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Principles of Pigment Dispersion

2026 NAPIM Summer Course
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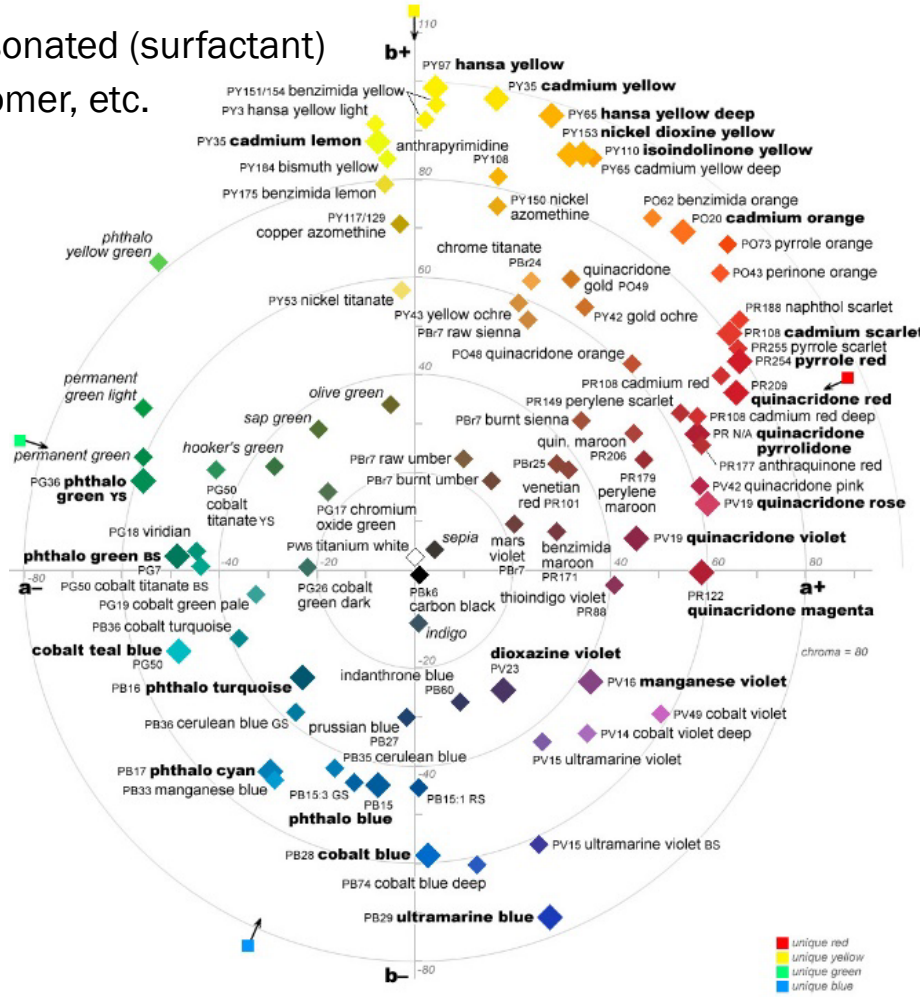
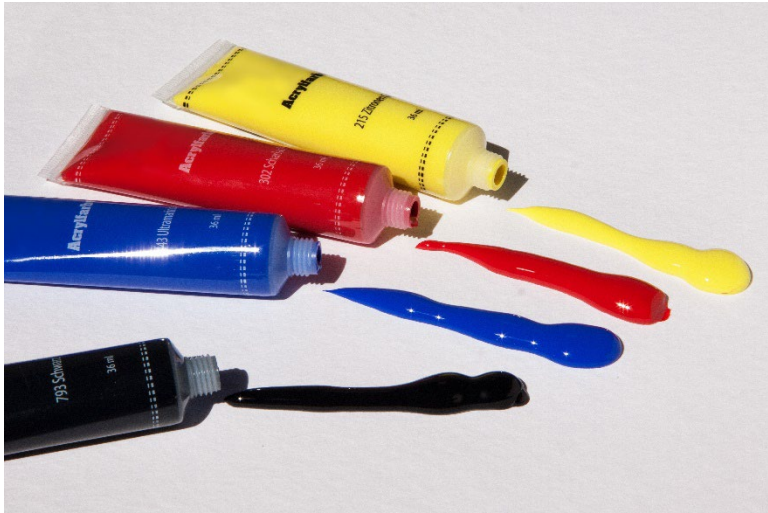
Dispersion Definitions

- Pigment ground in a suitable vehicle for incorporation into an ink or a coating.
- Pigment could be organic or inorganic
- Vehicle could be…
  - Resinated or non-resonated (surfactant)
  - Water, solvent, monomer, etc.
  - Paste or fluid



Dispersion Properties

- Color Shade
  - Pigment Choice
- Color Strength
  - Concentration
  - Pigment to Binder Ratio
- Fineness of Grind (Particle Size Distribution)
  - Milling Technique
- Compatibility
  - Suitability to ink/coating system (formulation)
- Stability
  - Dispersion Stabilization



The Dispersion Process

- Incorporation (or wetting)
- Deagglomeration
- Stabilization

Incorporation

This involves removing gases (such as air) and water (and other contaminants) from the pigment crystal surface and replacing it with vehicle.

Premix / Letdown (Paste – Offset & UV)

Not all the materials are necessarily added at the same time during the process of making dispersions. Items added before the milling stage are known as the Premix. Items added after milling are known as “Let down” materials.

- Offset – resin cut into oil (“varnish”) then pigment added; additional oils and modifiers (tack reducers) added at a later step

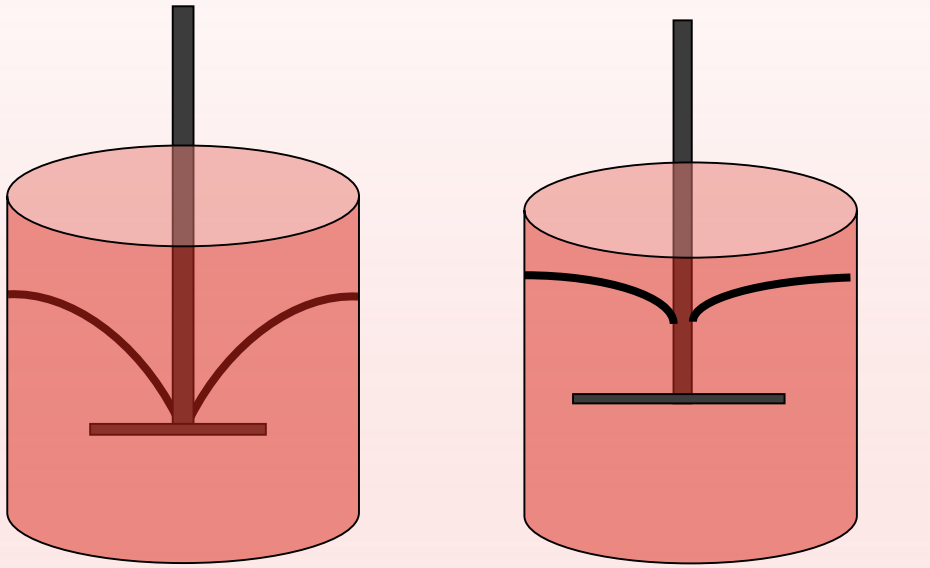
- UV – Oligomer(s), some monomer, and pigment combined Dispersants often used

Premix / Letdown (Liquid)

- The solution resin, solvents, water (amines?), defoamer, and surfactant are combined and mixed well before dry pigment is added to the premix. Some of the water (or solvent) can be held out to increase the rheology of the millbase and subsequent shear experienced in the mill.
- Due to low viscosity/high mobility considerations, order of addition can be more critical
- All liquids can be weighed in first, or some held back
- Surfactant can be added at various stages – either during the dispersion formulation, or as part of the solution resin cut
- State of resin solubility important – surfactants can affect this
- Pigment to binder ratio important
- Defoamers should not be added when dry pigment is present

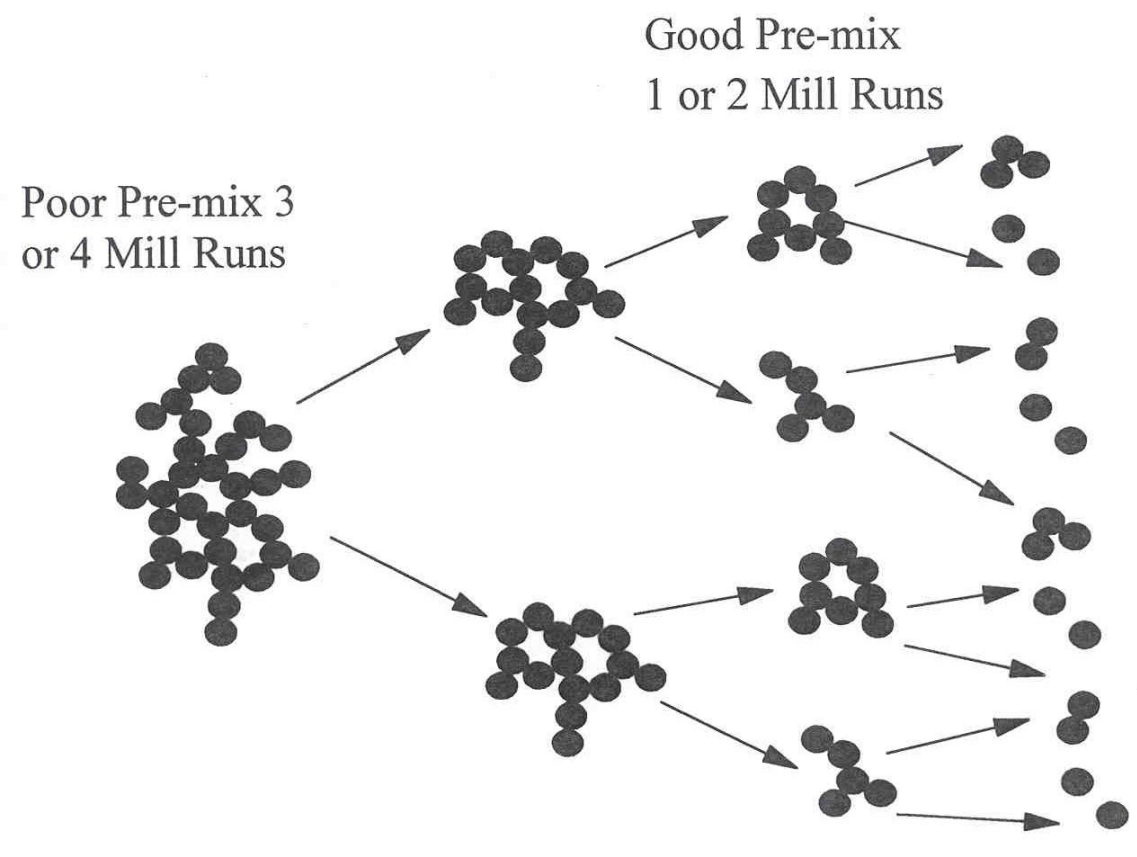
Premix Process

- Keep a good vortex
- Load pigment carefully
- Operate mixer at correct power setting
- Monitor batch temperature
- Better premixing leads to shorter milling times
- Do not allow cavitation to occur – entrained air is very hard to remove



Good vortex *Poor vortex*

Importance of Premix



Assuming 5 hours per mill pass..
10 hours * $50/hr
+$500 per batch!
Plus opportunity costs

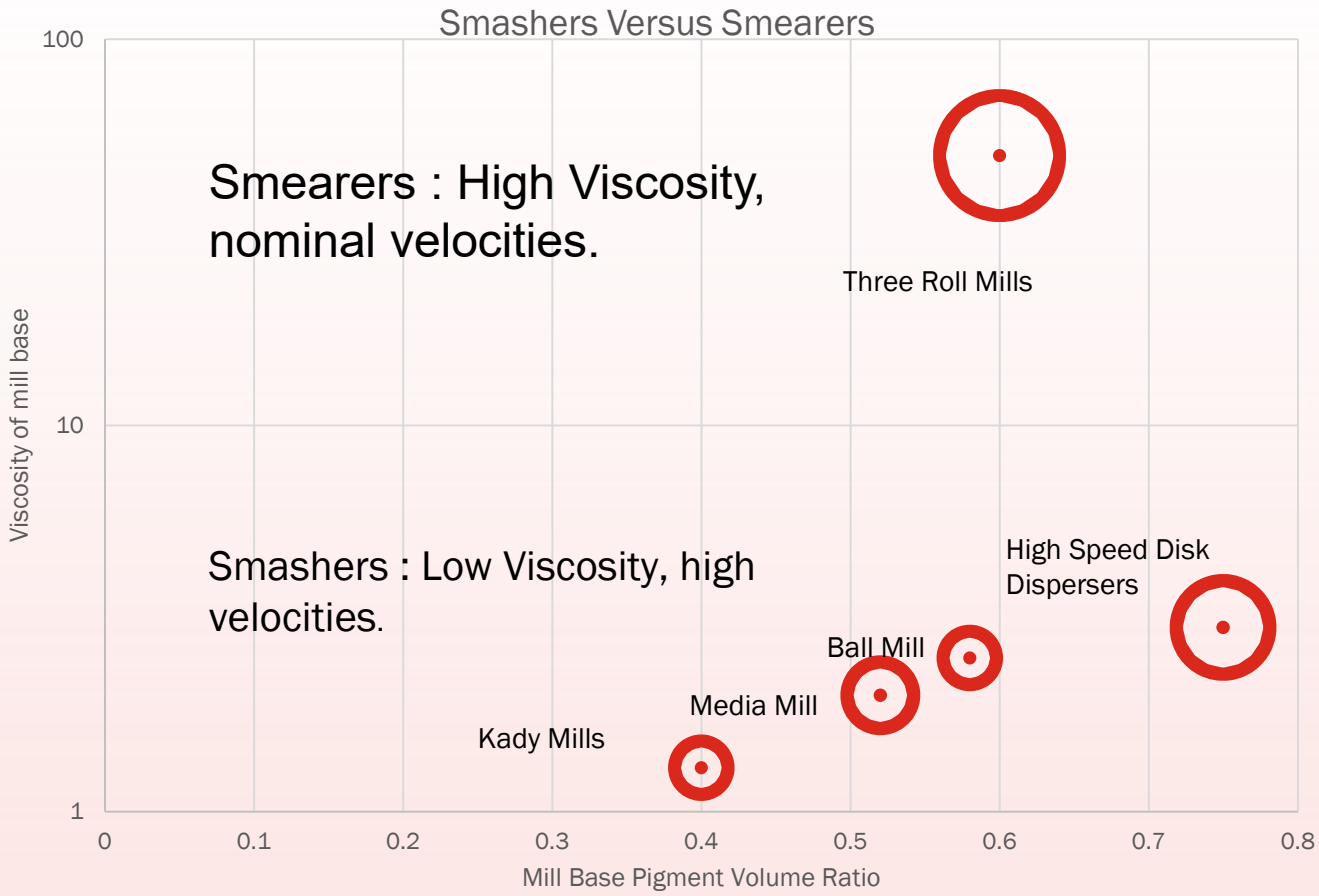
The Dispersion Process

- Incorporation (or wetting)
- Deagglomeration
- Stabilization

Deagglomeration

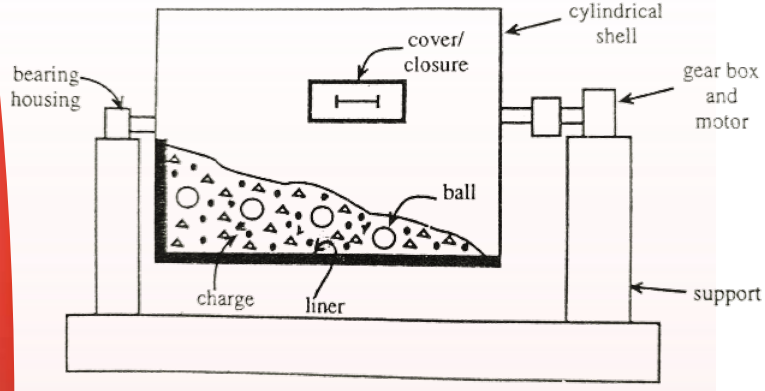
This is the breakdown, by mechanical work (shear), of pigment agglomerates into primary particles - such that each is surrounded individually and completely by solution resin (or dispersing additive).

Type of Milling
Hulk versus Granny's Butter Knife



Equipment

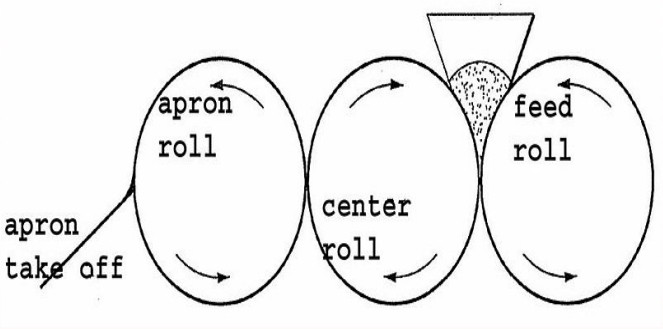
Ball Mill

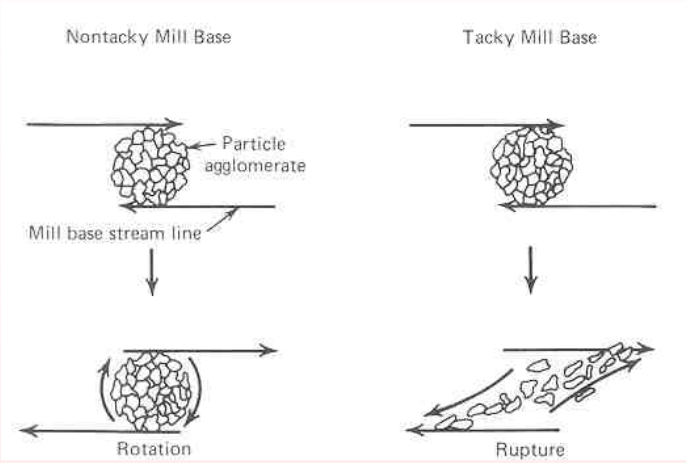


Horizontal Shot/Media Mill

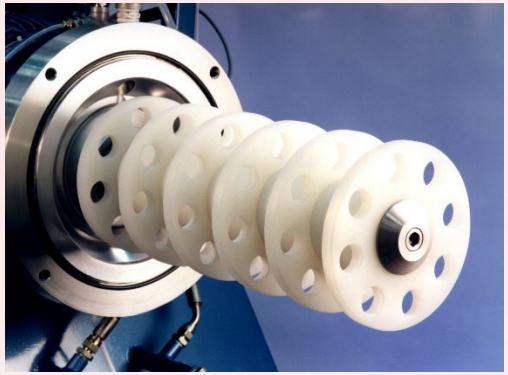
Milling

- Three roll mill (offset and UV ink dispersions only) Liquid ink dispersions not cohesive enough for three roll milling

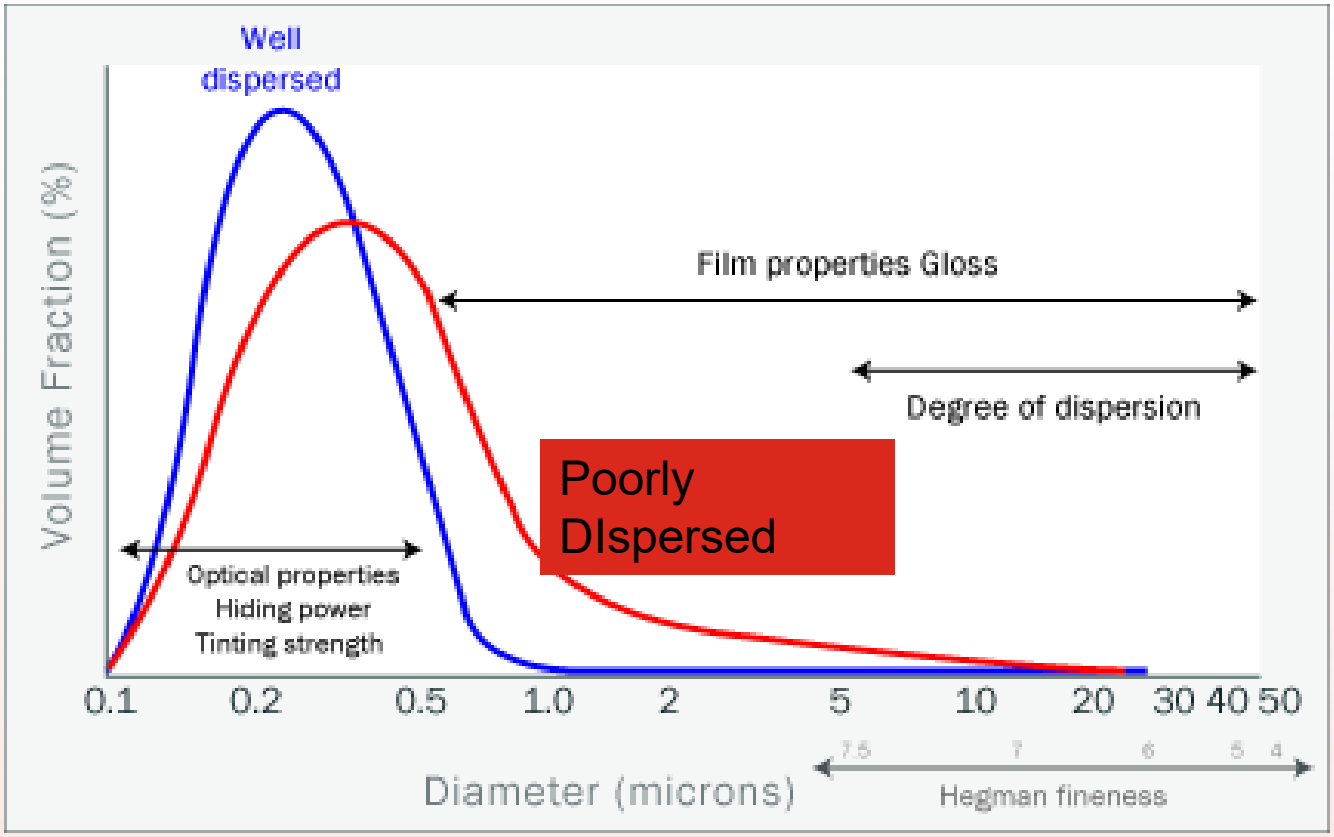




- Media mill (liquid ink dispersions, inkjet dispersions, and some UV ink dispersions)



Particle Size



- Grind Speed and Efficiency play an enormous role in color strength, shade, transparency/opacity, gloss, viscosity, etc.

Negative Effects of Heating

- Reduced chemical stability of pigment-dispersant interaction
- Solvent volatility
- Removal of “soft” surface coatings – TiO2
- Degradation of thermally sensitive pigments – diarylide yellow, rhodamine, methyl violet, e.g.

The Dispersion Process

- Incorporation (or wetting)
- Deagglomeration
- Stabilization

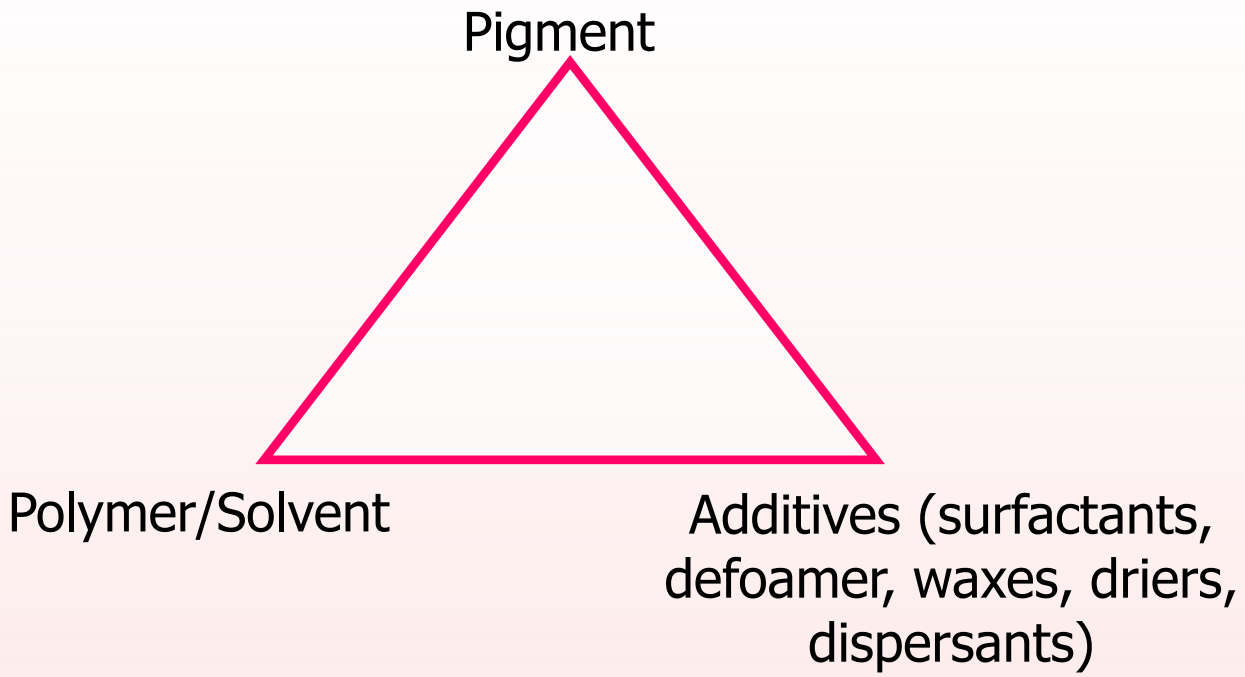
Stabilization

This is the maintenance of a uniform distribution of particles throughout the grind vehicle such that reagglomeration or flocculation is prevented from occurring.

Factors in Stabilization

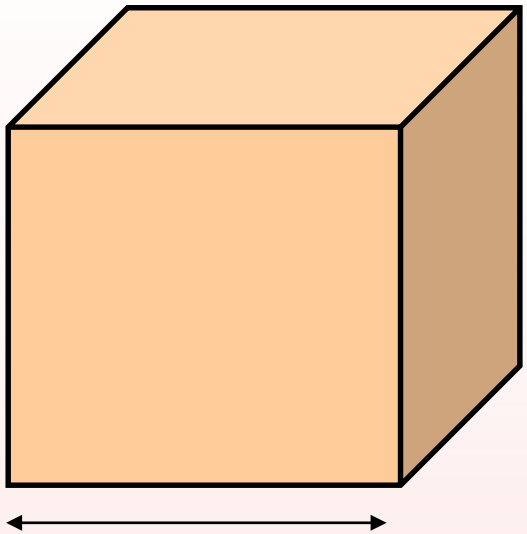
- Competitive Interactions
- Particle Size and its contribution to surface energy
- Interactions at a pigment surface and their contribution to surface energies

Competitive Interactions

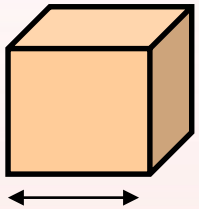


The interactions between the various major components of a dispersion are competitive in nature, making the prediction of stability very difficult. As depicted here, each ingredient has the potential to associate with two or more components. Efficacy of any one of these ingredients in the formulation will depend on the degree and type of interactions it has with the other species present. Varying the order of addition of the raw materials can affect which ingredients interact with one another.

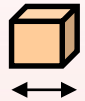
Particle Size / Surface Energy



8.4×10^5 ergs/cm



8.4×10^6 ergs/cm



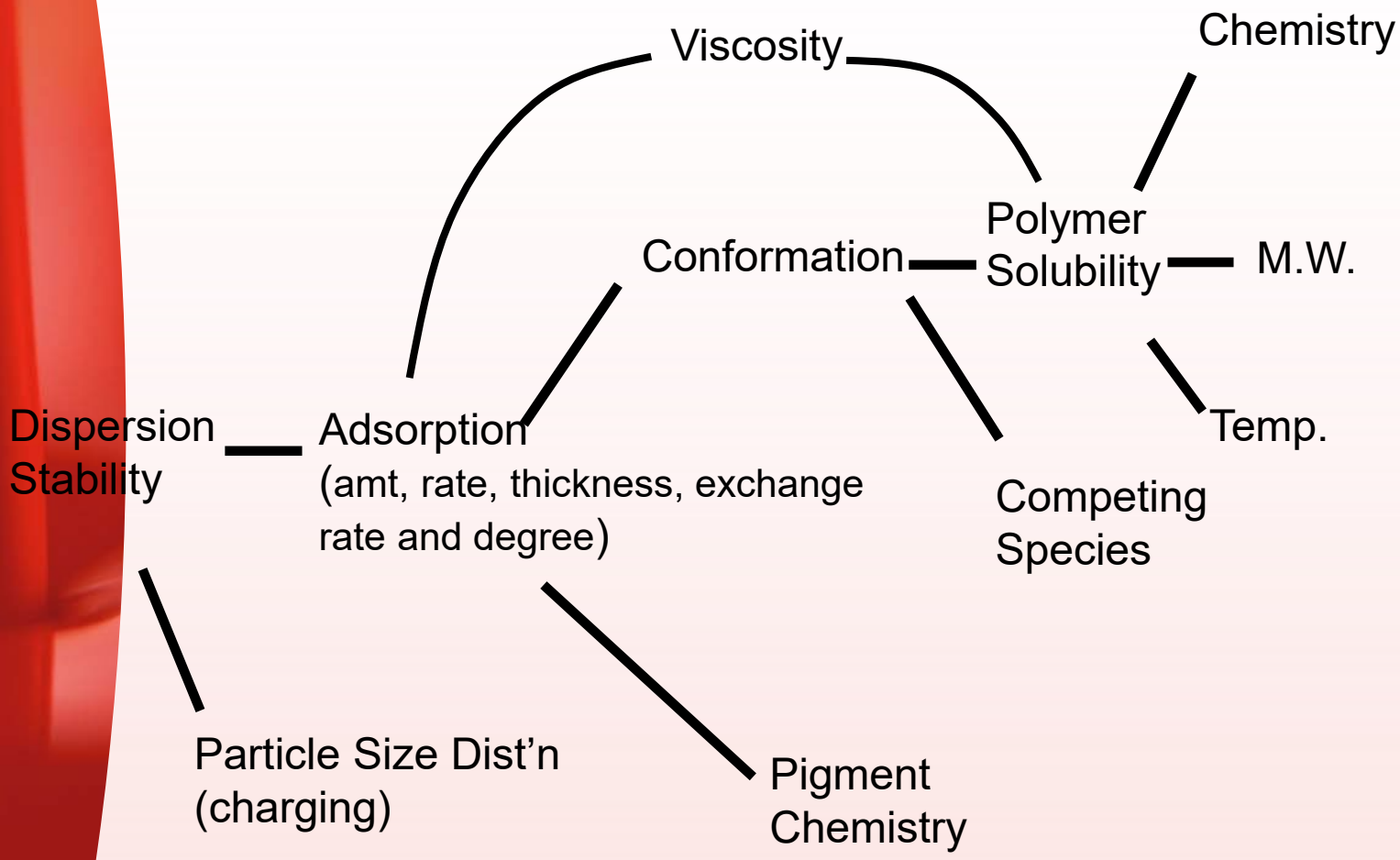
8.4×10^8 ergs/cm

The smaller the particle, the higher the surface energy. The system strives to lower its surface energy by minimization of surface exposure. This can occur by adsorption of polymers, solvents or surfactants OR by particle flocculation. Obviously, to maintain adequate dispersion properties, prevention of particle flocculation is desirable.

Surface Energy Reduction:

- *Flocculation* – a negative consequence which detracts from the color, rheology, gloss, transparency, conductivity, or protective characteristics of a dispersion
- *Adsorption* – a positive result which will enhance dispersion stability and maximization of the performance characteristics of the dispersion

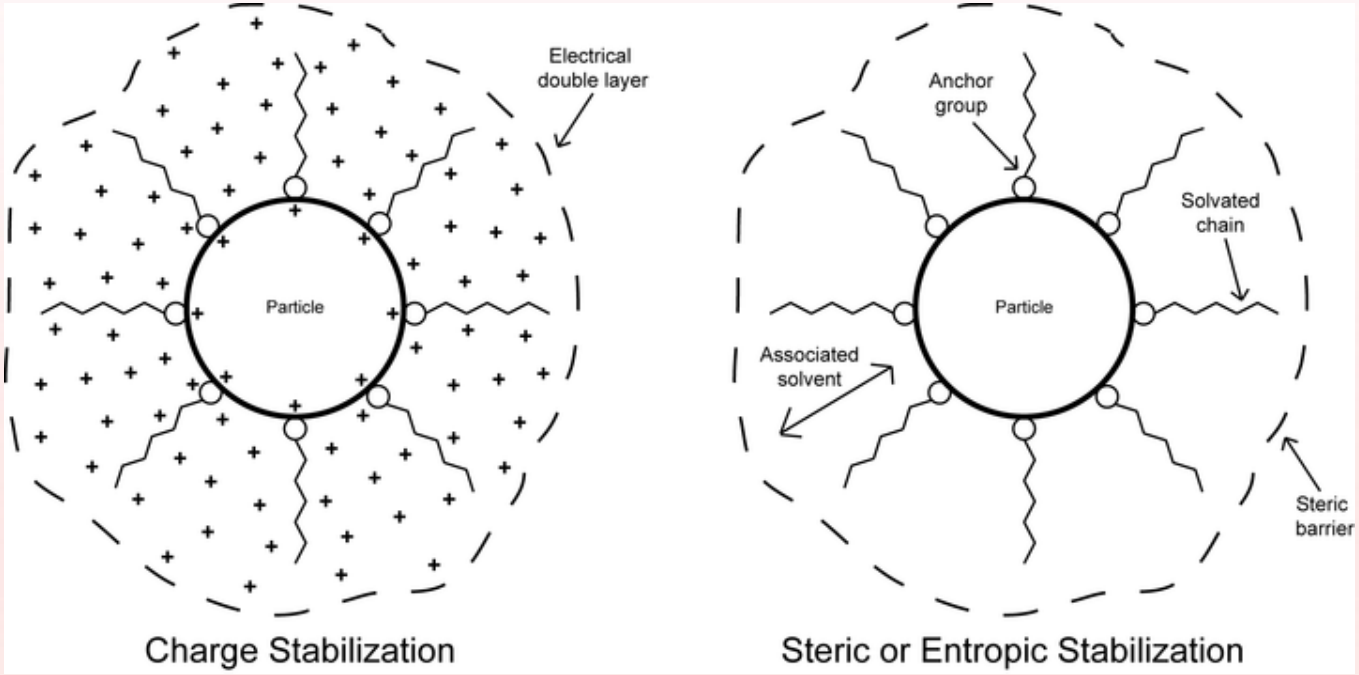
Interrelated Factors



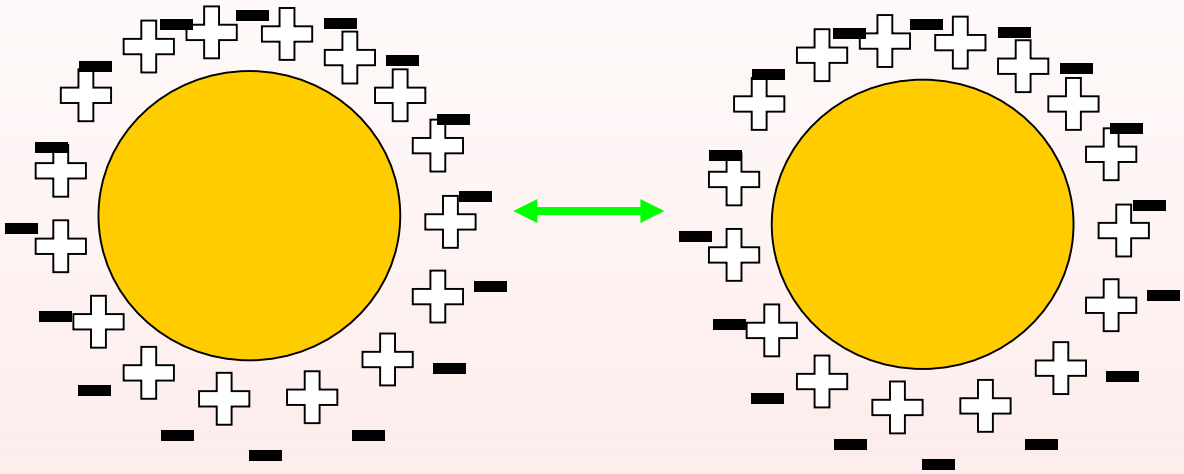
EVERYTHING DEPENDS ON EVERYTHING ELSE!

Two Types of Stabilization in Any Dispersion

- Electrostatic – relies on charging
- Steric – uses physical barriers



Electrostatic Stabilization



This involves the creation of an electrical double layer around each particle. The double layer consists of two parts: the inner part arising from the preferential adsorption of one species of ion at the surface of the particle, and the outer part. The outer part of the double layer is more diffuse, since the thermal motion acting on the counterions (of opposite charge to those adsorbed at the surface) offsets to a certain extent the electrostatic attraction which tends to keep them in the neighborhood of the preferentially adsorbed ions. Each particle is thus surrrounded by a cloud of "counterions" which screen off the particle charge.

DLVO Theory – Electrostatic Stabilization

Derjaguin and Landau, Verwey and Overbeek 1941

The total energy between any two particles is given by:

$V_T = V^{el}_R + V_A$ *where* V^{el}_R *and* V_A *are*

Repulsion term: $V^{el}_R = \frac{1}{2}(kr\varphi_0^2)$

Attraction term: $V_A = -(A/12\pi H^2)$ *where* $H = R - 2r$

LET'S LOOK AT THIS IN STEPS:

Repulsion Term

Repulsion term: $V^{el}_R = \frac{1}{2}(kr\varphi_0^2)$

Assume an interaction between any two particles. The surface potential on the two particles is assumed to be the same (φ_0^2) and is a similar term to q_1q_2 (magnitude of two charges) – from Coulomb's Law

r describes the radius of the two particles.

k is the dielectric constant of solvent; it is high for aqueous systems and low for solvent systems.

So.....

- Repulsion is high for larger radius particles (means that dispersing things finer detracts from repulsion – and good repulsion is necessary for dispersion stabilization!)
- High particle charge leads to better repulsion
- High dielectric constant leads to better repulsion, generally

Attraction Term

Attraction term: $V_A = -(A/12\pi H^2)$
where $H = R - 2r$

H^2 describes the distance between the surface of one particle to the surface of the other, since R is the distance between the centers of the two particles, and r is the radius of the two particles.

So…..

- Attraction depends primarily on the separation of the particles themselves. This can be influenced by spacing (aka *concentration – more particles indeed decrease the spacing available between them!*) and inherent size of the dispersed particles.
- *Pigment to Binder Ratio!*

DLVO Theory – Electrostatic Stabilization, Part II

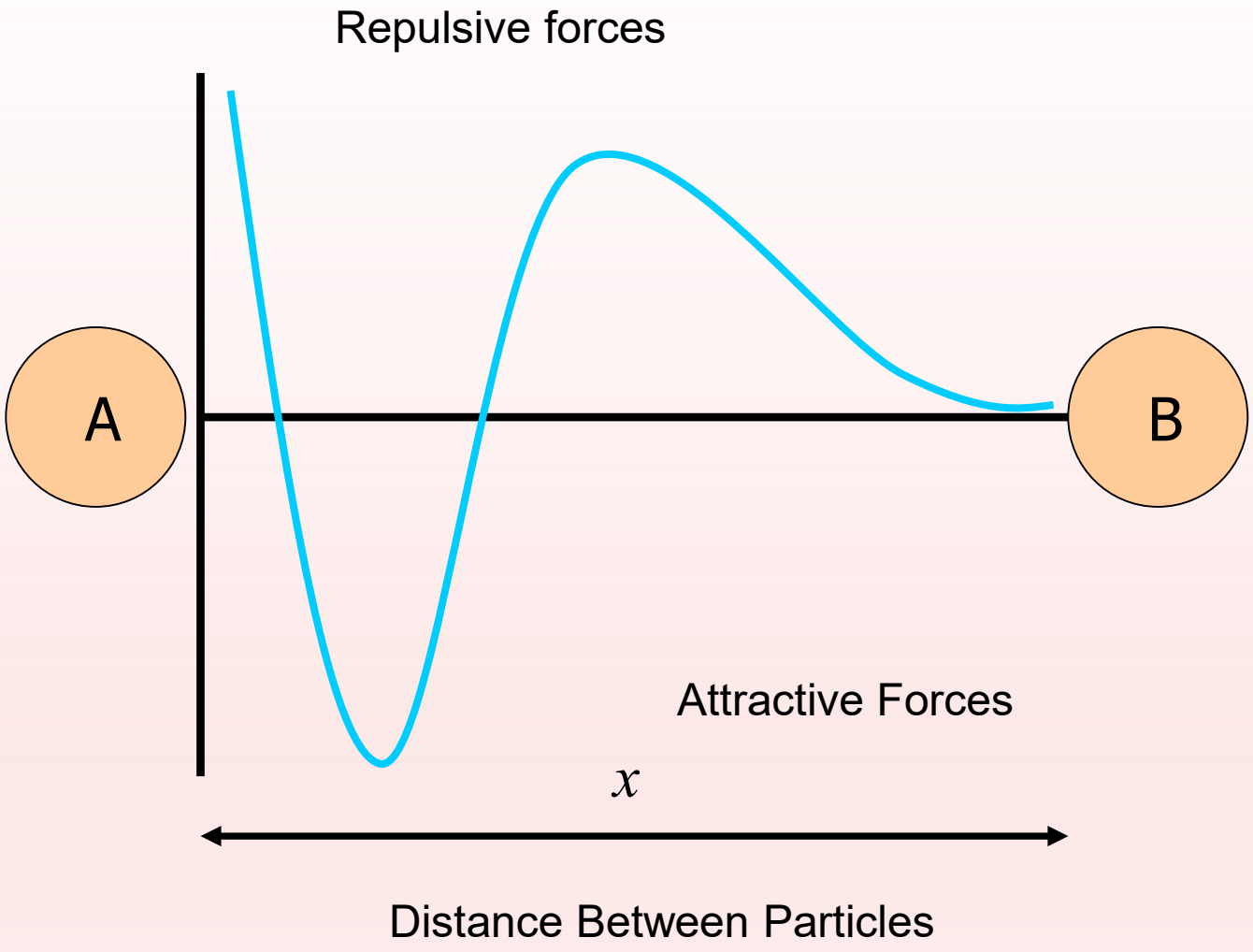
Substituting into the equation of V_T :

$$V_T = \tfrac{1}{2}(kr\varphi_0^2) - (A/12\pi H^2)$$

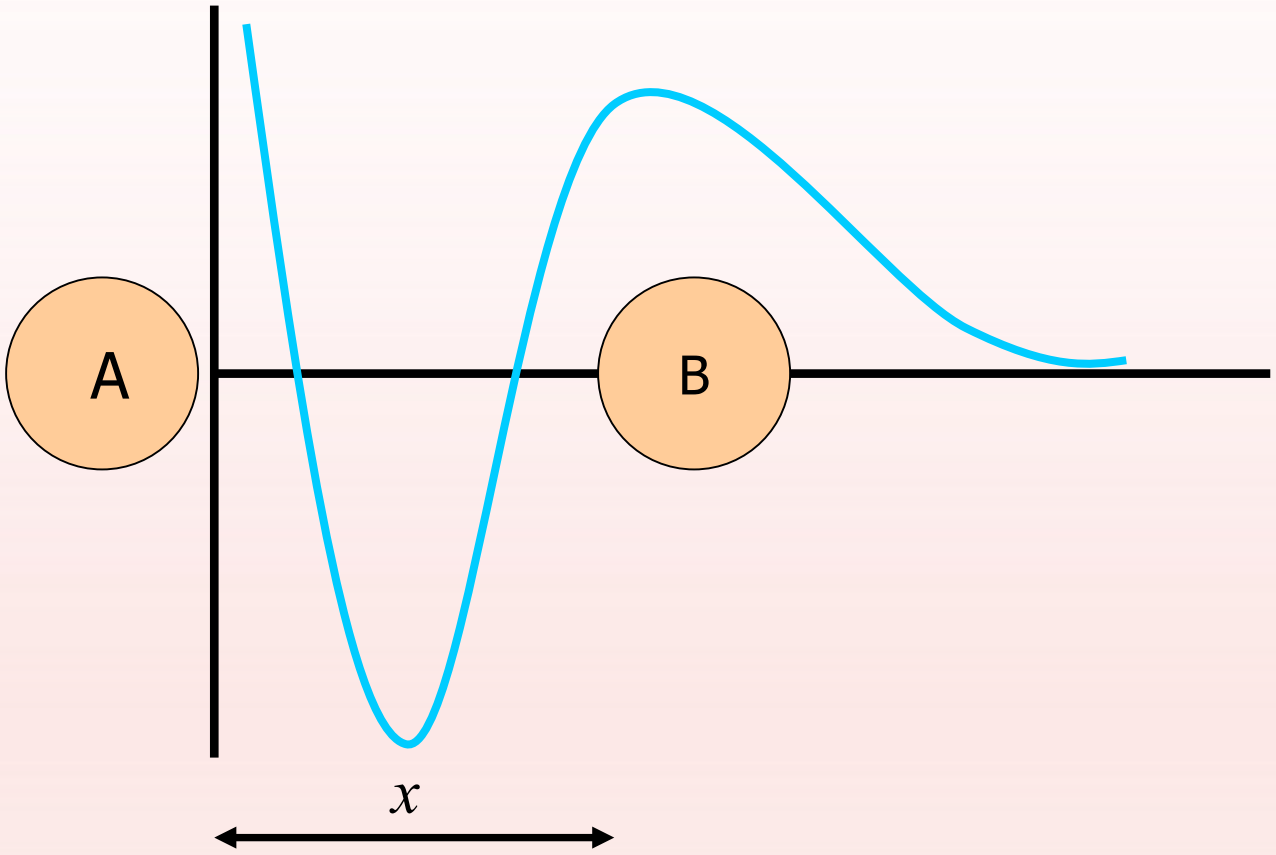
repulsion attraction

As *r* (radius of particles) decreases, the magnitude of the repulsive term in the equation for V_T decreases. This will cause H^2 in the attractive term to increase (which will also decrease the attractive term to a small degree). But overall, attraction will start to dominate. Result: flocculation!

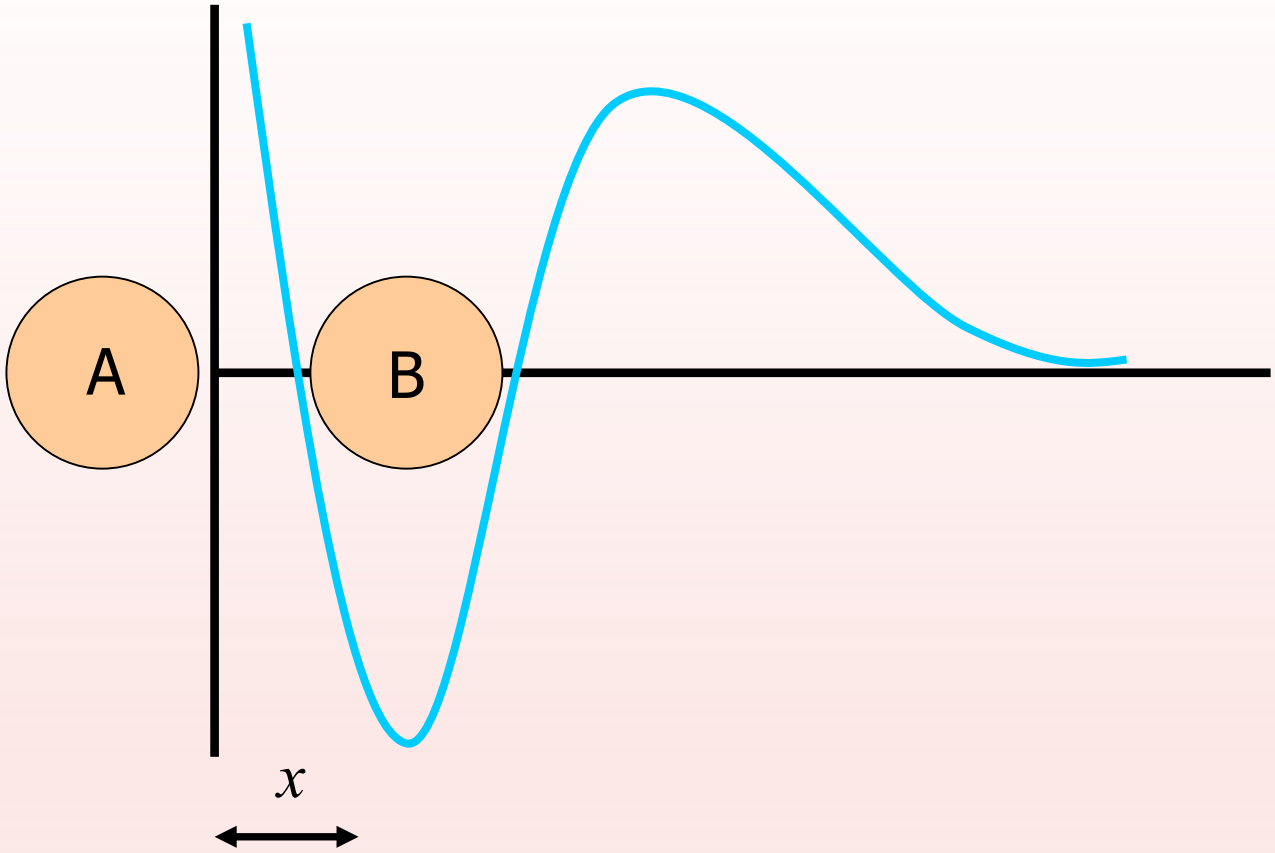
No Interaction Between Two Particles



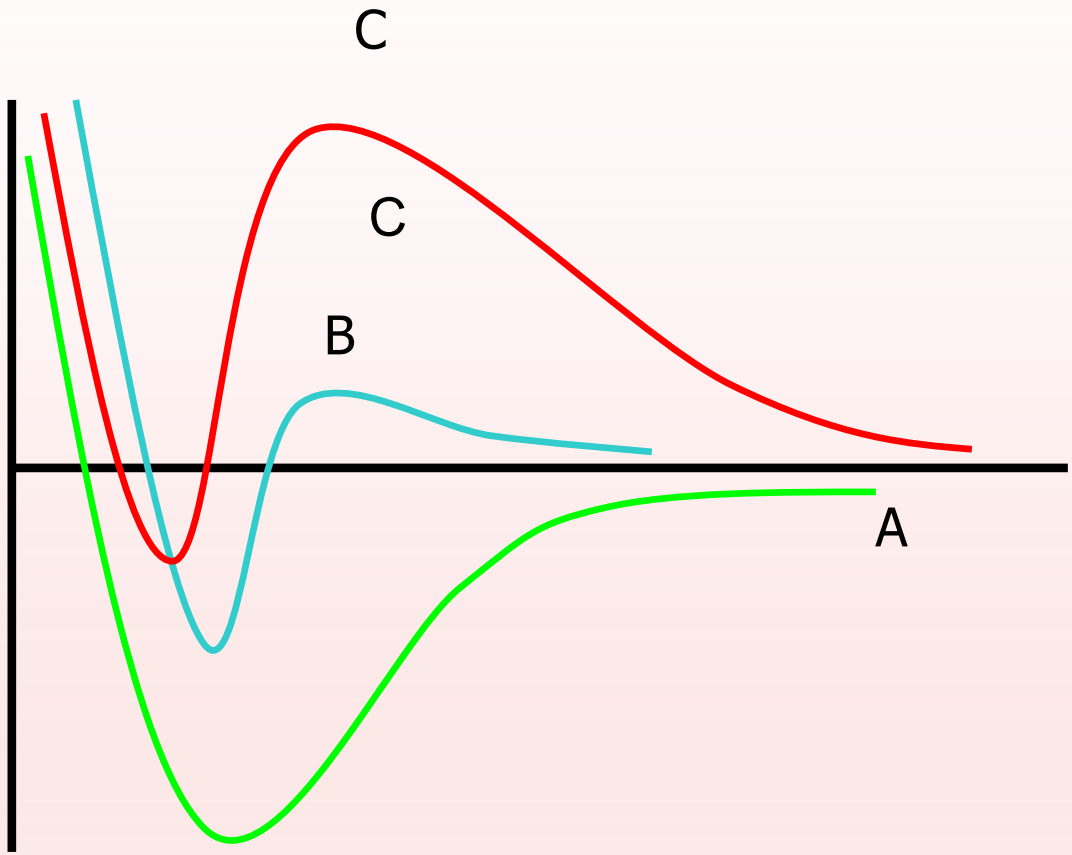
Repulsion Between Two Particles



Attraction Between Two Particles



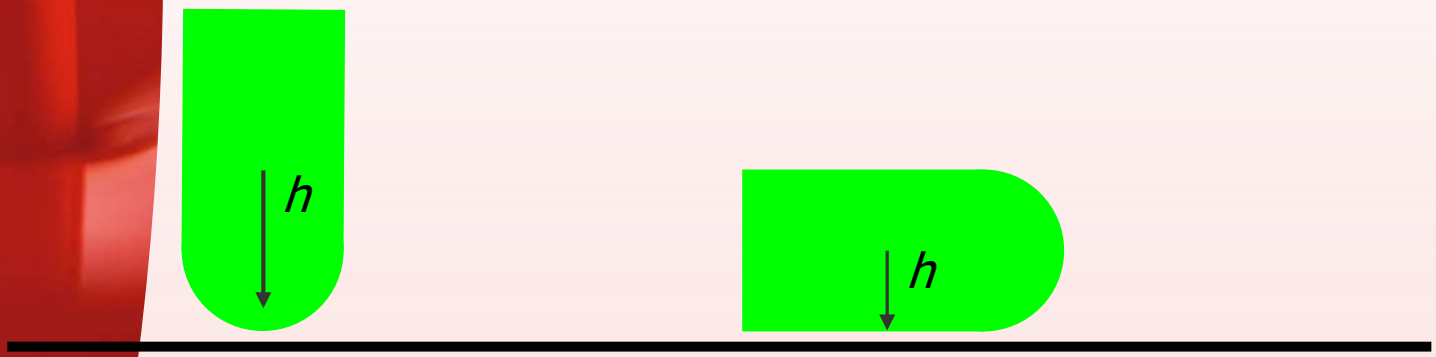
Other Energy Diagrams



Trying to make a “stable” dispersion…..

Is like trying to stand a rounded brick on end!

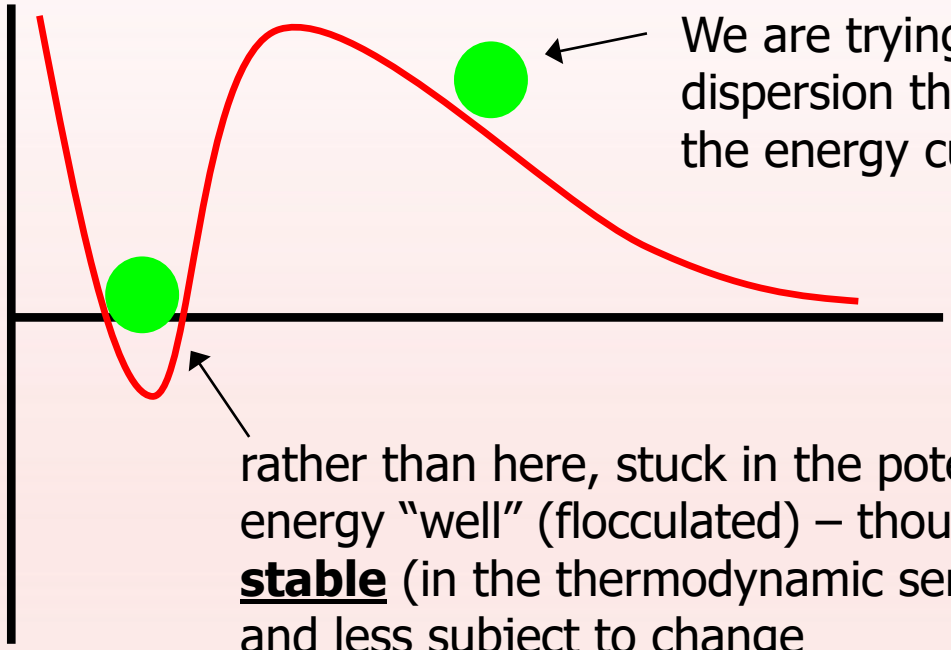
The potential energy of the brick = mgh



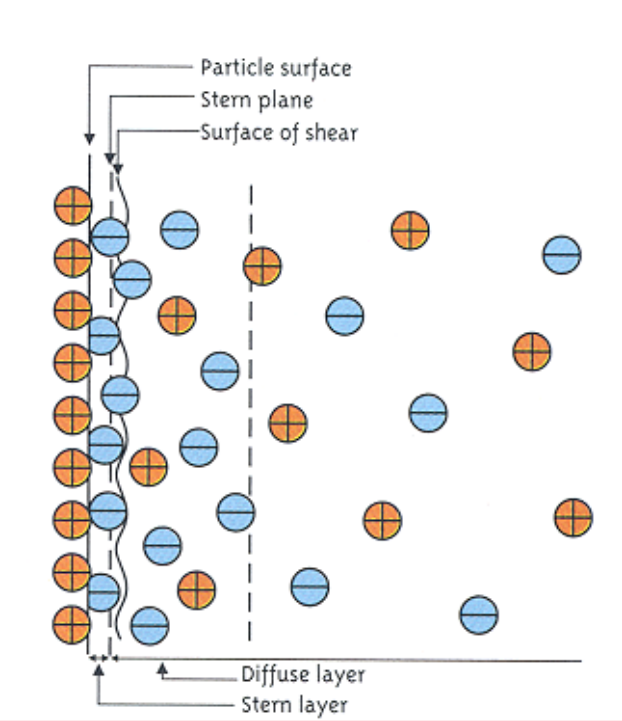
C.G. closer to ground = lower energy state – but this represents particle FLOCCULATION!

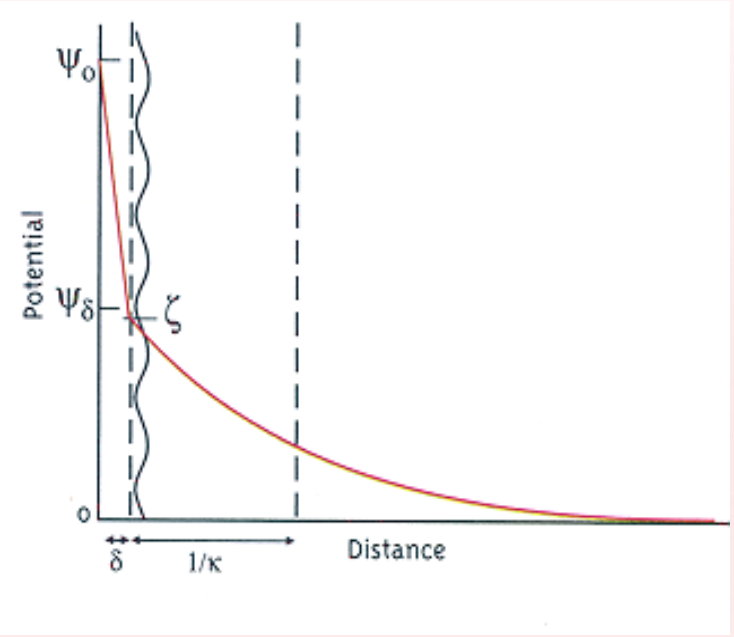
What We Call "Stability"

in making pigment dispersions is really a "metastable" state!



What is Zeta Potential?





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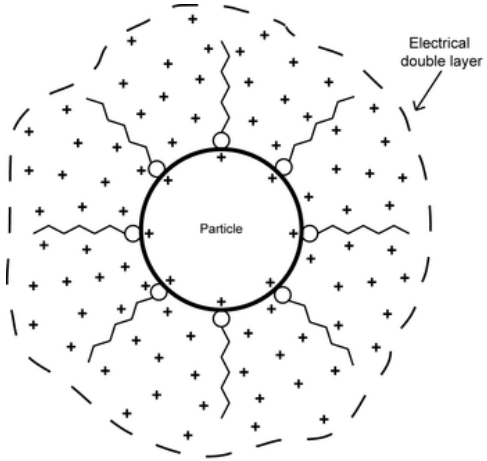
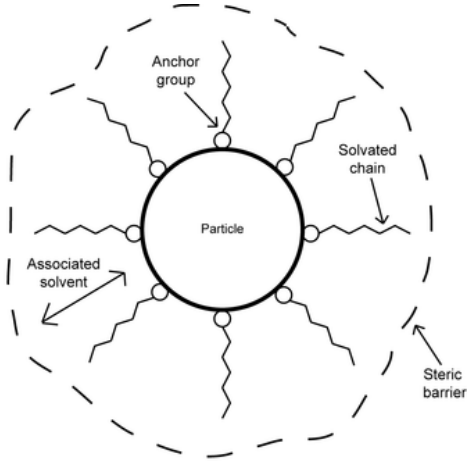
- Steric – uses physical barriers



Charge Stabilization

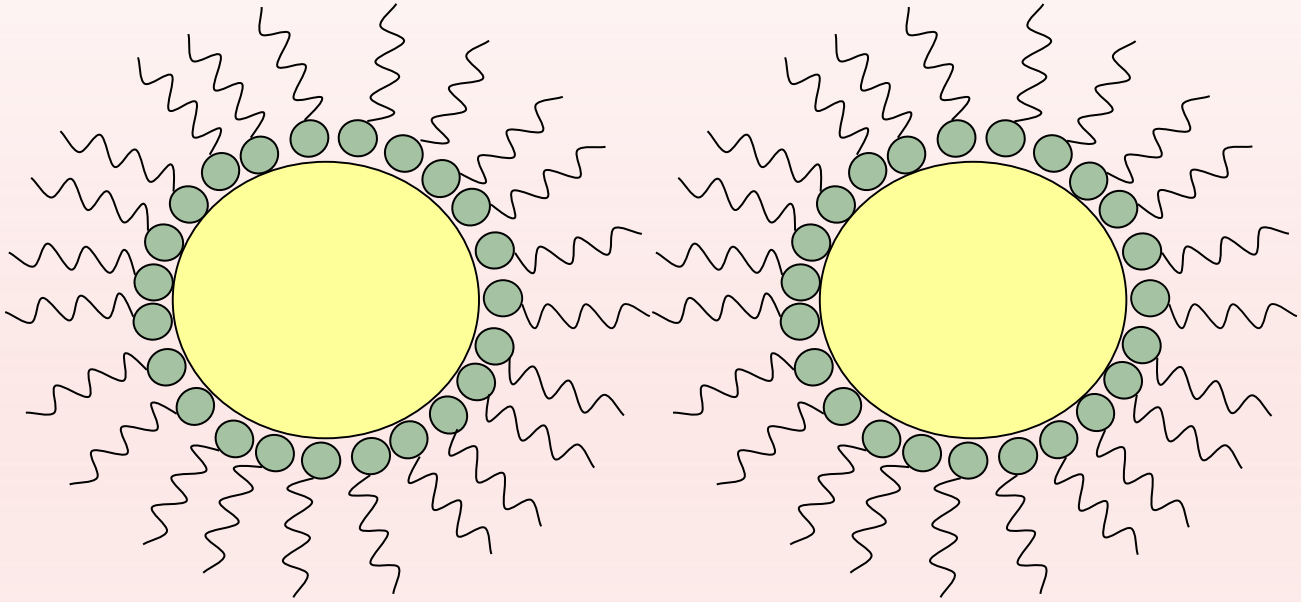


Steric or Entropic Stabilization

Steric Stability

Effective steric stabilization depends on:

1. High surface coverage
2. Efficient anchoring of adsorbed segments
3. Extended tails/loops
4. Good solvent environment for segments in tails

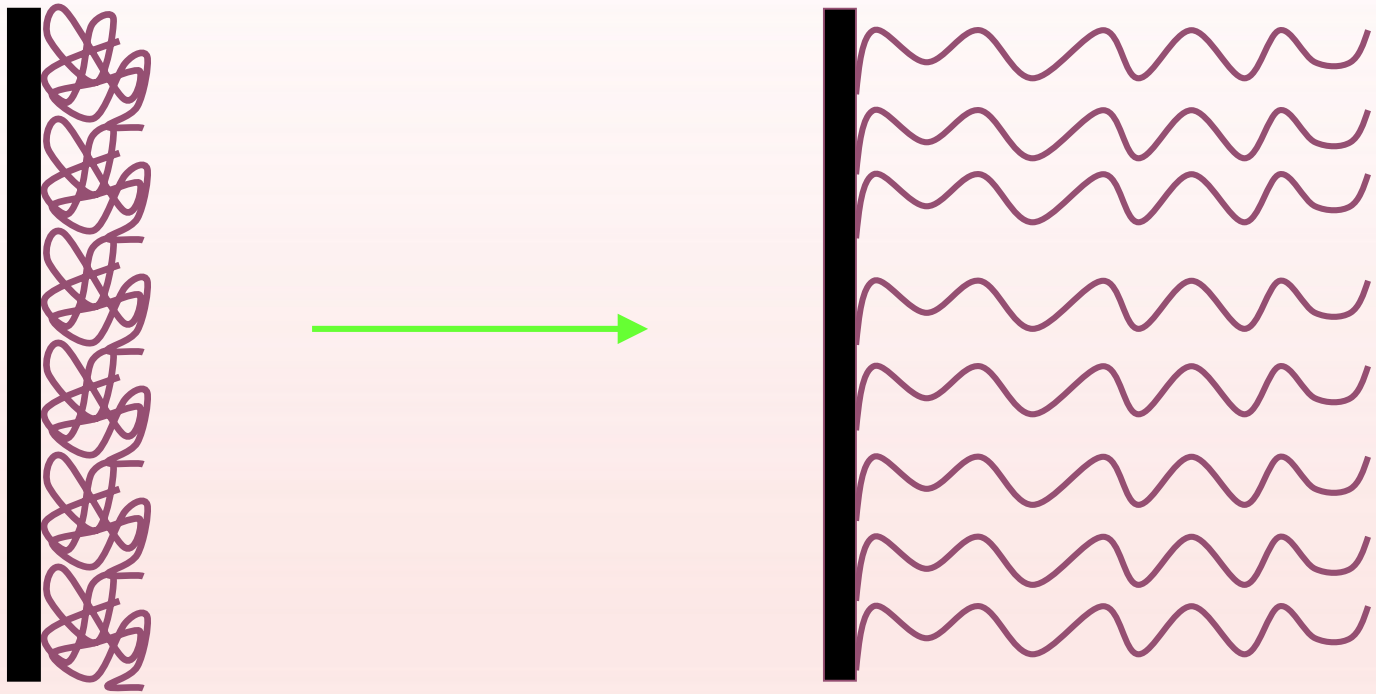


Steric Stability

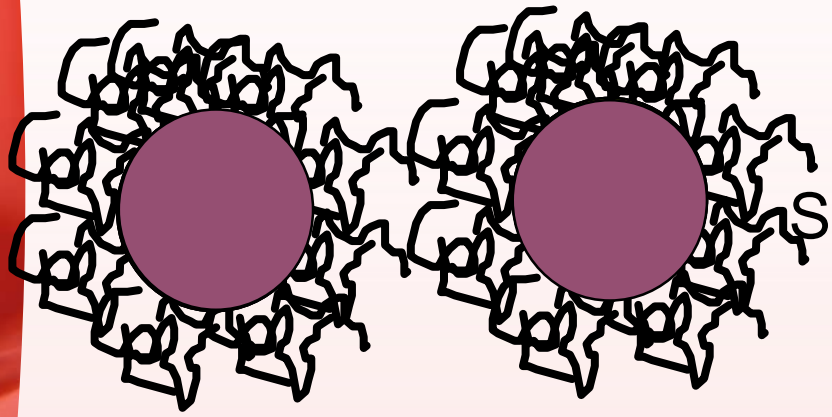
$$V_T = V^{el}_R + V_A + V^{st}_R$$

Adds a steric repulsion term to the equation for total interaction energy

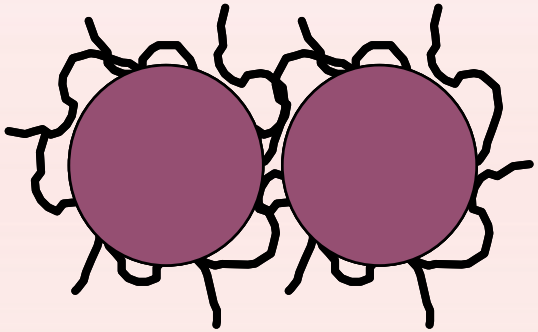
Steric Stability – Adsorption Layer Thickness



Adsorption Layer Thickness

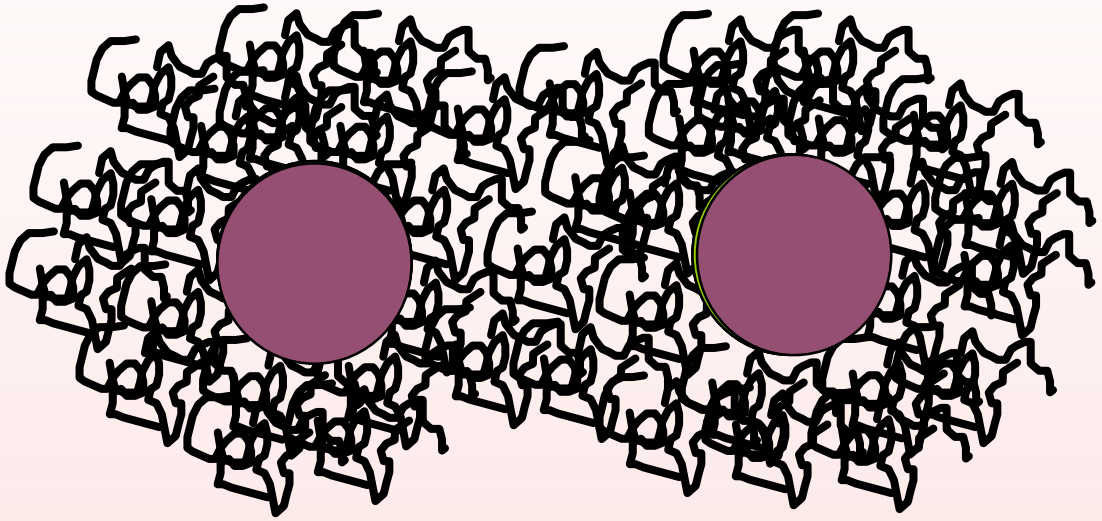


Steric Stability



Flocculation

Adsorption Layer Thickness

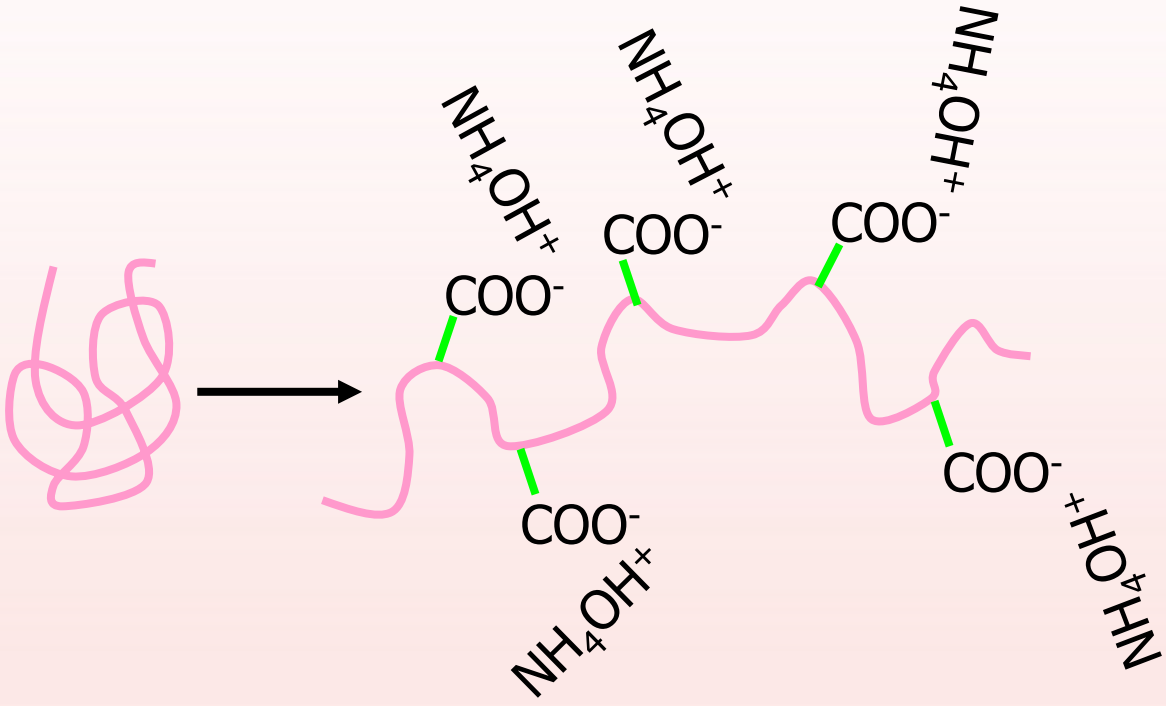


However, too thick an adsorption layer is not ideal, either!

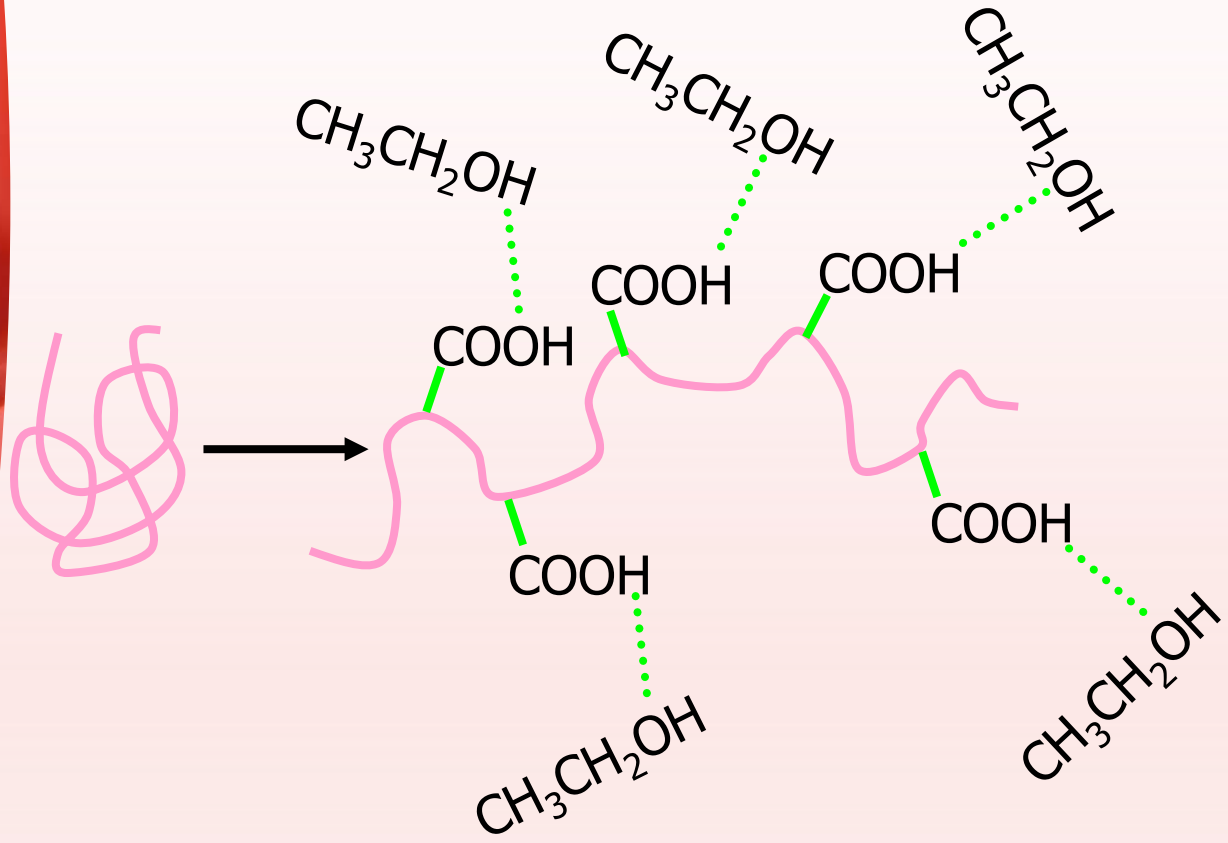
The Quality of the Adsorbed Layer at the Pigment Surface Depends On:

- Polymer solubility
- Polymer molecular weight
- Polymer conformation
- Polymer functional groups
- Pigment surface chemistry
- Temperature
- Competing species (surfactant)
- Intermolecular association (polymer)

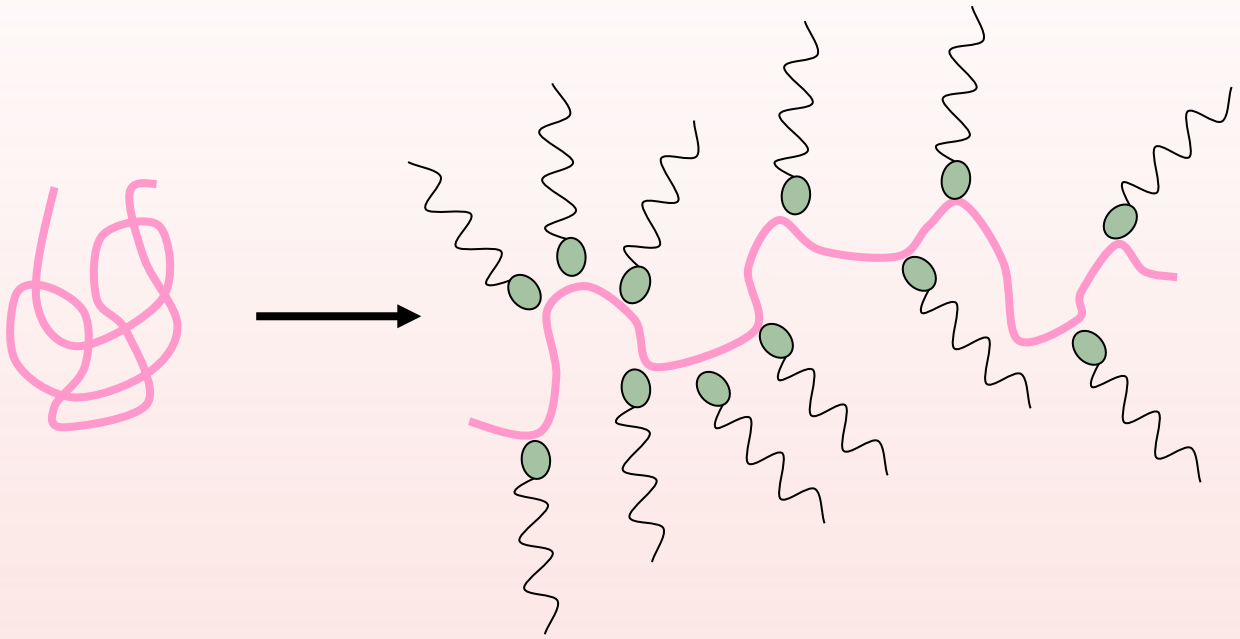
Polymer Solubility – via ionization



Polymer Solubility – via solvation



Polymer Solubility – via surfactant association



Liquid Inks: Effect of Surfactant Association on Solution Polymer Viscosities

	Viscosity, cps
Control	90,000
Anionic sulfate surfactant, 15 EO - A	11,120
50/50 A/B	14,220
Nonionic surfactant, 70 EO - B	26,690

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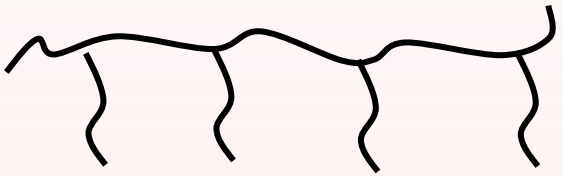
Polymer Conformation @ Pigment Surface

- Adsorbing sites (pigment)
- Adsorbable functional groups (polymer)
- Size and degree of branching of polymer molecule
- Accessibility of polymer functional groups (solubility)

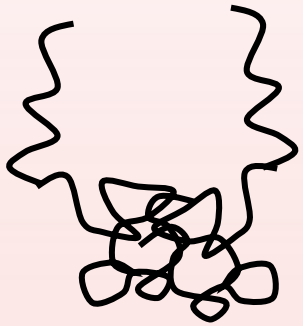
Single Point Attachment

Loop

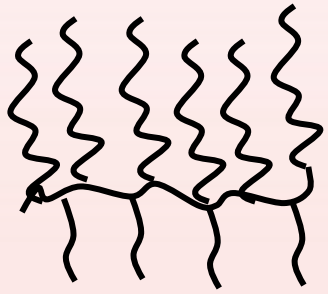


Train

Random Coil



Nonuniform Segment Dist'n



Multilayer

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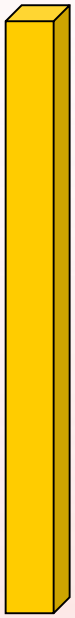
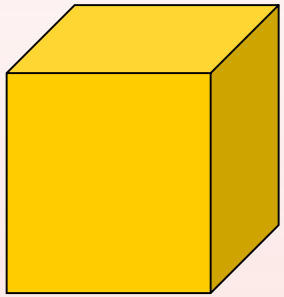
- Intermolecular association (polymer)

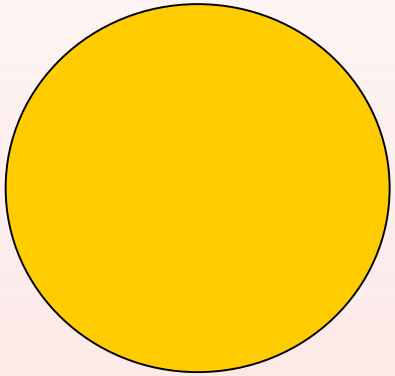
Pigment Chemistry Model – affects adsorption of polymer and dispersing additives



Rods: highly oleophilic



Cubes: oleophilic



Spheres: hydrophilic (inorganic pigments)

The Quality of the Adsorbed Layer at the Pigment Surface Depends On:

- Polymer solubility
- Polymer molecular weight
- Polymer conformation
- Polymer functional groups
- Pigment surface chemistry
- Temperature – can affect mobility of the adsorbing species
- Competing species (surfactant)
- Intermolecular association (polymer)

The Quality of the Adsorbed Layer at the Pigment Surface Depends On:

- Polymer solubility
- Polymer molecular weight
- Polymer conformation
- Polymer functional groups
- Pigment surface chemistry
- Temperature
- Competing species (surfactant) – can occupy sites that would be taken by polymer, due to the higher mobility of the low molecular weight surfactant species
- Intermolecular association (polymer)

The Quality of the Adsorbed Layer at the Pigment Surface Depends On:

- Polymer solubility
- Polymer molecular weight
- Polymer conformation
- Polymer functional groups
- Pigment surface chemistry
- Temperature
- Competing species (surfactant)
- Intermolecular association (polymer) – polymer sites may be more attracted to sites on adjacent polymer molecules, rather than to the pigment surface sites themselves

When Stability Is Not Attained: Causes of Flocculation

- Too much or too little dispersant present (bridging flocculation)
- Colloidal shock during letdown
- Presence of multivalent cations in the formulation (aqueous systems)

Summary

- Dispersed systems intrinsically unstable
- Flocculation is an attempt of the system to stabilize at lowest potential energy level
- Surface treatment of pigments can increase stability of dispersions by modifying interfacial chemistries
- Interaction of additives with polymers can improve dispersibility and dispersion rheology. Advantage: increased solids loading
- Adsorption on pigment surfaces is a DYNAMIC process

Theory versus Reality

- Theory is all well and good, but often practice takes precedence.
- Quicker to test than analyze for zeta potential
- Work with your pigment and dispersant suppliers to determine optimal materials and formulations.
- Key is to make sure that your testing in the lab will “scale” to the plant.

Dispersion Production

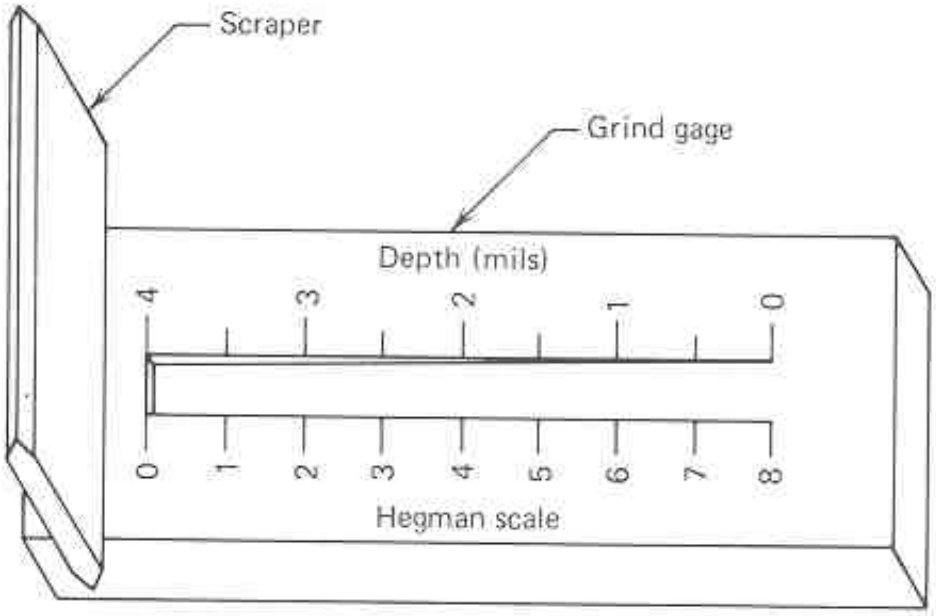
- Once formulation is developed, production control is necessary
- Temperature! (Gap distances, milling time, etc)
- Maintenance
  - Is there shot in the mill?
- Procedures

Pigment Dispersion QC

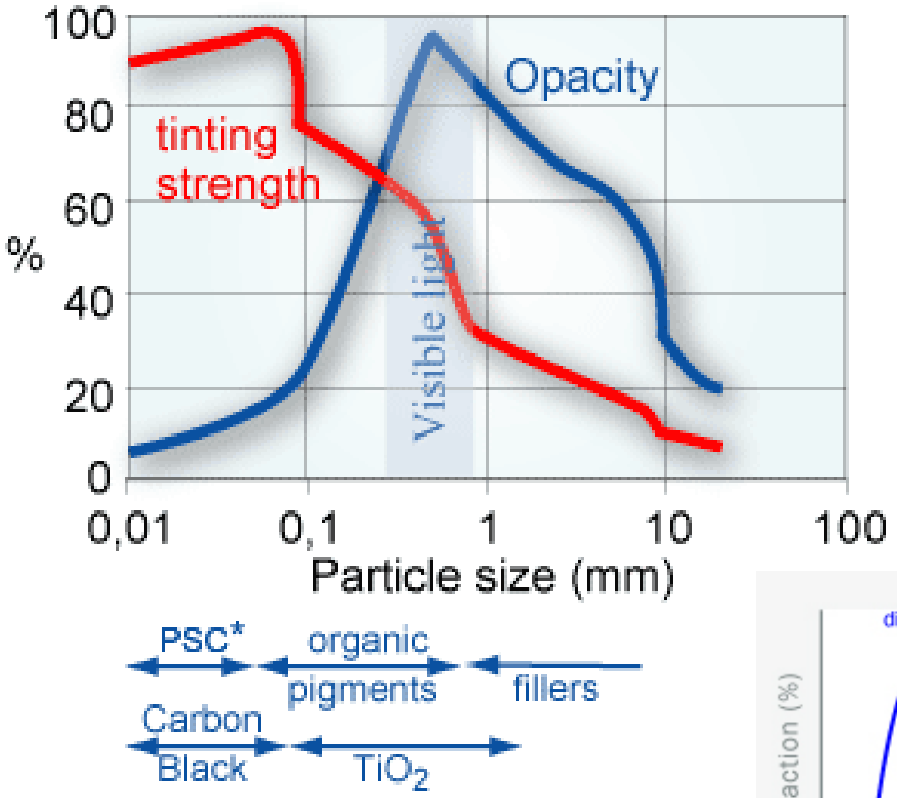
- Grind / Particle Size
  - Grind Gauge / Laser Diffraction
- Tint strength (color development) / Shade
  - Let backs and bleaching
- Gloss and transparency in finished ink
  - Opacity charts
- Viscosity
- Color and viscosity stability (time and temperature)
- Settling Studies
- Compatibility with ink vehicles
- Shock sensitivity

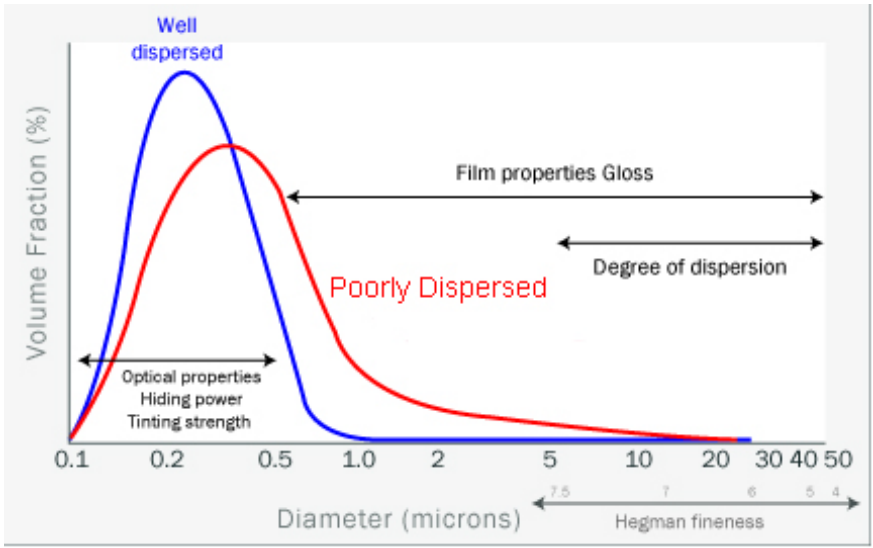
Grind / Particle Size Analyses

- Grind Gauges
- Sieve Analyses
- Laser Diffraction



Relationship of Particle Size to Strength and Opacity





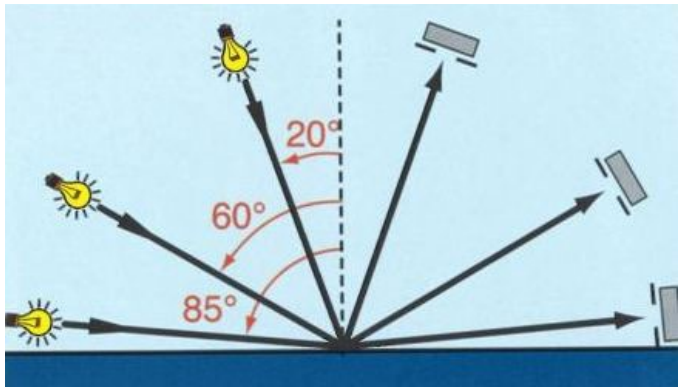
Tint Strength Assessment

- Paint shaker (liquid inks) or Hauschild (DAC) mixer (paste inks and liquid inks)
- 45.0/5.0 parts of white to dispersion (or whichever works for your facility)
- Make sure dispersion is compatible with base
- Commercial Flat White Tint Base or well controlled equivalent
- Paste ink tints have been made with standard NPIRI bleaching white or similar. Strength differences evaluated immediately to avoid floatation affects

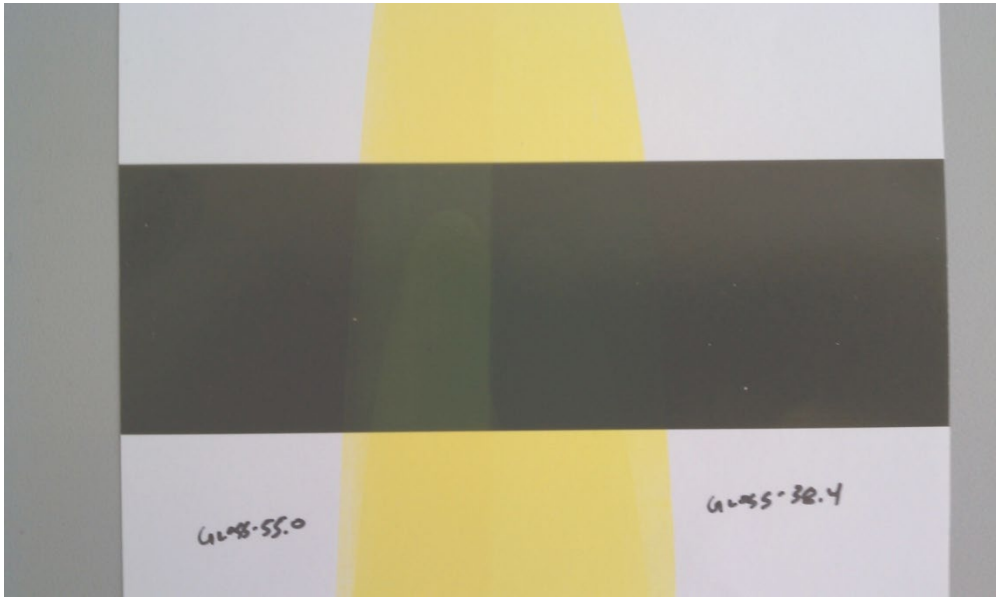
Testing Dispersion Quality

- Grind
- Tint strength (color development)
- Gloss and transparency
- Viscosity
- Color and viscosity stability (time and temperature)
- Compatibility with ink vehicles
- Shock proof

Gloss and Transparency



Gloss and Transparency



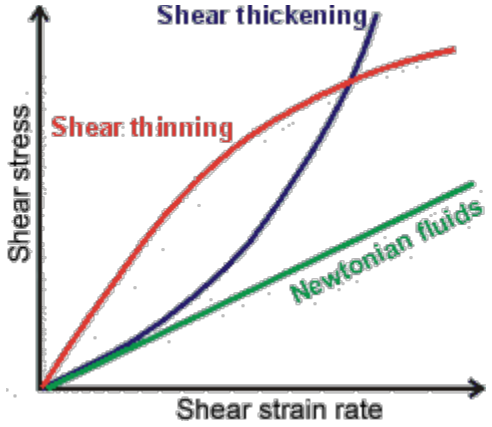
The more well-dispersed the pigment, the better the transparency will be! (for whites, the reverse is often true: better dispersion equals better opacity).

Viscosity – Resistance to Flow

- Newtonian
  - Visc not affected by shear rate
- Non-Newtonian
  - Pseudo-plastic (shear thinning)
    - Viscosity reduces with shear
  - Dilatant (shear thickening)
  - Plastic
    - Requires initial stress for flow than constant
  - Thixotropic
    - Viscosity reduces over time at constant stress

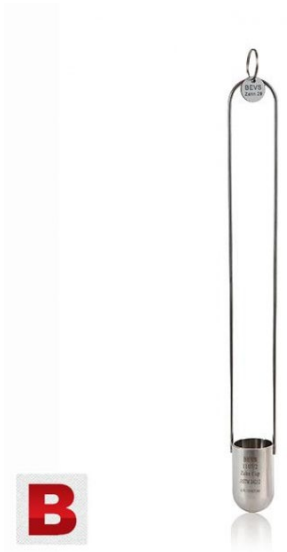
Viscosity / Rheology

- Basic
  - Flow Cups (zahn, din, shell, etc.)
  - Flow plates
- Intermediate
  - Rotational
  - Falling Body
- Advanced – (Non-Newtonian)



Flow cups

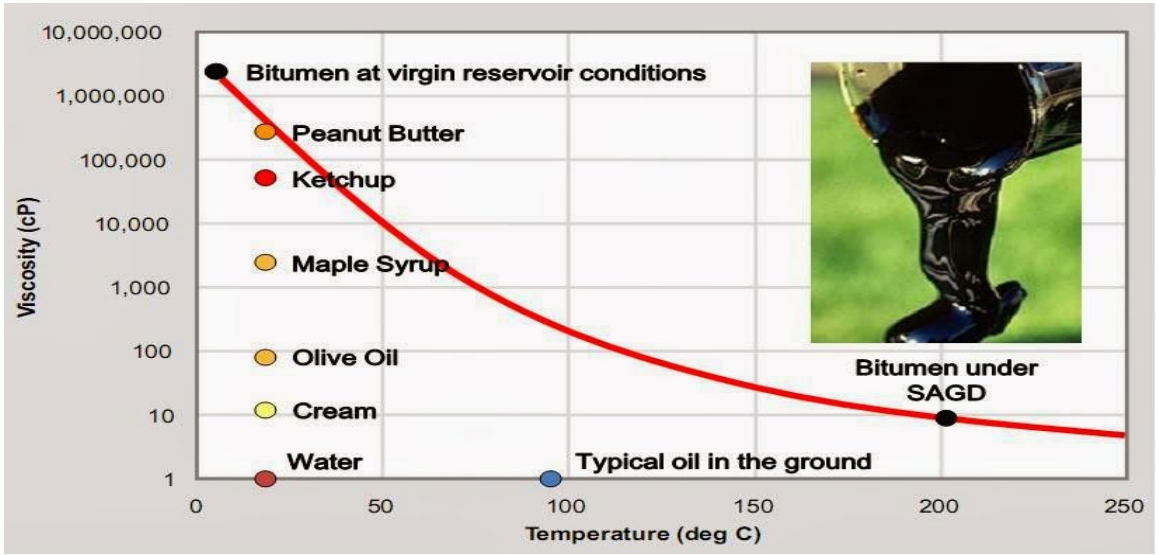
- Measure time of flow as a function of a certain outlet diameter and volume. (seconds)
- MUST be calibrated. Not all are equal.



Rotational Viscometer – Liquid Inks

*** Viscosity & Temperature ****

- Remember that viscosity will definitely be affected by temperature!
- Measurements must be made at consistent temperature.



Testing Dispersion Quality

- Grind
- Tint strength (color development)
- Gloss and transparency in finished ink
- Viscosity
- Color and viscosity stability (time and temperature)
- Compatibility with ink vehicles
- Shock proof

Color Strength Viscosity Stability

- Check initial tint strength and cup/Brookfield/Laray viscosity
- Place tightly closed samples at elevated temperature (120F or 140F) for one week
- Check for loss (or gain) of color, change of color, rise in viscosity

Testing Dispersion Quality

- Grind
- Tint strength (color development)
- Gloss and transparency in finished ink
- Viscosity
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Compatability with Ink Vehicles

- After the dispersion is fully processed, it is combined with other materials (the “letdown” components) to make the finished ink
- Assess rheological behavior and color properties when combined with different ink vehicles
- An adverse rise in viscosity/pseudoplasticity often occurs when a dispersion is less compatible with a given vehicle
- For liquid inks, alcohols, surfactants, defoamers, glycols, and glycol ethers can all affect how a letdown vehicle interacts with a pigment dispersion. Consider modifications in these areas before overhauling the entire system

Testing Dispersion Quality

- Grind
- Tint strength (color development)
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- Viscosity
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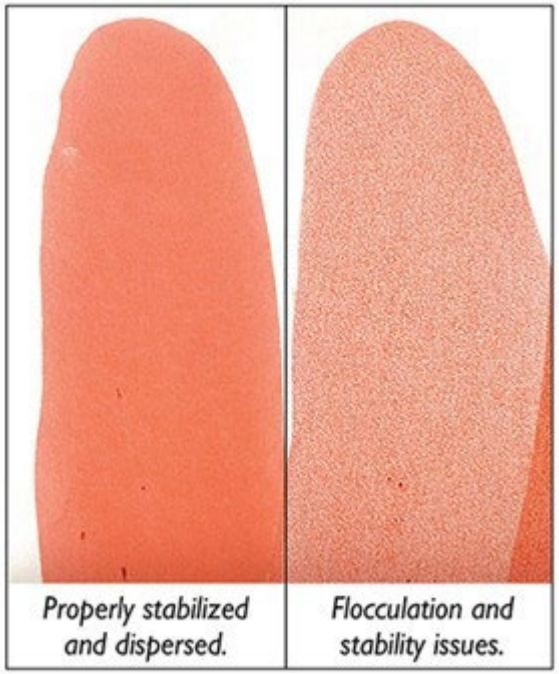
Checking Shock Stability

- Consequence of poor dispersion quality and/or stability
- Usually only a factor in lower viscosity (i.e. *liquid*) inks
- Can occur in high pigment:binder formulations, e.g. 5:1 and higher
- Increases opacity
- Decreases gloss
- Increases settling
- Decreases color strength
- Increases pseudoplastic behavior



Conclusions

- Making a dispersion is easy. Making a STABLE dispersion takes knowledge, patience, and work.
- Don’t skimp on the Premix! Trying to rush the process will only make things worse
- Optimize particle size. A narrow distribution is always better than a broad one
- Formulate the dispersion for stability, Be aware of pigment to binder ratios and/or surfactant loading
- Make sure dispersion is suitable for application

Questions?

If you are interested in learning more, I can be reached at

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Thank you!