dispersing aid to avoid re-agglomeration
  - Energy to break agglomerates into primary particles
    - Pump & stirrer or ultrasound

Check for Wetting

- Sprinkle particles on of target dispersant. If the particles float on top and do not penetrate the water surface, they are not wetted. This is usually a bad sign.
- If the particles break through surface and sink, they are a) wetted or b) so big that gravity is more important than surface tension. If it is case a, you are in luck.





Particle Wetting

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Measurement of Contact Angle (θ)

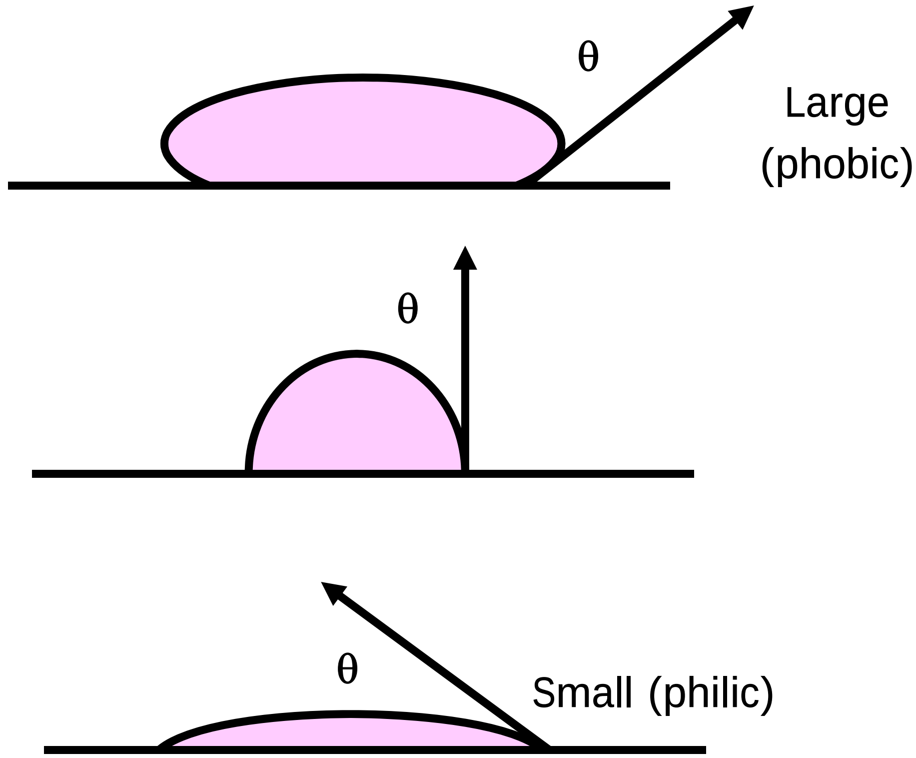
The contact angle is a measure of how well the liquid drop adheres to the surface of a solid

Large angles indicate poor wetting ability.

Small angles indicate good wetting ability.

Surfactants reduce surface tension and thereby are conducive to good wetting.

(Instruments are available for measuring contact angle)



Drop of a liquid on a solid

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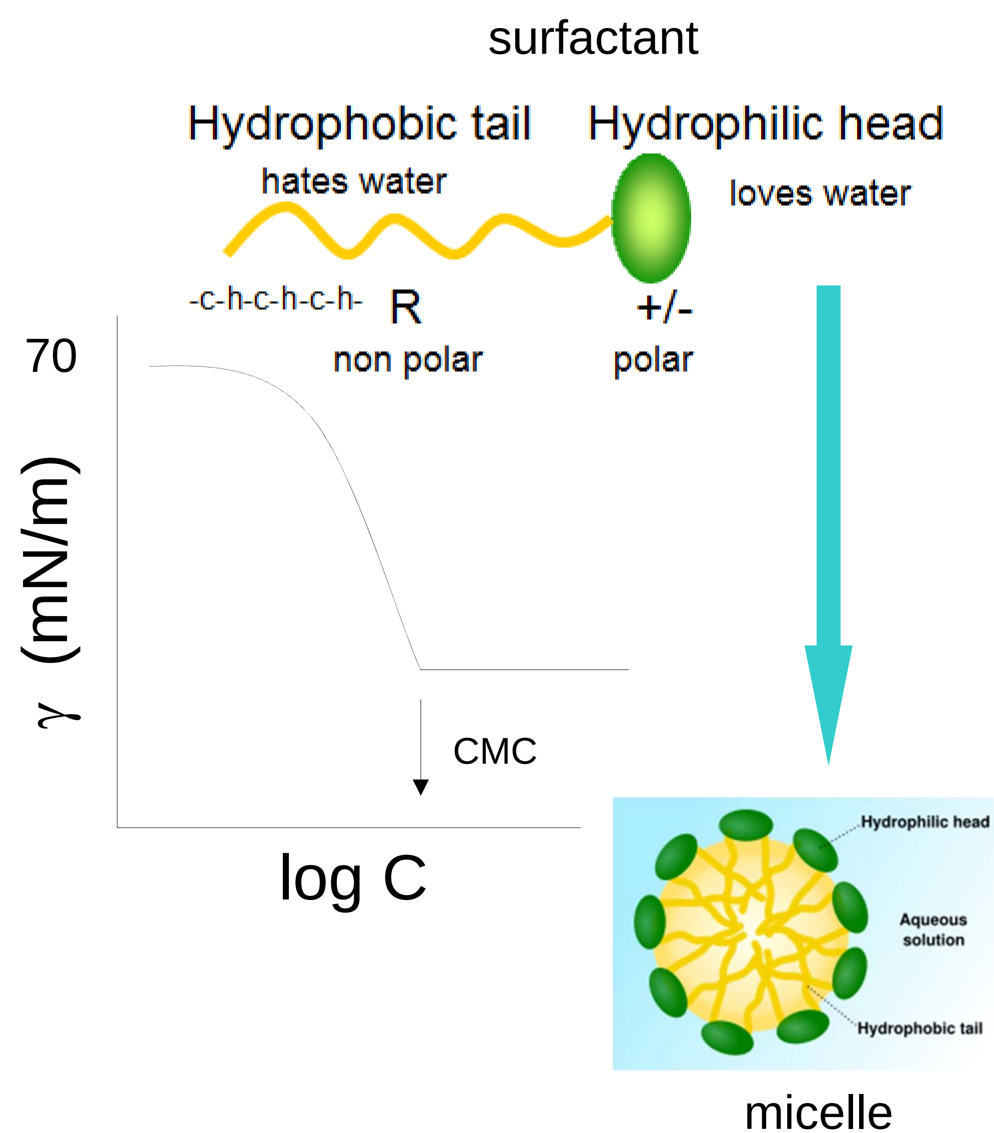
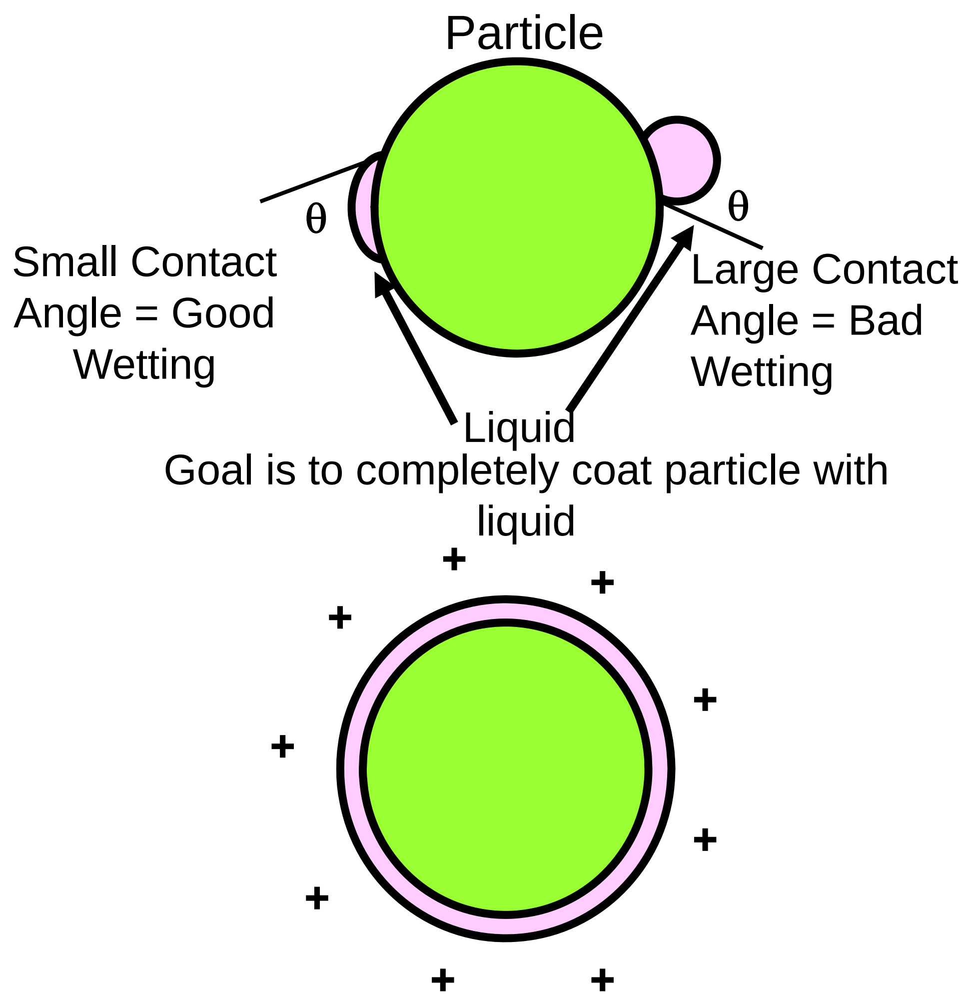
Surfactant Reduces Surface Tension

- Non-polar surfaces (hydrophobic) have low surface energy, need surfactant in aqueous phase to aid wetting
- Surfactant lowers surface tension from ~70 to 30 mN/m
- Slight decrease, linear decrease, then becomes constant at CMC



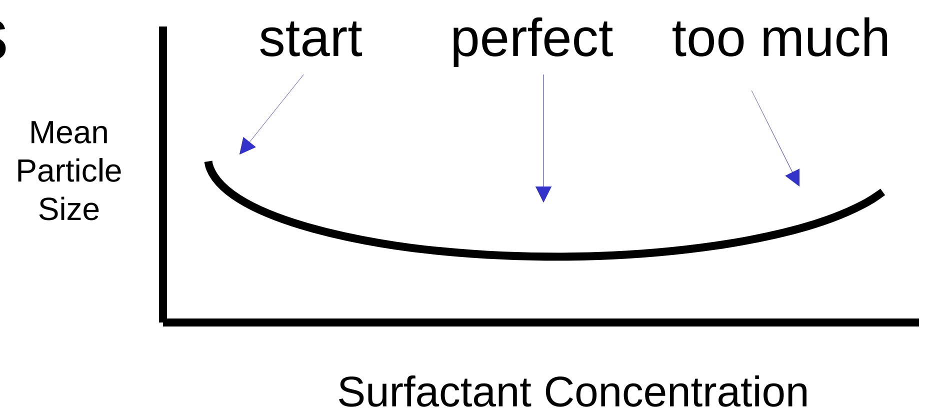
Particle Wetting

Surface tension must be lowered so liquid will adhere to particles.



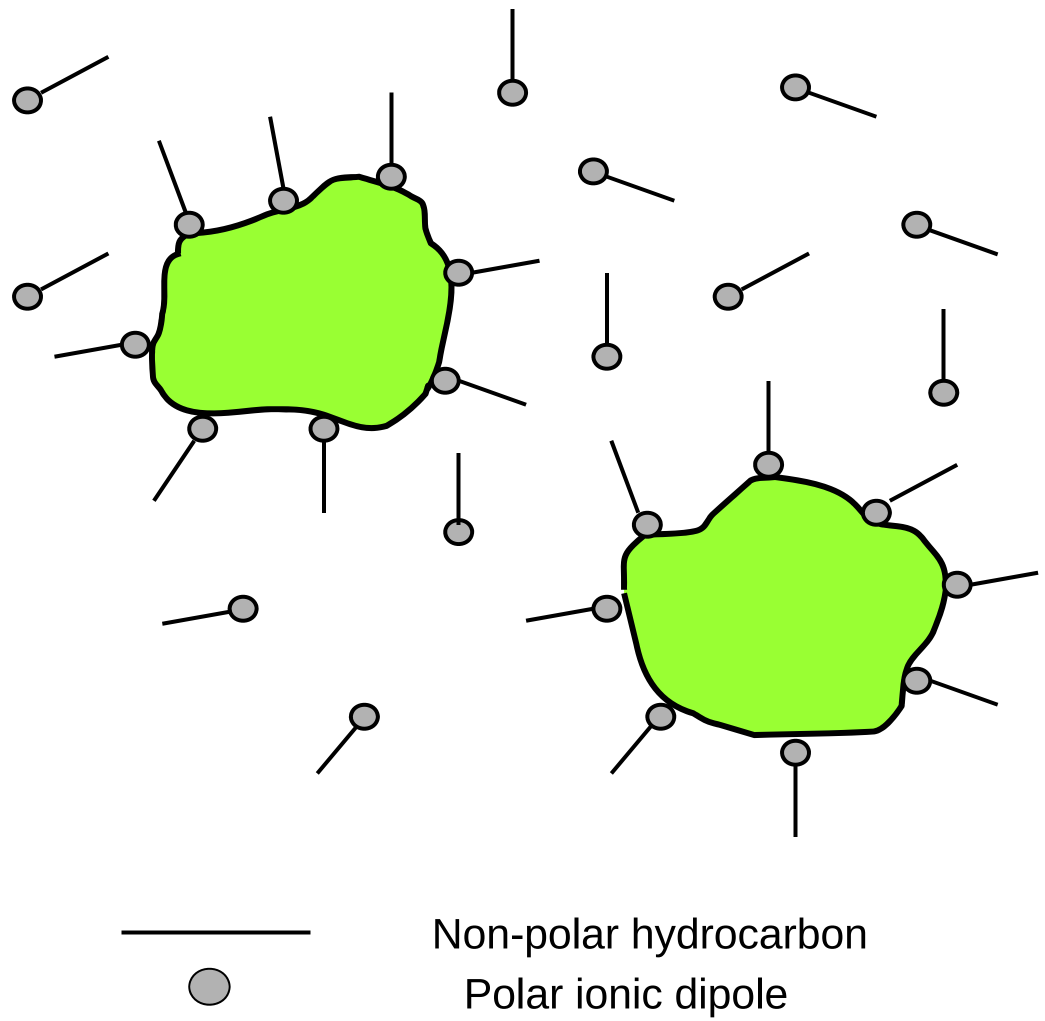
Effect of Surfactant Addition

- Surfactant addition will disperse particles for good measurement
- Particle size first decreases
- Reaches minimum @ proper concentration
- Add too much: particle size increases - agglomeration
- Common concentration: 0.01-0.1%

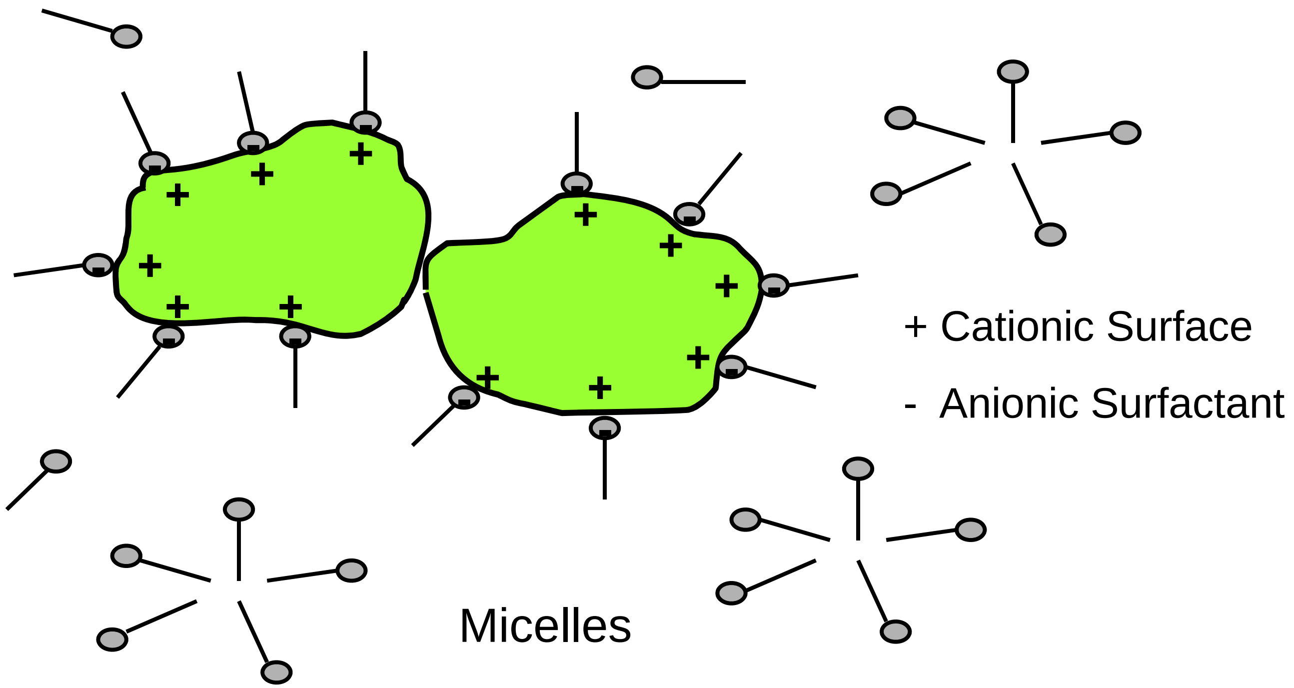


Surfactant Mechanism

Equilibrium established between surfactant on particles and surfactant in solution



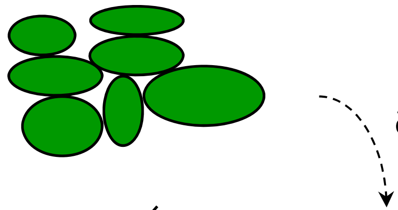
Critical Micelle Concentration



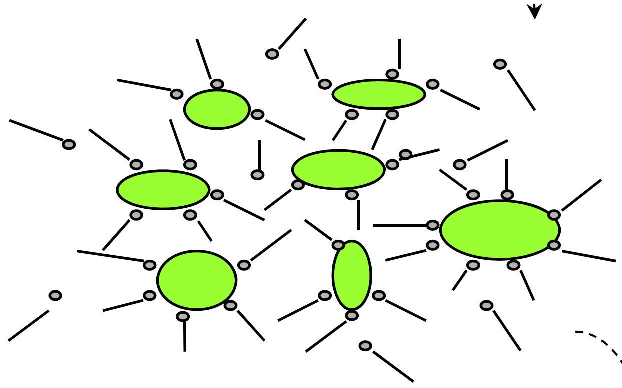
As more surfactant is added, equilibrium shifts. Surfactant leaves surfaces to start formation of micelles. This is called the Critical Micelle Concentration (CMC).

Particle surfaces are no longer repulsed, and energy of the system favors reagglomeration

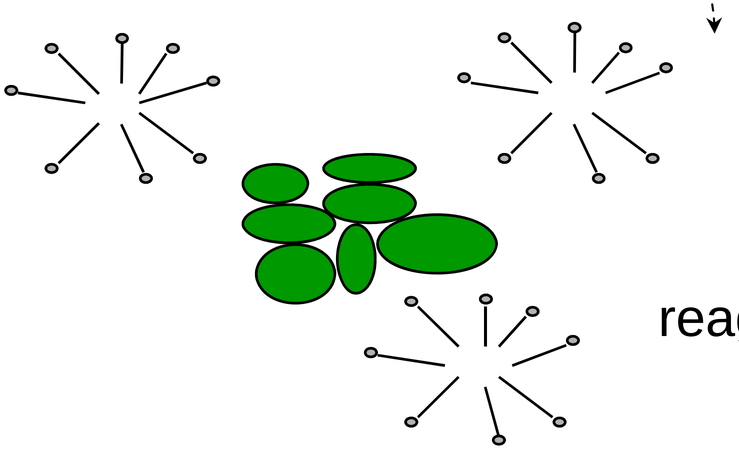
Effect of Surfactant Addition



No surfactant - agglomerated particles



Optimum concentration – proper particle dispersion



Excess surfactant- reagglomeration of particles

Types of Surfactants

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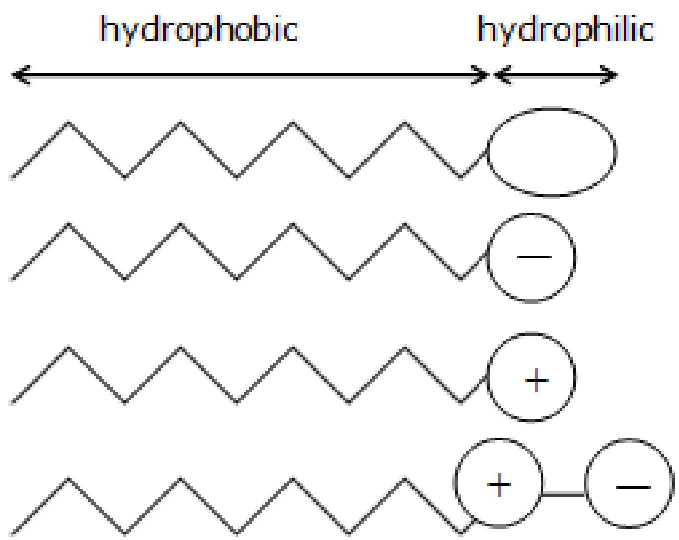
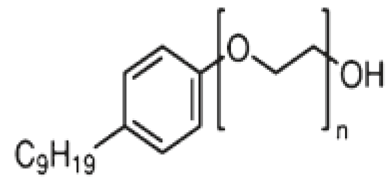
- H-C chain is hydrophobic
- Polar head is hydrophilic

- Nonionic
- Anionic
- Cationic
- Zwitterionic

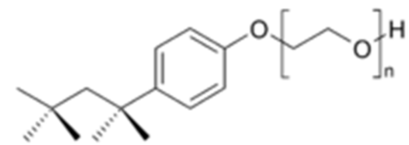


Types of Surfactants

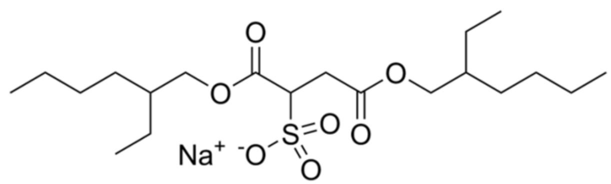
- Igepal, nonionic



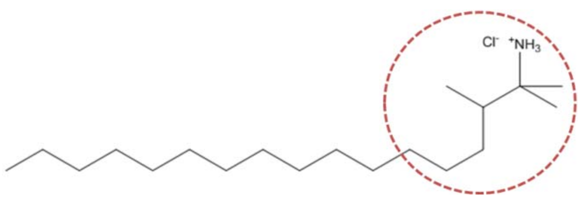
- Triton X-100, nonionic



- Aerosol OT, anionic

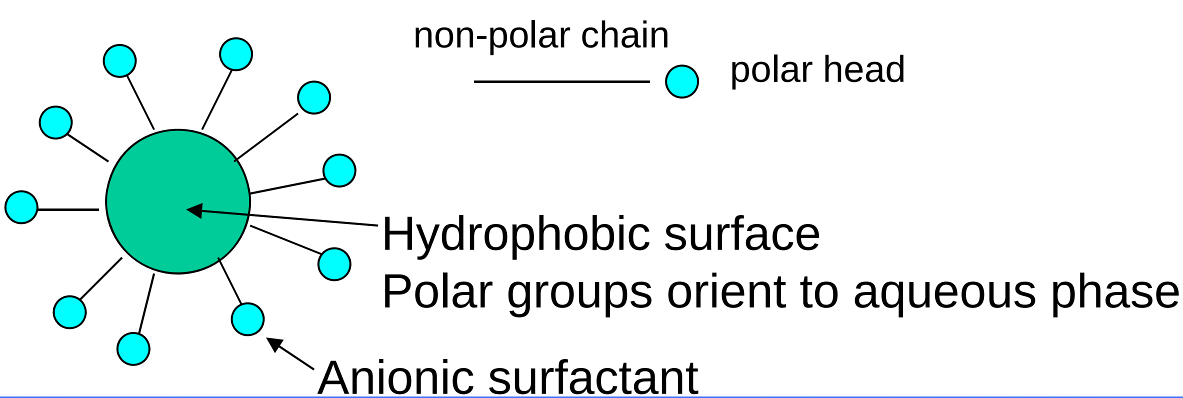


- Trimethylhexadecyl ammonium chloride, cationic



Common Surfactants

- Nonionic surfactants adsorb to charged and neutral surfaces, create steric barrier
- Igepal CA630 Ethoxylated octyl phenol Nonionic
- Triton X100 Octylphenoxypolyethoxy ethanol Nonionic
- Tween 20 Polyoxyethylene sorbitan Nonionic
- Aerosol-OT Dioctyl ester Na Sulfo succinic acid Anionic
- Cationic surfactants often used for biological samples, strongly bonds to negatively charged surfaces



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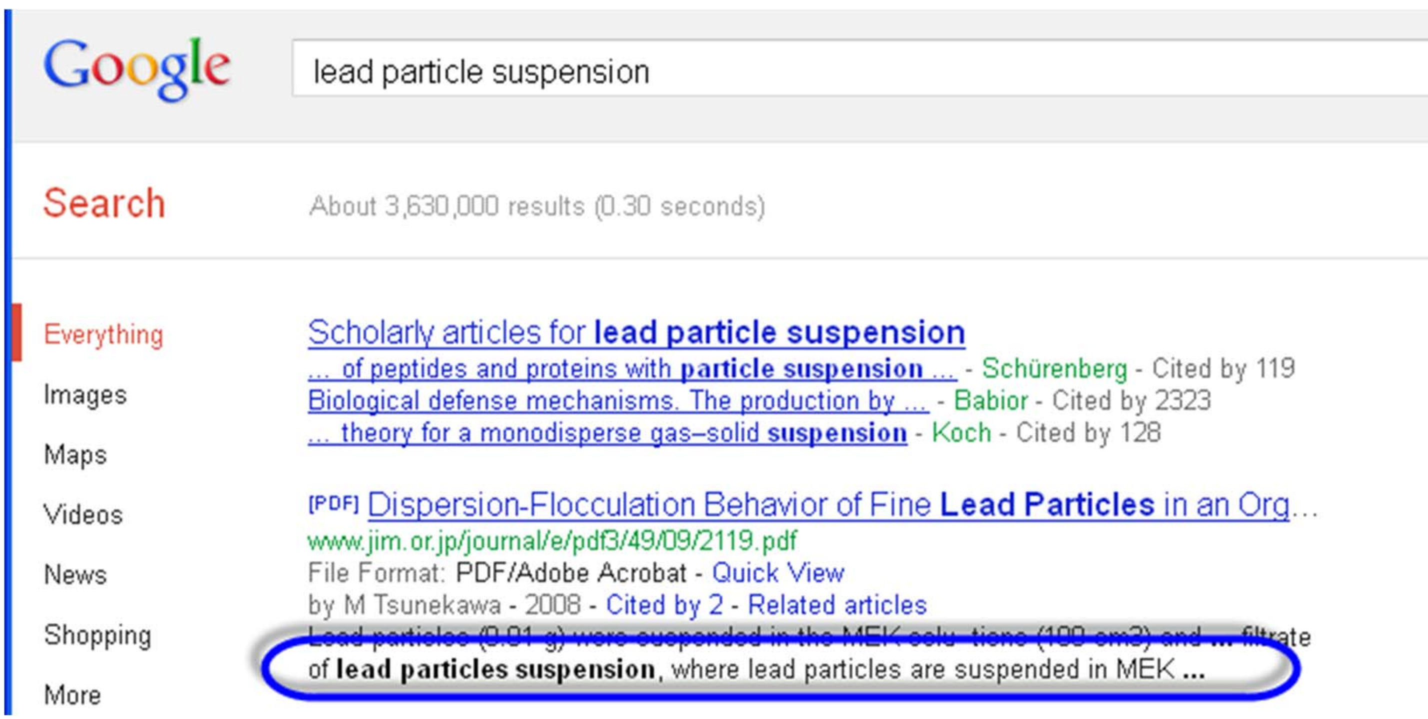
Changing Solvents

- Working with aqueous systems is usually easier for many reasons.
- But don’t forget to try a less polar solvent such as isopropyl alcohol.
- And, don’t forget that organic solvents are more difficult to handle due to fire and health hazards.

Search for Answers

- Check the literature and the web and see what other people use.
- Google to get the idea to use MEK with lead.



Experiment

- Try a series of options.
- Here is a series of suspensions and check them by eye, then measure.

ISO 14887

- Provides rigorous approach to dispersion
- Need to understand powder properties and ionic strength in suspension
- Match powder to liquid to liquid, dispersant, and conditions

INTERNATIONAL STANDARD

ISO 14887

First edition
2000-09-01

Sample preparation — Dispersing procedures for powders in liquids

ISO 14887

Categorize the Powder

- Does your powder best fit into the following categories
  - Metal
  - Metal oxide
  - Ionic salt
  - H-bonding organic
  - Non-polar organic
  - Weakly polar
  - Organic amine
  - Fluorocarbon

Category	Solid
metal hydroxide (pH_{iso} = 8,3)	boehmite
weakly polar	boron carbide
metal oxide	boron oxide
ionic salt	cadmium sulfide
ionic salt	calcium carbonate

Powders	
Category	**Example**
metal	aluminum
metal oxide	aluminum oxide
ionic salt	calcium carbonate
H-bonding organic	cellulose
organic acid	adipic acid
non-polar organic	latex
weakly polar	silicon carbide
organic amine	naphtylamine
fluorocarbon	perfluoroalkane

Choose the Liquid

- Possible liquid categories include:
  - Water
  - Non-polar
  - Weakly polar
  - Highly polar
  - H-bonding organic

Liquids	
Category	**Example**
water	water
non-polar	iso-octane
weakly polar	methyl ethyl ketone
polar	cyclohaxanone
highly polar	acetone
H-bonding organic	ethylene glycol

Choose Dispersant*

- Consider possible dispersants
  - Copolymer
  - Organic: acids, amines, esters, phosphate, sulfate, sulfonate
  - Phospholipid
  - Polyester
  - Polyionic salt

Dispersants (incomplete)	
Category	**Example**
PEO/PPO copolymer	Pluronic
organic acids	sodium dodecanoate
organic amines	alkanolamide
organic esters	lanolin
organic phosphate	alcohol phosphate
organic sulfate	sodium alkyl sulfate
organic sulfonate	sodium alkyl sulfonate
phospholipid	lecithin
polyester	polyacrylate
polyionic salt	sodium silicate
PEO: Polyethoxy = (-CH2-CH2-O-)n	
PPO: Polyisopropoxy = (-CH2-CH(CH3)-O-)n	

*will discuss later

Put it All Together

Solid category	Liquid category	Condition	Dispersing-agent category
metal	water		PEO/mercaptan
		Encapsulation in gelatine is also effective	
	organic		organic amine
carbon	water		PEO/alcohol
	organic		PPO/alkane
metal oxide	water	IS < 0,1	adjust $pH < pH_{iso} - 2$ or $pH > pH_{iso} + 2$
		IS > 0,1	polyion
	organic		organic acid or organic amine
metal hydroxide	Use the same guidelines as for a metal oxide		
ionic salt	water	IS < 0,1	try common-ion effect
		IS > 0,1	polyion
	H-bond organic		PEO/PPO copolymer
	highly polar		PEO/PPO copolymer
	weakly polar		PEO/alkane
	nonpolar		PEO/alkane

Avoid IEP

Put it All Together

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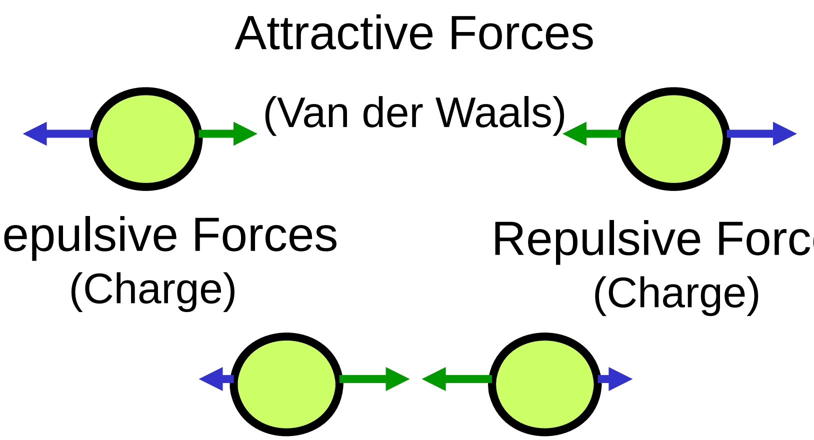
Summary

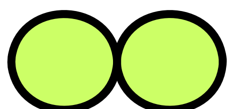
Powder	Liquid	Dispersing agent
H-bonding organic	water	PEO/PPO copolymer
H-bonding organic	organic	phospholipid
ionic salt	highly polar	PEO/PPO copolymer
ionic salt	weakly polar	PEO/alkane
metal oxide	water	adjust pH away from IEP
metal oxide	organic	organic acid
		or organic amine

Personal experience: prefer electrostatic stabilization and avoid use of polymers

Dispersants: Particle Interactions



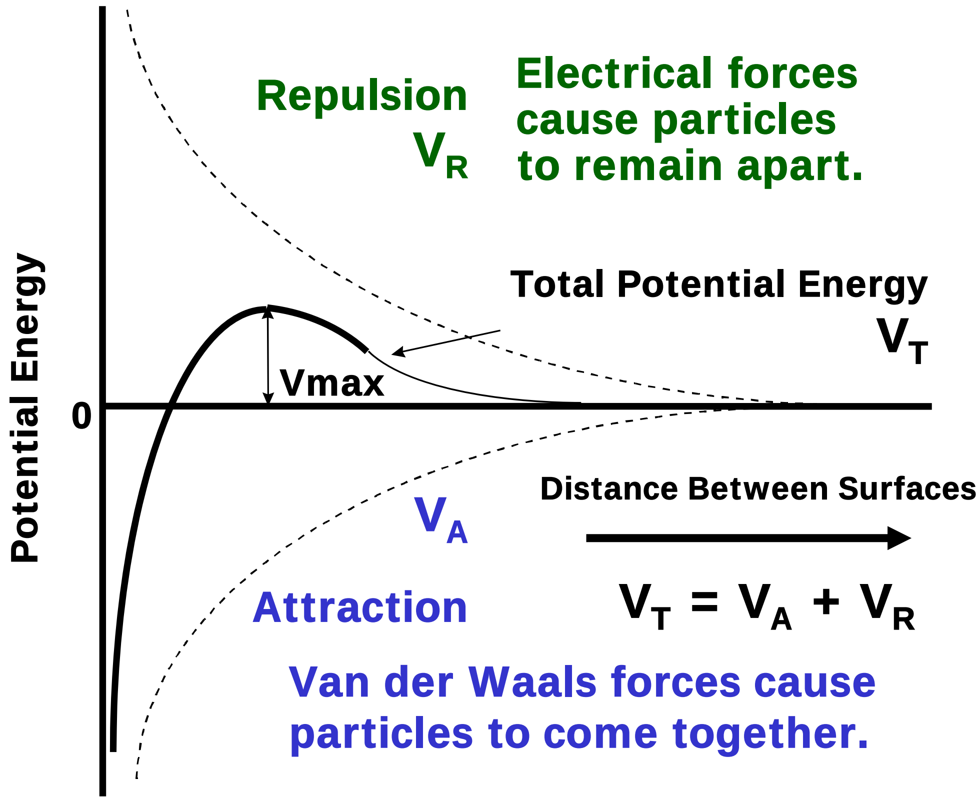
When particles approach close enough to cross the potential barrier (when attractive forces exceed repulsive forces), they come together (agglomerate).



Goal: repulsive forces strong enough to keep particles apart, even during close approach. Can be accomplished by surfactant coating of particle surfaces.

Energy of Interaction

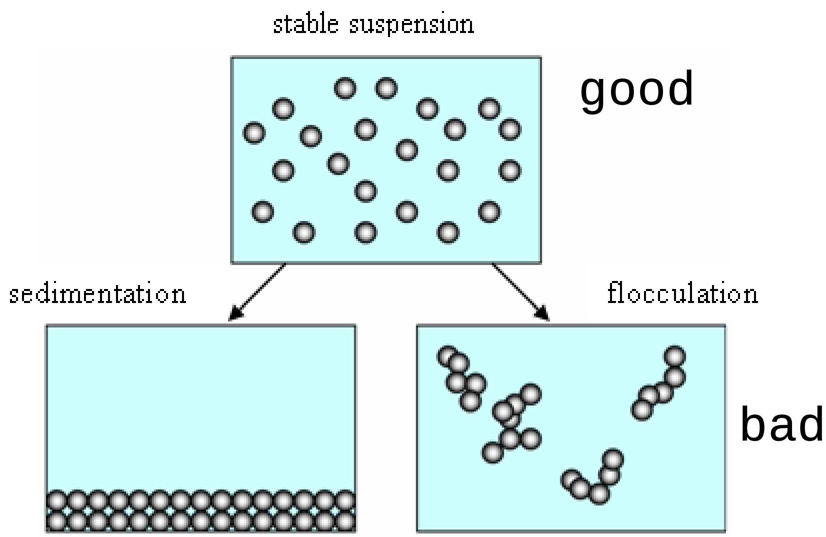
Interaction of Two Charges Surfaces/Particles

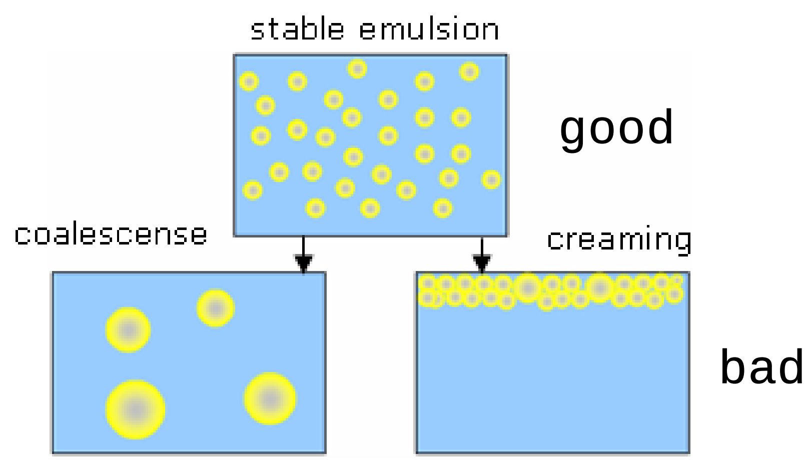


- Stability depends on balance of forces. Attractive due to Van der Waals, & repulsive due to electrical double layers around particles.
- If V_T lower than average thermal energy, K_T, then high probability two adjacent particles will eventually collide & remain attached due to strong Van der Waals forces at very close distances.

Dispersion Stability

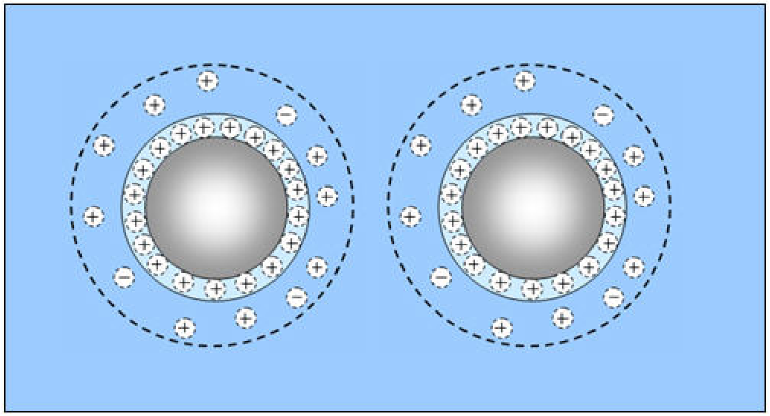
- Want to disperse to individual particle state
- Need sample to stay dispersed during the measurement
- Avoid reagglomeration, sedimentation, flocculation



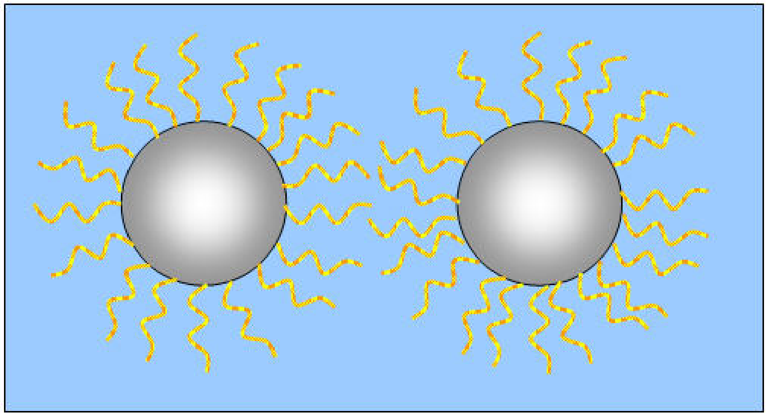


Dispersion Stability

- Electrostatic stabilization better when relative dielectric permittivity greater than 30, and ionic strength < 0.1 mol/L

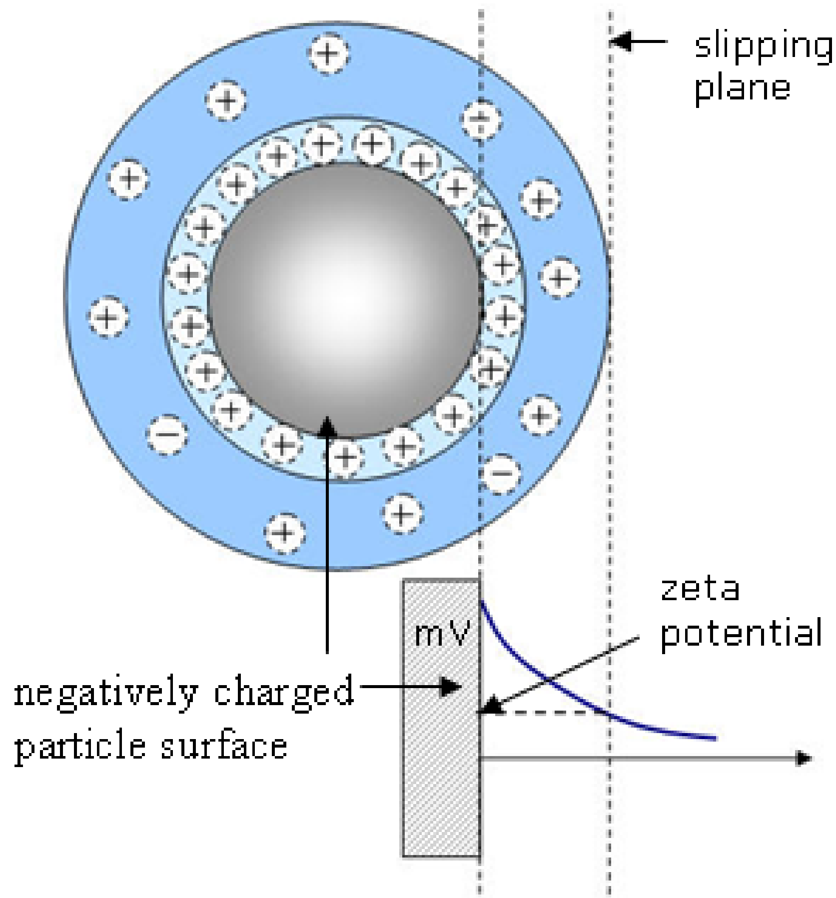


- Steric stabilization better when relative dielectric permittivity < 30 or an ionic strength greater than 0,1 mol/L



Zeta Potential

- If surface has + charge, then - ions attracted to surface
- + ions attracted to – ions, builds electric double layer
- Slipping plane: distance from particle surface where ions move with particle
- ZP = potential (mV) at slipping plane



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Dispersants

- Add charge to particle surface
- Need surfactants to wet
- Need energy to separate
- Need dispersants to keep apart

Polyionic salts

Dispersing agent	Commercial examples (manufacturer)
sodium tripolyphosphate = $Na_3PO_4 \cdot 12H_2O$	Maypon (Stepan), SuperPro® (Stepan)
sodium tetrapyrophosphate = $Na_4P_2O_7 \cdot 10H_2O$	Numerous
sodium hexametaphosphate = $Na_6(PO_3)_6$	Calgon® (Nalco), (Solutia)
sodium silicate	Numerous
sodium citrate = $Na_3C_6H_5O_7 \cdot H_2O$	Numerous
sodium polyacrylate	Dispex® 40 (Ciba Spec. Chem.), Good-rite® (BF Goodrich)
NOTE Any alkali metal ion or amminium ion may be used in place of sodium.	

Dispersants

PEO/alcohol

Dispersing agent	Commercial examples (manufacturer)
alkyl phenoxy PEO ethanol	Igepal® (Rhodia), Lissapol® NX, Nonidet® P40 (BP), Praewozell® W-ON 100, Renex® 648, Triton® 100 (Union Carbide), Merpol® 100 (Rohm & Haas), Polyfac® NP-40 (Westvaco)
PEO/alkanol	Neodol® (Shell), Merpol® (Rohm & Haas), Tergitol® (Union Carbide)
PEO/acetylenic glycol	Surfynol® 104 (Air Products)

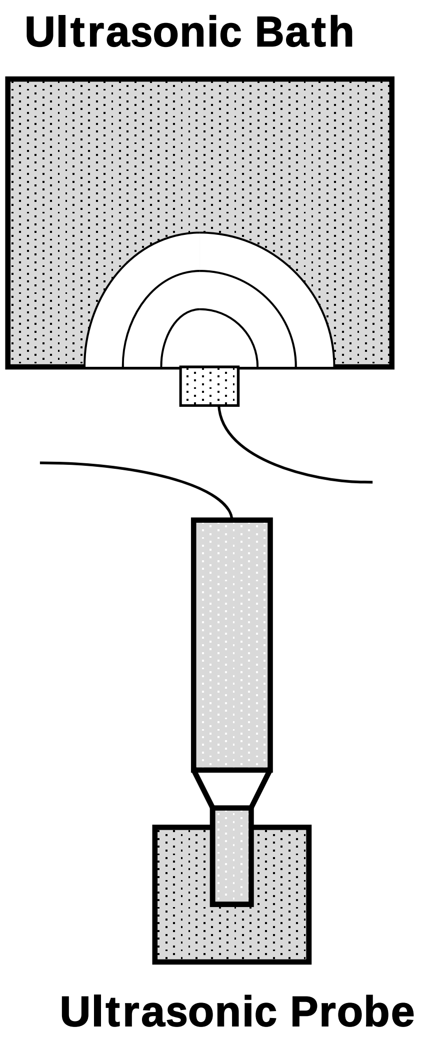
Water soluable organic

Dispersing agent	Commercial examples (manufacturer)
formaldehyde-naphthalene sulfonate	Daxad® (Grace), Blancol® N (Rhodia), Tamol® N Micro (Rohm & Haas), Petro 425 (Witco)
sulfonated lignin	Polyfon® (Westvaco), Marasperse® (Reed Lignin)
tannic acid	Durtan® (Durkee)
sorbitan laurate	Span® 20 (Uniqema), Liposorb® L (Lipo), Sorbac® 20 (Speciality Industrial Prod.)
PEO/sorbitan stearate	Tween® 20, Liposorb® L-20 (Lipo), Polysorbac® 20 (Speciality Industrial Prod.)
tall-oil acid salts	Polyfac® MT (Westvaco)

Add Energy

- Ultrasonic waves generate microscopic bubbles or cavities (cavitation) which produce shearing action causing the liquid and suspended particles to become intensely agitated.

- Agglomerates are broken apart.
- In some cases fragile particles are shattered.
- The selection of appropriate type and level of ultrasonic energy must be made carefully.



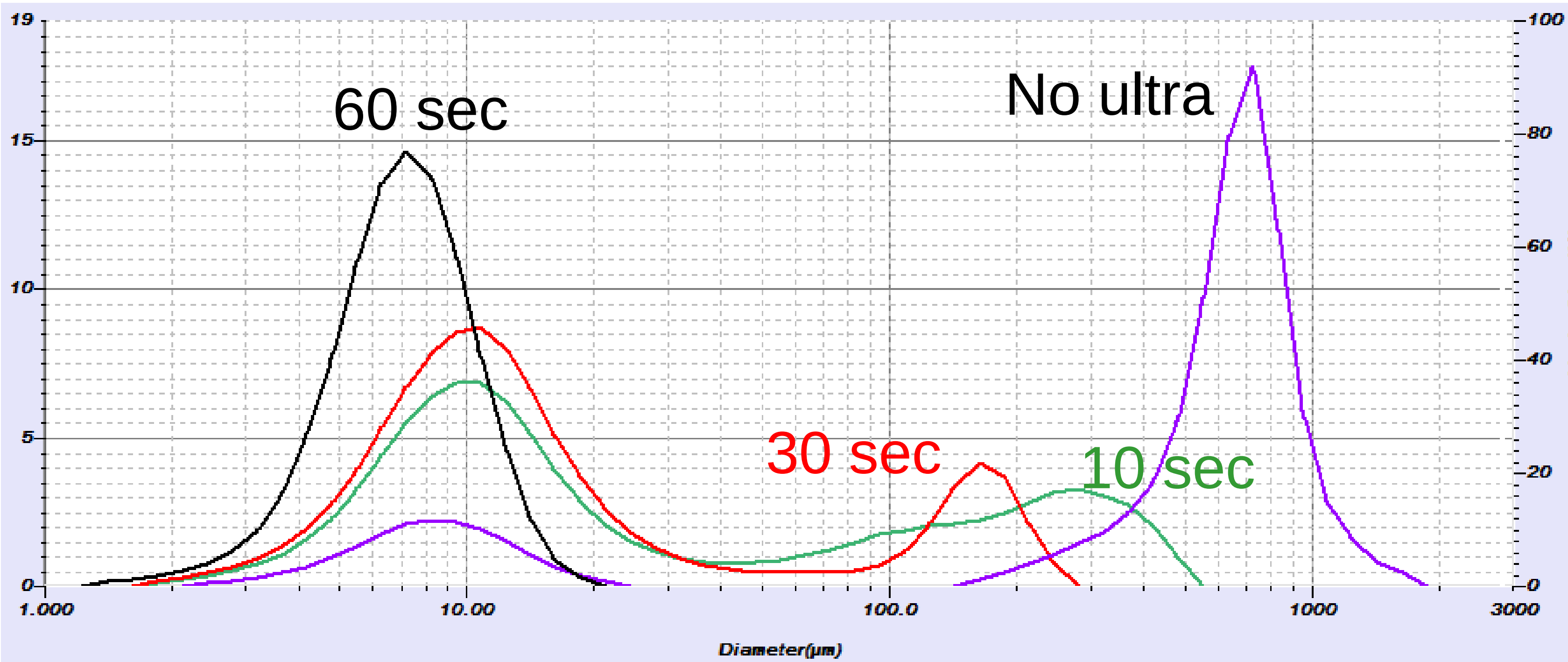
Case Studies

Effect of Energy

Effect of Dispersant

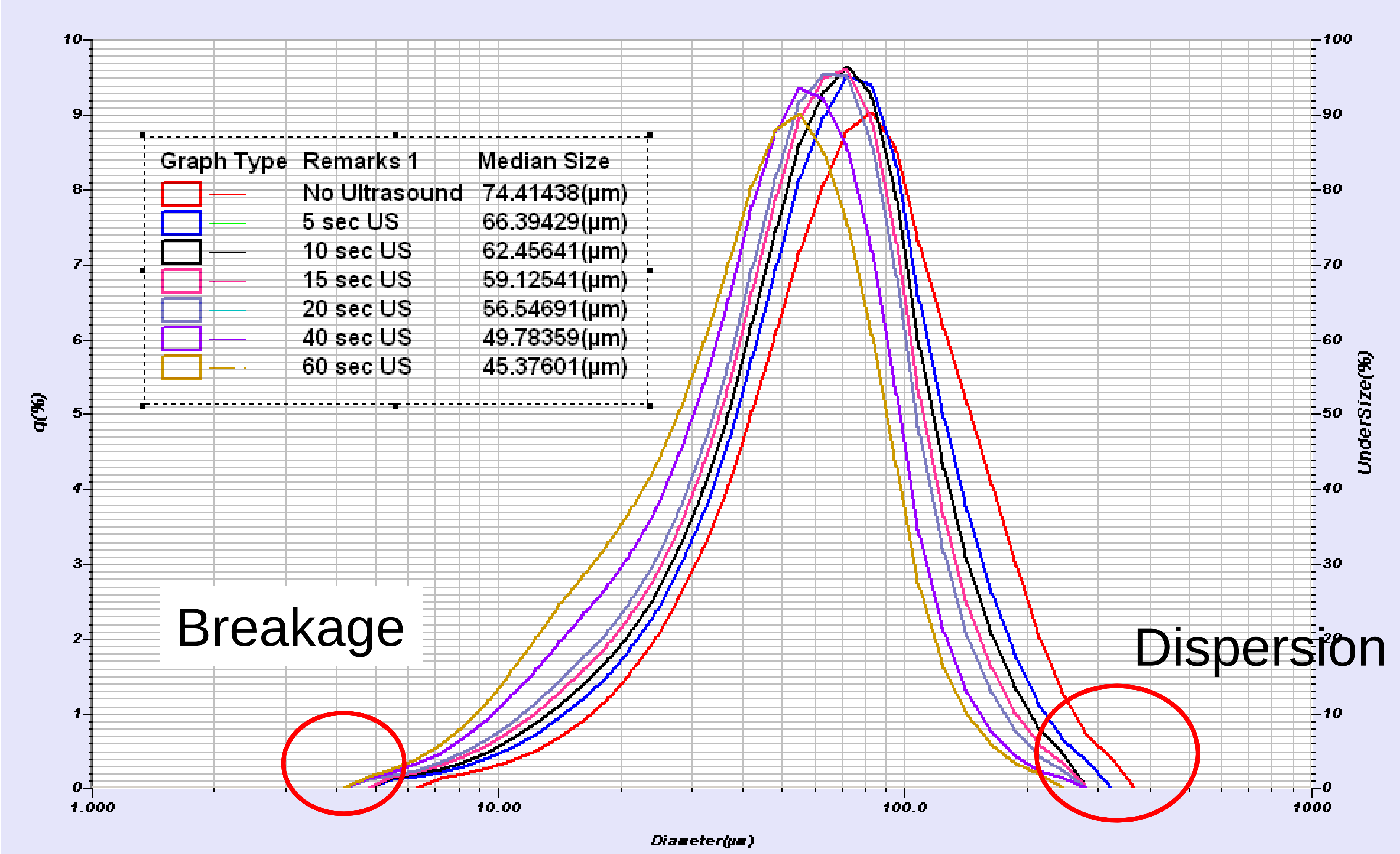
Add Energy

Effect of Ultrasound using LA-950



If powder naturally wets, energy best way to disperse powder

Effect of Ultrasound



TiO2; no Dispersant

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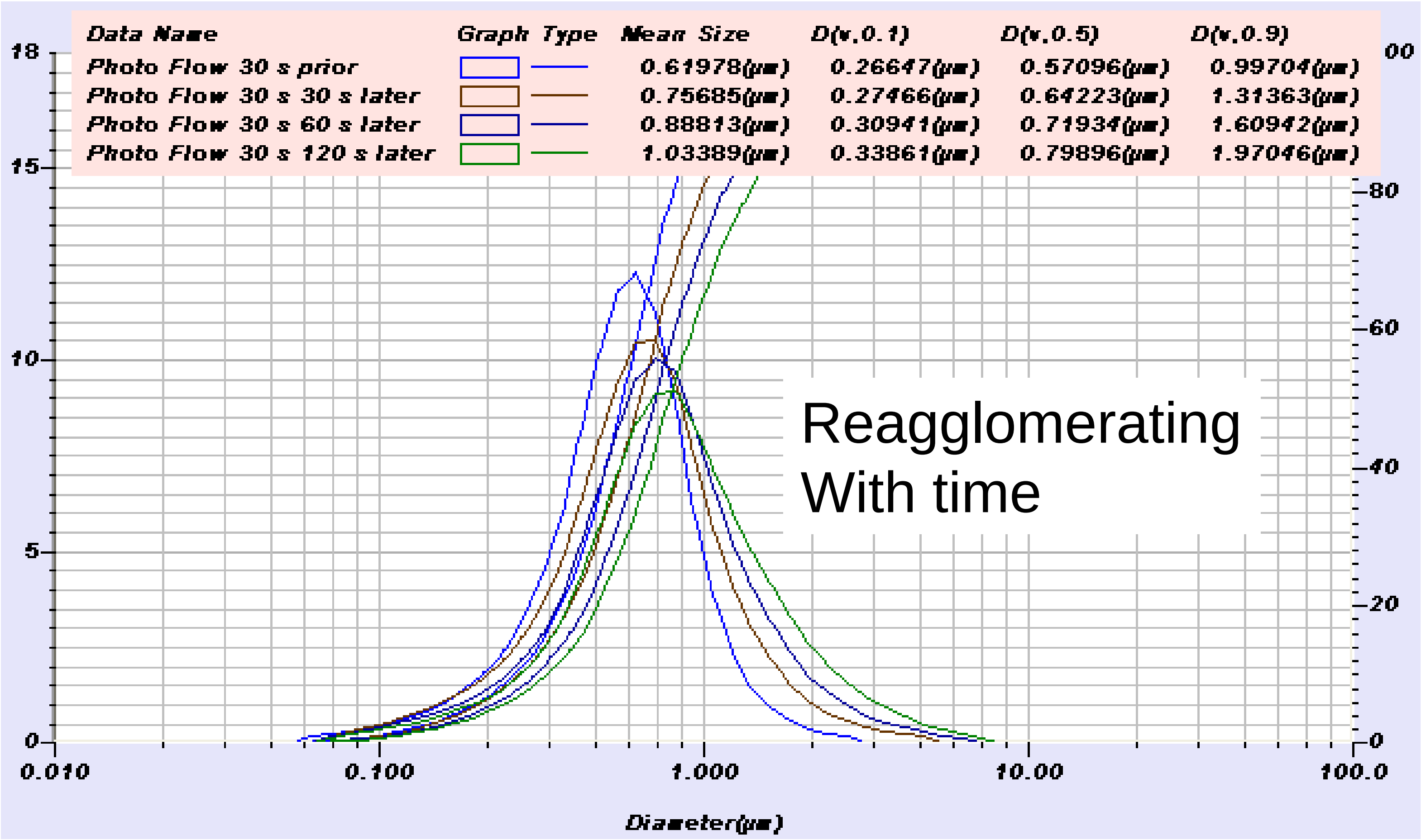
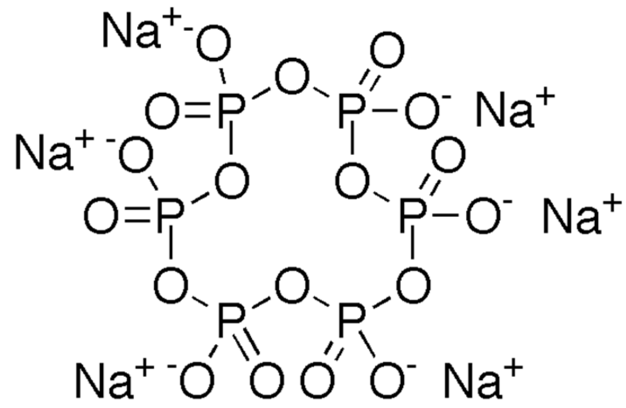
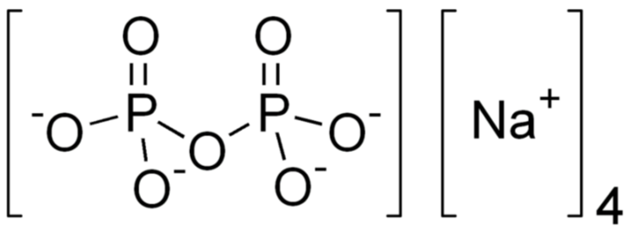


Sodium Hexametaphosphate

- Most common stabilizer
- Abbreviated NaHMP
- Keeps particles from re-agglomerating
- Disperse sample in 0.01 – 1.0% $(NaPO_3)_6$ rather than DI water
- Tetrasodium pyrophosphate also used (sodium pyrophosphate, NaPP)





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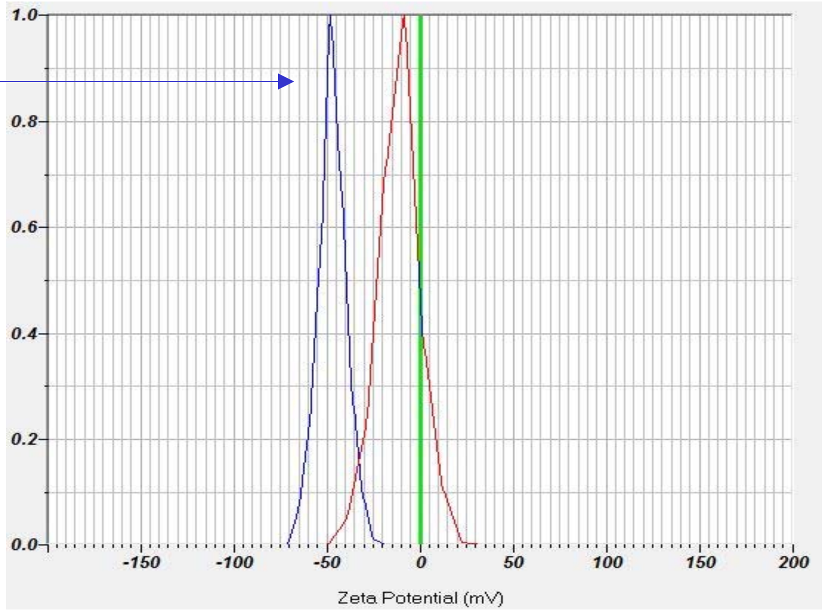
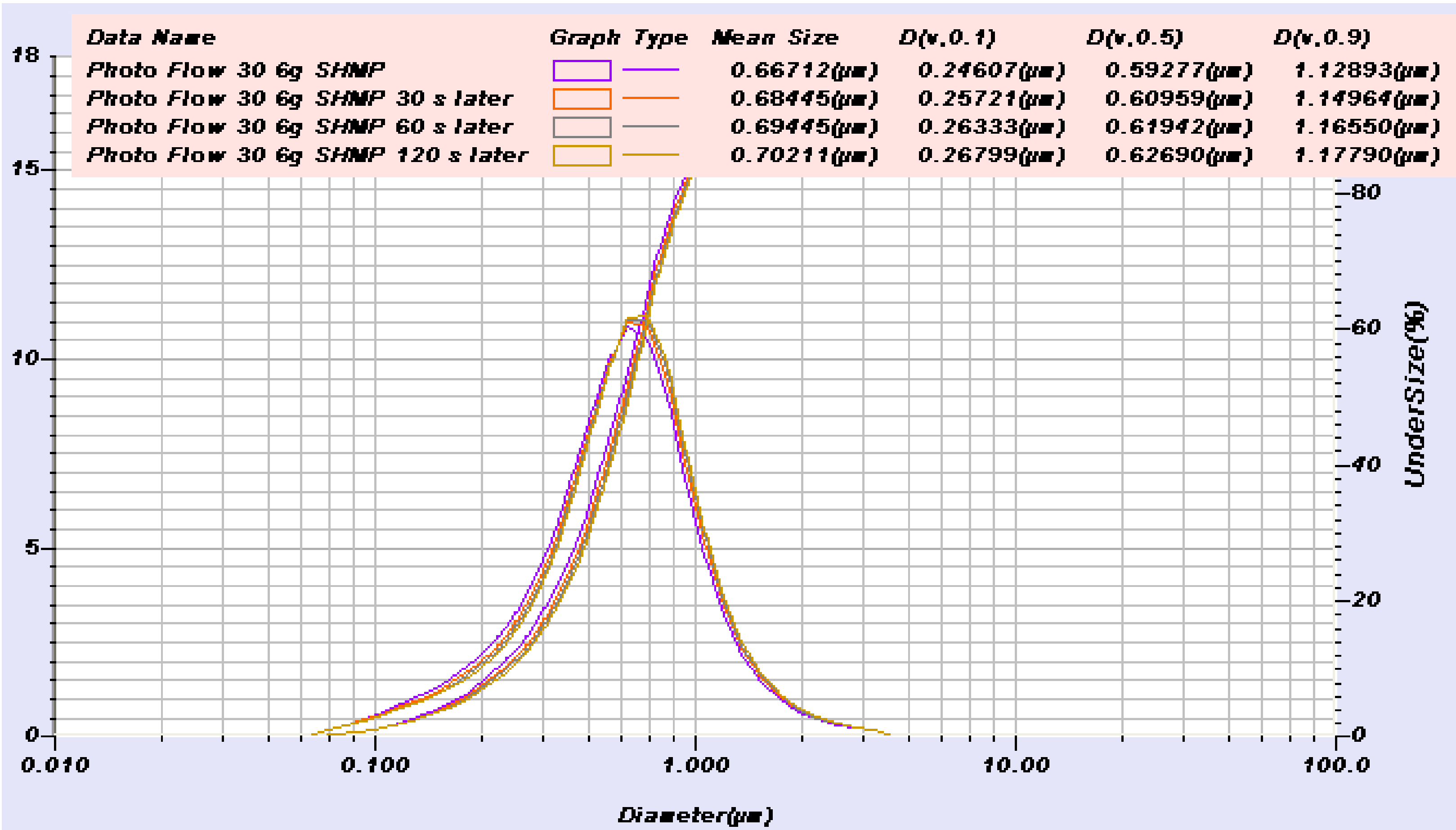
Dispersant Increases ZP

- Measured zeta potential on SZ-100 of sample in DI and in NaHMP
- DI water in red = -11.1 mV, unstable
- NaHMP in blue = -47.5 mV, stable



TiO2; with NaHMP



Summary

- Surfactants wet powders
- Use dispersants/admixtures to alter surface chemistry
  - Sodium hexametaphosphate
  - Sodium pyrophosphate
- Ultrasound reduces size
  - De-agglomeration and/or breakage
- Need methodical approach, but now have a basis

Resources: www.horiba.com/particle

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