Dispersants –

An overview on their purpose, value, and application

Tony Moy, September 11, 2018

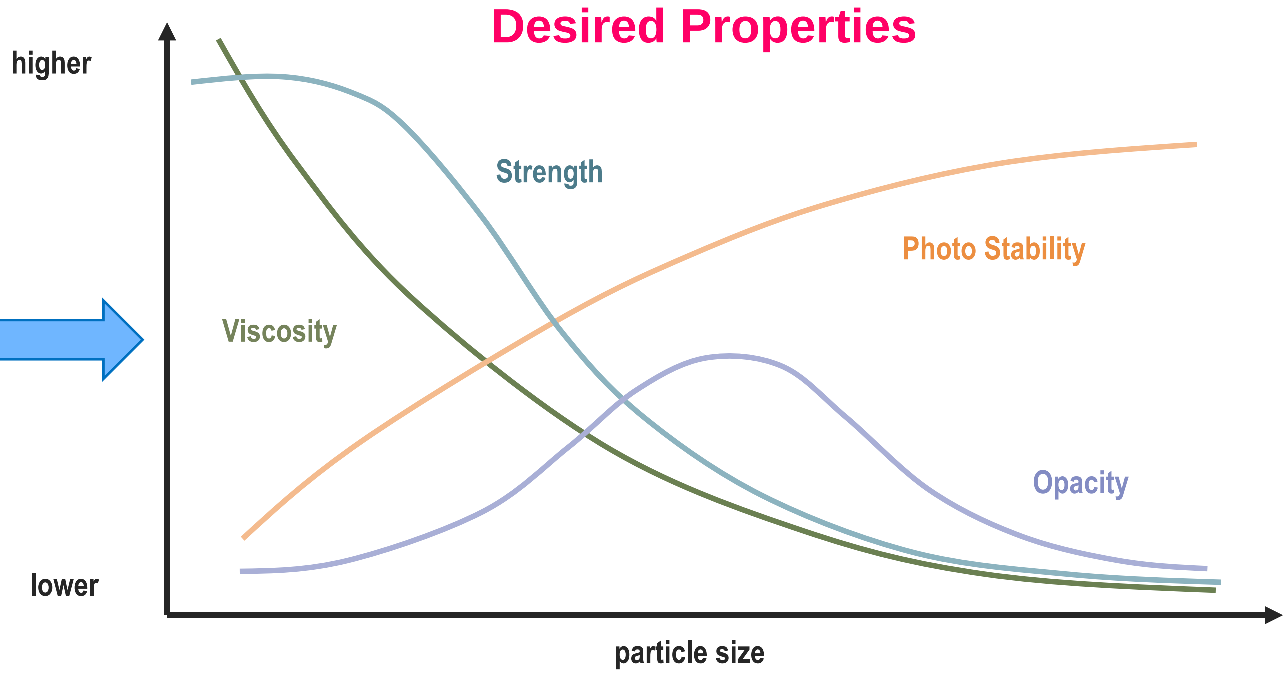
Agenda

- What are dispersants?
- Why use dispersants?
- How do dispersants work?
- Dispersant types, associated pigment applications, and considerations
- Optimizing dispersant concentration/level in a formulation
- Process considerations
- Examples of dispersant applications
- Questions?

What are Dispersants

What are Dispersants?

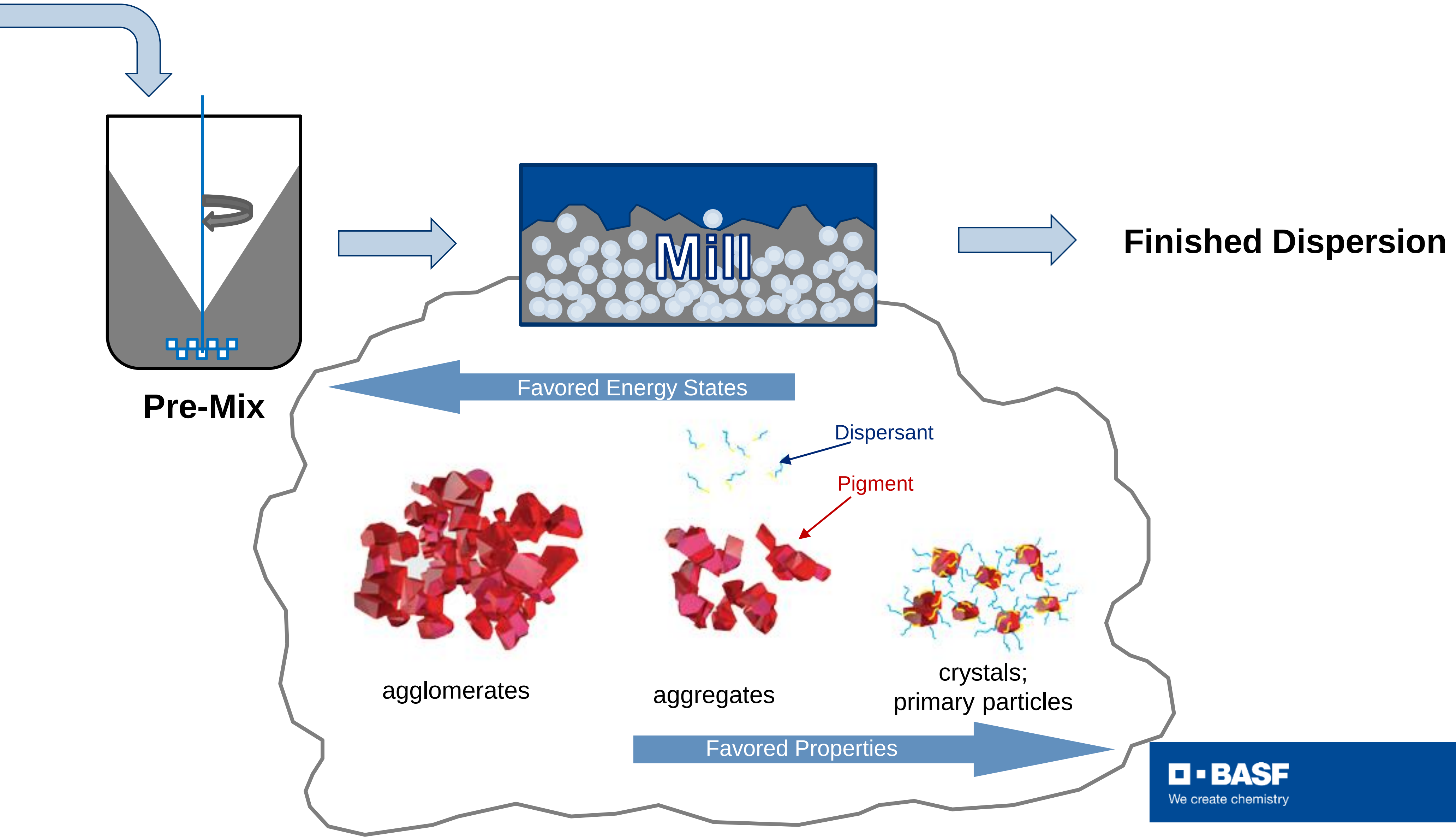
- **Dispersants** are chemical substances that serve to **stabilize** solids/**particles** (pigments) in a liquid **dispersion**/suspension
- In the coatings industry these are in the form of: surface actives (surfactants) and polymers



Making a Dispersion

Raw Materials

- Water/solvent
- Dispersant
- Other Additives
- Resin



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Why use Dispersants?

Value of Dispersants

- Minimize interaction of pigments
  - Reduce viscosity
  - Enhance stability of pigment and dispersion
  - Reduced settling and kick out
  - Maximize performance contribution of pigments (color, protection, etc.)
  - Minimize the amount of pigment required to do the job ($$$)
- More formulation latitude: ability to load more (solids) into formulation
  - Introduce filler/extender pigments
  - Use less resin to achieve mechanical properties
  - Use less primary pigment ($$$)
- Productivity ($$$)
  - Shorter dispersion time
  - Transfer product with less energy and time

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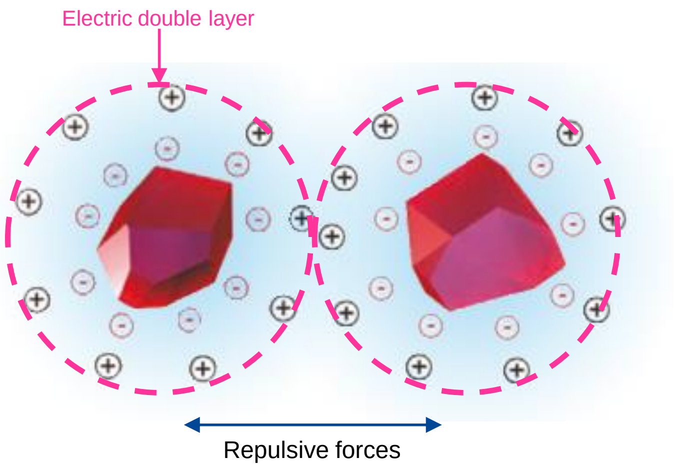
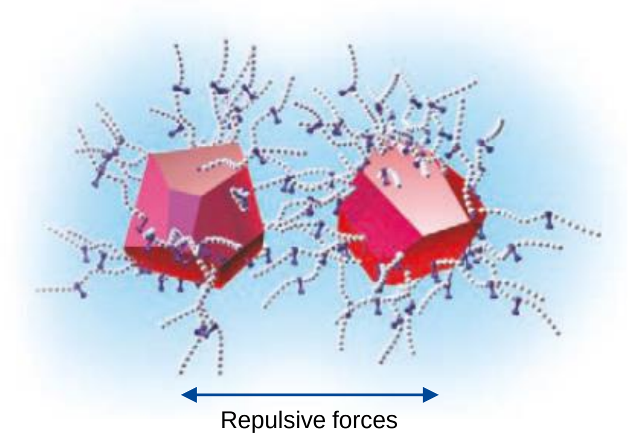
How do Dispersants work?

Dispersant Mechanisms

- Electrostatic
  - Dispersant attaches to pigment and establishes electric double layer causing repulsive forces



- Steric
  - Dispersant attaches to pigment and has segments which stand out from pigment surface to provide mechanical repulsive forces

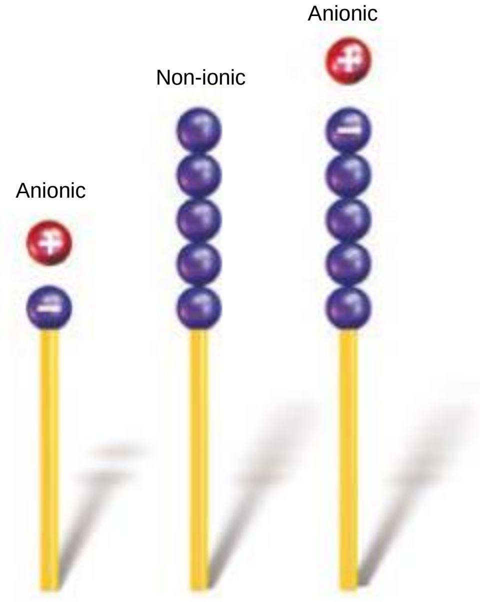


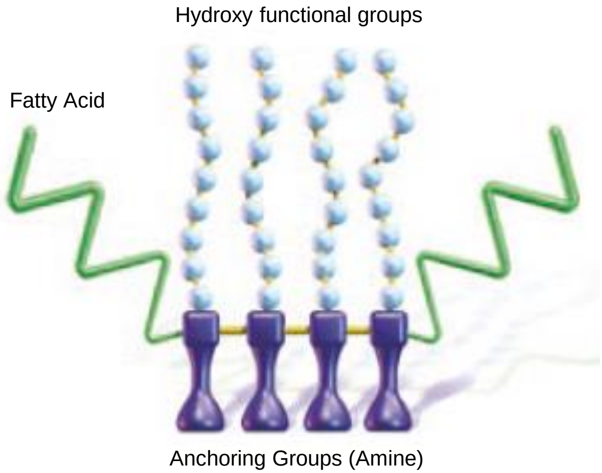
- Electrosteric
  - A combination of both

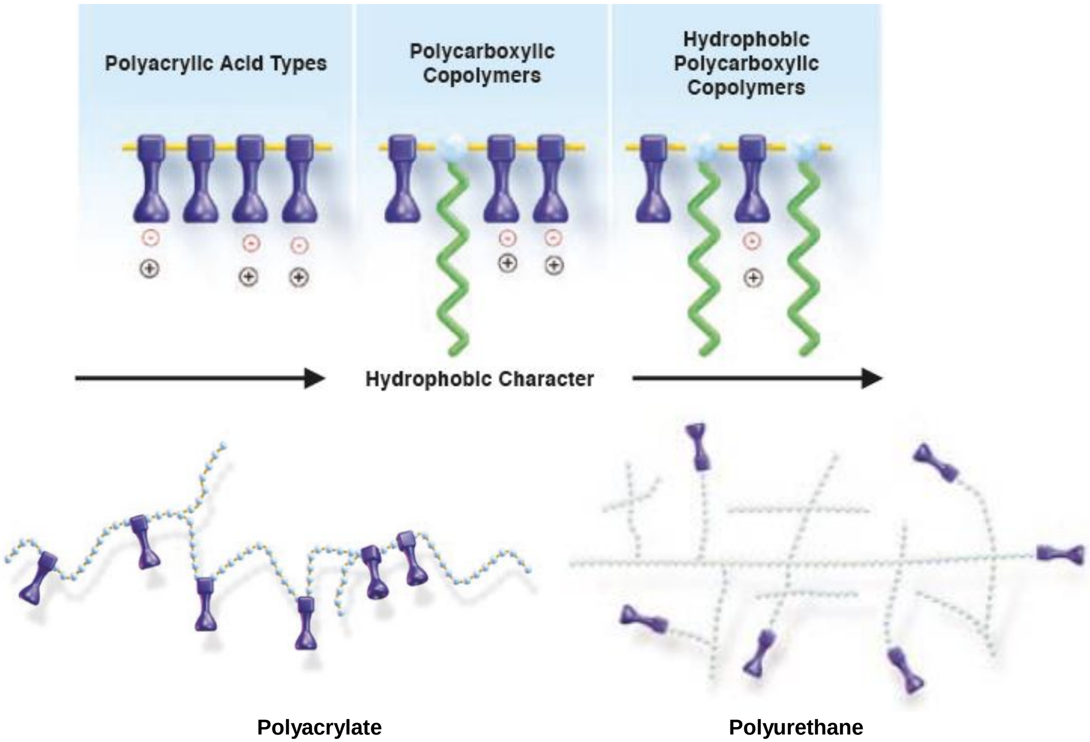
- Ultimately the force of repulsion created by dispersant must overcome the attractive forces of the pigment particles to realize a stable state

Types of Dispersants

Types of Dispersants







Low Molecular Weight

- Surfactant Types
  - Ionic and Non-ionic

MW < 1000

Examples:
- Sulfates/sulfonates
- Phosphate esters
- Fatty acids
- Quaternary ammonium/Imidazolium salts

Oligomeric Medium Molecular Weight

- Fatty Acid Modified Ester
  - Anionic

MW: 1000 - 3000

High Molecular Weight

- Polyacrylic Acid
- Polycarboxylic Copolymers
- Polyacrylates
- Polyurethanes

MW > 5000

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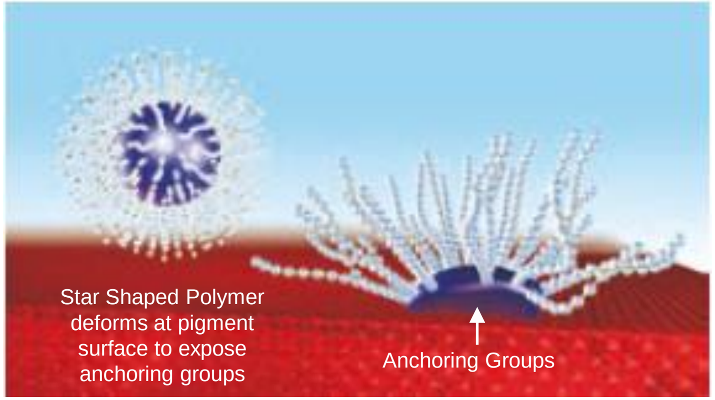
Types of Dispersants



Star Shaped Polymer

Block Copolymer

Advanced High Molecular Weight

- Star Shaped Polymers
- Block Copolymers via Controlled Free Radical Polymerization (CFRP)

MW > 5000

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Selecting a Dispersant

Selecting a Dispersant

- Key Questions to consider when selecting/using dispersants

1. What is being dispersed?
2. What is it dispersed in?
3. How is it dispersed?
4. What is the objective?

Dispersant(s) to trial

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Consideration No. 1: What is being dispersed?

- Pigments
  - Inorganic, Organic, or both together?
  - Type, Grade, Color Index
  - Surface Treated?!
- Clay
  - Ceramics, e.g. via “slip casting”
- Calcium Carbonate
  - Recovery from waste water
- Catalysts
  - For further processing as slurry

Consideration No. 2: What is it dispersed in?

- Water
  - What is the pH? Is it neutralized?
- Solvent (blend)
  - What is the polarity?
- 100% System
  - What’s the Chemistry (EP, PU, …)?

The dispersant must be compatible with the medium in which it is dispersed!

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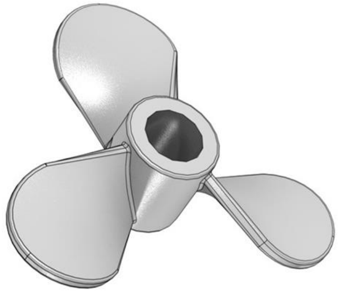
Consideration No. 3: How is it dispersed?



Paddle Blade (Low Shear)

Cowles Blade

Roller Mill

Vertical Sand Mill

Horizontal Mill

Basket Mill

Typically, the type of pigment will dictate what is required

Consideration No. 4: What is the objective?

<u>Process Aid</u>

- Improved pigment wetting
- Increased mill efficiency
- Viscosity control

<u>Performance</u>

- Increased color strength
- Improved compatibility
- Higher gloss
- Stability

<u>Formulation Effect</u>

- Higher pigment loading
- Improved color stability
- Improved rheology control
- Improved economics

Typically, coatings must be a balance of several objectives;
Dispersant types and level of usage must be chosen accordingly!

Selecting a Dispersant: General Guidelines – Pigments & Benefits

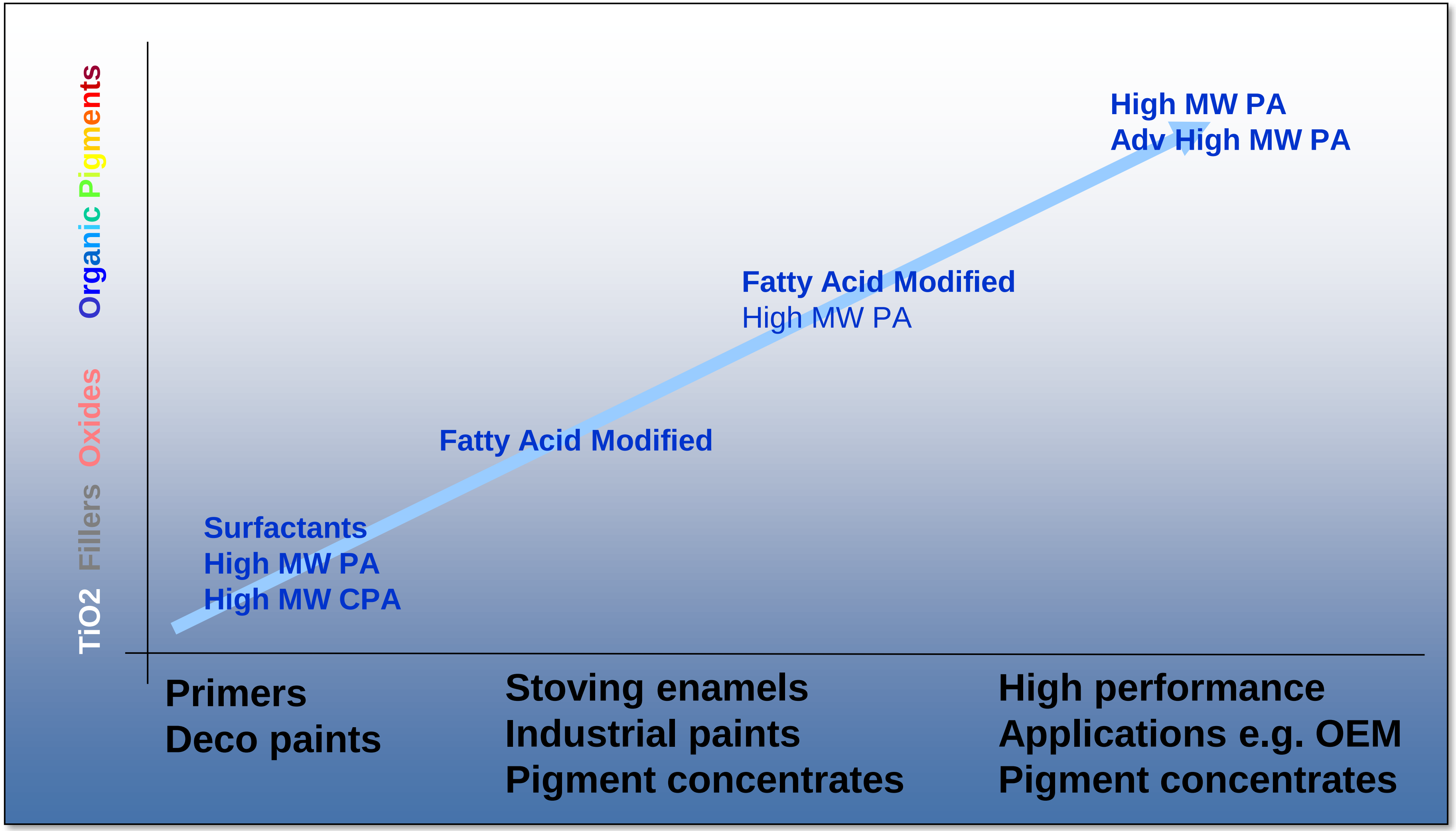
- **Ionic Dispersants:**
  - Fillers, extenders, TiO_2
  - Economic solutions
  - Combined with resin

- **Medium MW dispersants and smart blends:**
  - Broadest compatibility
  - Universal application

- **LMW dispersants:**
  - Fillers, extenders, TiO_2
  - Economic solutions with less demand for performance
  - Combined with resin or HMWD
  - Solvent and water borne

- **HMW dispersants:**
  - For organic and inorganic pigments
  - Lowest viscosities
  - Highest color strength
  - Highest gloss

Dispersants – Pigments – Applications
Water-based



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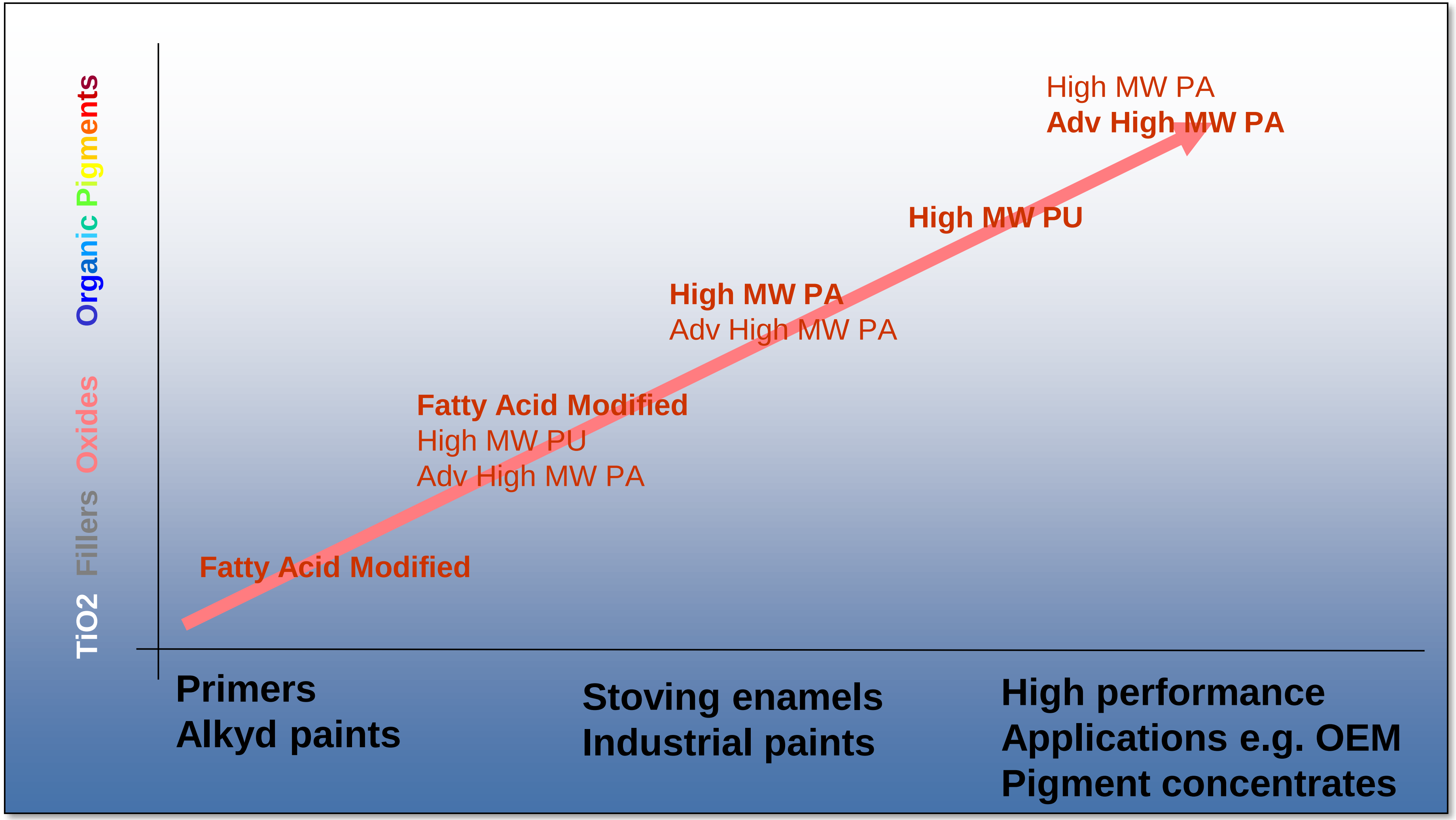
Dispersants – Pigments – Applications
Solvent-based



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Dispersant Application Recommendations by Market/Industry

<table>
<tr><th>Application Markets</th><th colspan="2">Recommended Products for Given Application Types</th></tr>
<tr><td>Architectural / Deco</td><td>Interior decorative coatings (WB)
- High MW Polyacrylic Acids
Exterior decorative coatings (WB)
- High MW Copolyacrylates</td><td>Trim paints (SB)
- Fatty Acid Modified
Trim paints (WB)
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer</td></tr>
<tr><td>Industrial Coatings</td><td>Can & Coil Coatings (SB)
- High MW Polyacrylates
- Adv High MW Polyacrylates
Furniture & Flooring Coatings (WB/SB)
- Fatty Acid Modified
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer</td><td>Industrial Maintenance (WB/SB)
- High MW Polyacrylates
- High MW Polyurethanes
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer
Marine Coatings (SB)
- Fatty Acid Modified
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer
Industrial Mixing Systems
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer
- Grind Resins</td></tr>
<tr><td>Automotive OEM</td><td colspan="2">To achieve best jetness and blue undertone with carbon black pigments (WB/SB)
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer</td></tr>
<tr><td>Printing & Packaging</td><td>WB pigment concentrates and inks
- High MW Polyacrylates
- High MW Polyurethanes
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer
- Wetting Agents</td><td>SB ink formulations
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer
- Grind Resins
UV curable inks (SF)
- Adv High MW Polyacrylates
- Adv High MW Block Copolymer</td></tr>
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BASF Dispersant – Pigment Reference
Some suggestions/starting points

Pigment Type	Water	Solvent	Solvent-free
White	Dispex AA 4144 Dispex CX 4230/4320 Dispex Ultra PX 4585	Efka FA 4608/4609/4620 Efka PU 4010/4047 Efka PX 4330	Efka FA 4608/4620
Inorganic Fillers	Dispex Ultra FA 4420/4431/4483 Dispex AA 4135/4140/4144	Efka FA 4609/4620/4642	Efka FA 4620/4642 Efka PU 4046
Aluminum, Pearls (Mica)	Efka FA 4620 Dispex Ultra FA 4437	Efka FA 4609/4620 Efka PU 4047	Efka FA 4620/4665 Efka PU 4046
Black (Organic)	Dispex Ultra PX 4585	Efka PX 4310/4320	Efka PX 4731 / 4732 / 4733 / 4751+Efka MI 6745
Blue (Phthalo)	Dispex Ultra PX 4585	Efka PX 4350/4751+Efka MI 6745	
Violet (Quinacridone)	Dispex Ultra PX 4585	Efka PX 4310	
Red (DPP)	Dispex Ultra PX 4585	Efka PX 4310	
Red (Quinacridone)	Dispex Ultra PX 4585	Efka PX 4310	
Green (Phthalo)	Dispex Ultra PX 4585	Efka PX 4350/4751+Efka MI 6745	
Yellow (Isoindoline) (Benzimidazalone) (Bizmuth Vanadate)	Dispex Ultra PX 4550 (B, BV) / 4585 (I, B)	Efka PA 4401 (I, B) Efka PX 4330 (I, B, BV)	Efka PX 47** series (I,B)
Trans Iron Oxide (Red, Yellow)	Dispex Ultra PX 4550/4575	Efka FA 4608/4609/4620 Efka PA 4401 Efka PX 4330	Efka 4608/4620

Pigment Grinding Reference

Pigment Type	Grind	Grind Equipment
White	Easy	HSD or Sandmill
Inorganic Fillers	Easy	HSD
Aluminum, Pearls (Mica) – Effect Pigments	Don’t grind	Paddle mixer
Black (Organic)	Difficult	HSD Premix + High Energy Mill
Blue (Phthalo)	Difficult	HSD Premix + High Energy Mill
Violet (Quinacridone)	Difficult	HSD Premix + High Energy Mill
Red (DPP)	Difficult	HSD Premix + High Energy Mill
Red (Quinacridone)	Moderate to Difficult	HSD Premix + High Energy Mill
Green (Phthalo)	Difficult	
Yellow (Isoindoline) (Benzimidazalone) (Bizmuth Vanadate)	Moderate	Sandmill
Trans Iron Oxide (Red, Yellow)	Moderate to Difficult	HSD Premix + High Energy Mill

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Optimizing Dispersant Level in a Formulation

Some Best Practices after a dispersant has been selected

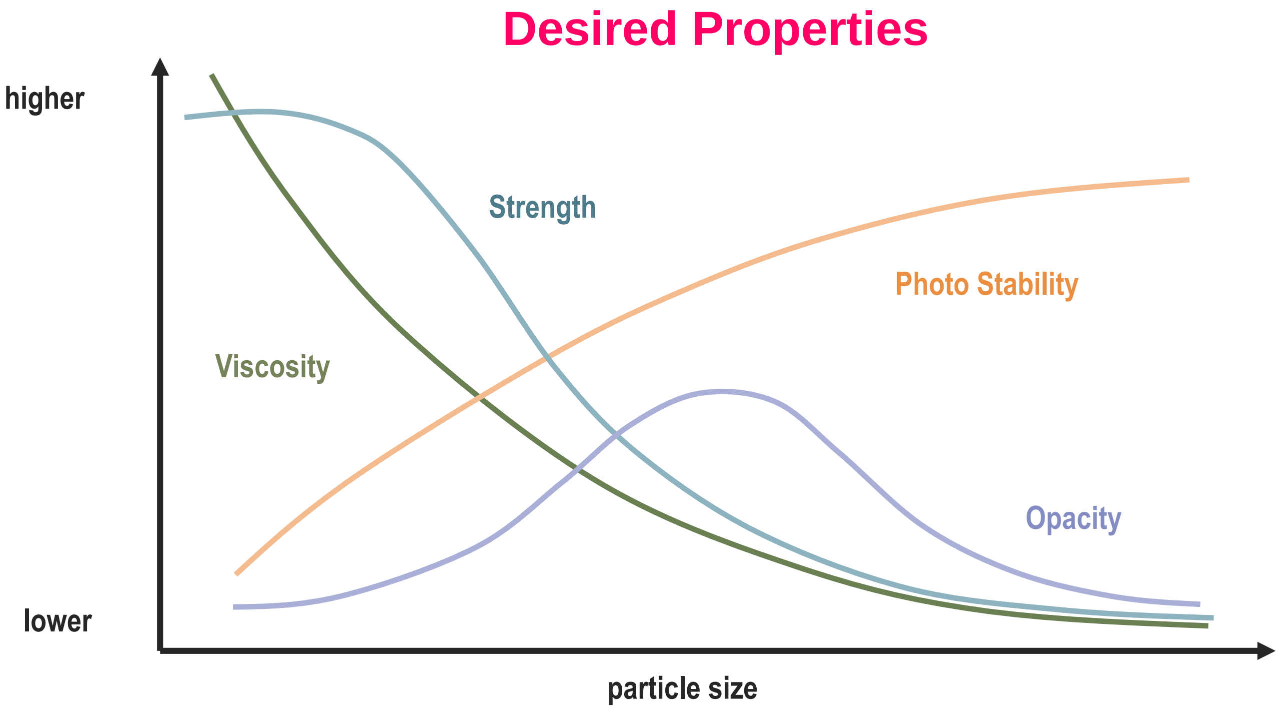
- Avoid mixing pigment types in a single dispersion if possible
- Use of a single, universal dispersant for pigments can be advantageous if compatibility is important
  - Note that these types of dispersants may not give best dispersing results for all pigments; compromise for compatibility
- Confirm compatibility of dispersant with key liquid ingredients in formulation
- If replacing an existing dispersant with a new one, account for substitution based on active solids
- Run a Dispersant Demand Ladder Experiment to determine optimal concentration
- Once an optimal dispersant level is chosen, run grind experiments
- Correlate property development vs grind time to determine optimal grind time
- Perform 2 week accelerated aging study (120 °F) to confirm dispersion stability
  - Test properties before and after aging
- If other pigmented dispersions will be mixed then check for compatibility
  - Flood, float, color acceptance
  - May need a fatty acid (compatibilizer/emulsifier) or controlled flocculation type of dispersant

Dispersant Demand Curves

- For a given formulation with:
  Fixed pigment, resin, solvent/water concentrations
- Run ladder experiment varying dispersant concentration
  - Low to High
  - Refer to supplier TDS for recommended range or
  - Use rough rule of thumb for center point:

    Active dispersant amt = Pigment Surface area/4
    on pigment (%)

  - Measure key property of interest
  - Plot measured Property vs Dispersant Concentration
  - Identify Dispersant Concentration which matches most positive Property value
  - May need to balance a variety of Properties



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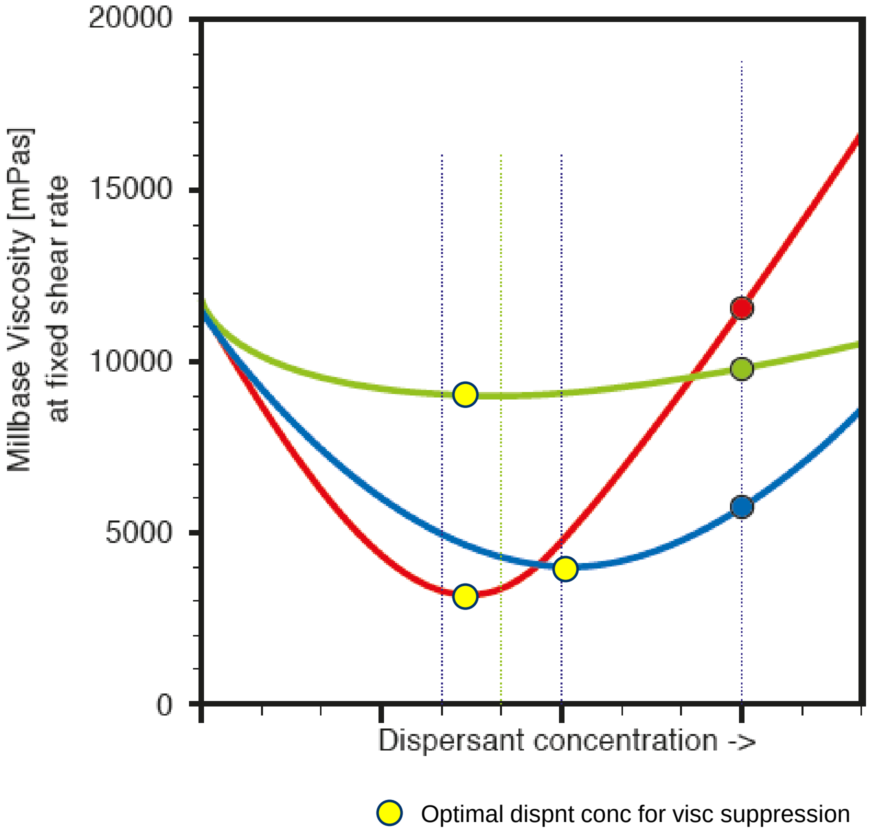
Dispersant Demand Curve – Viscosity Example

- For a given formulation with:

  Fixed pigment, resin, solvent/water concentrations
- Run ladder experiment varying dispersant concentration
  - Low to High
  - Refer to supplier TDS for recommended range or
  - Use rough rule of thumb for center point:

    Active dispersant amt on pigment (%) = Pigment Surface area/4
  - Measure low shear viscosity

    (e.g., Brookfield at fixed RPM)
  - Plot measured viscosity vs Dispersant Concentration
  - Low point on curve corresponds to optimal dispersant concentration for viscosity suppression



Dispersant performance

Ladder study 1 > 3 >> 2

Dispersant demand

minimum viscosity curve

Dispersant level

determined with ladder study

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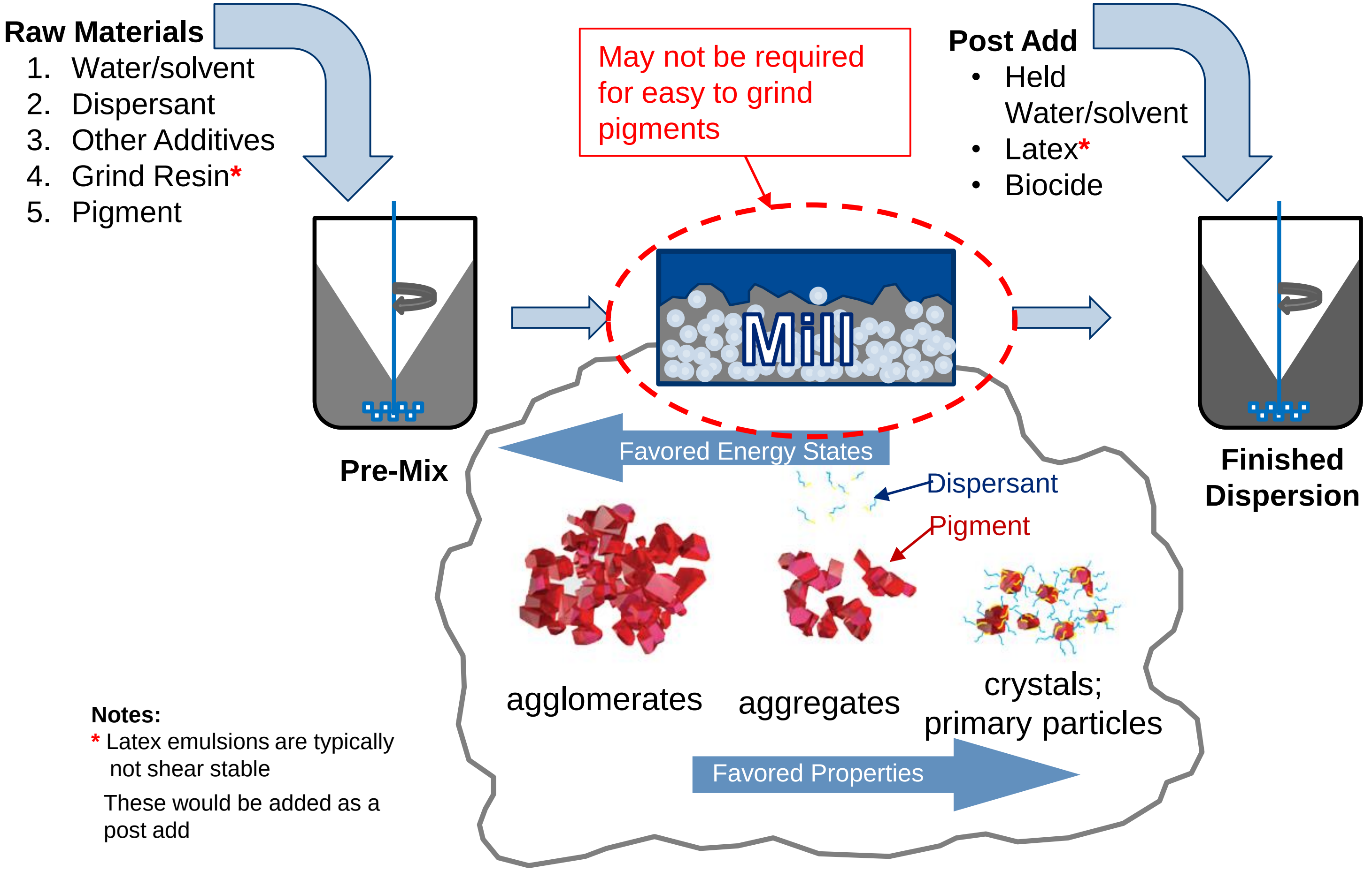
Processing Considerations

Processing considerations

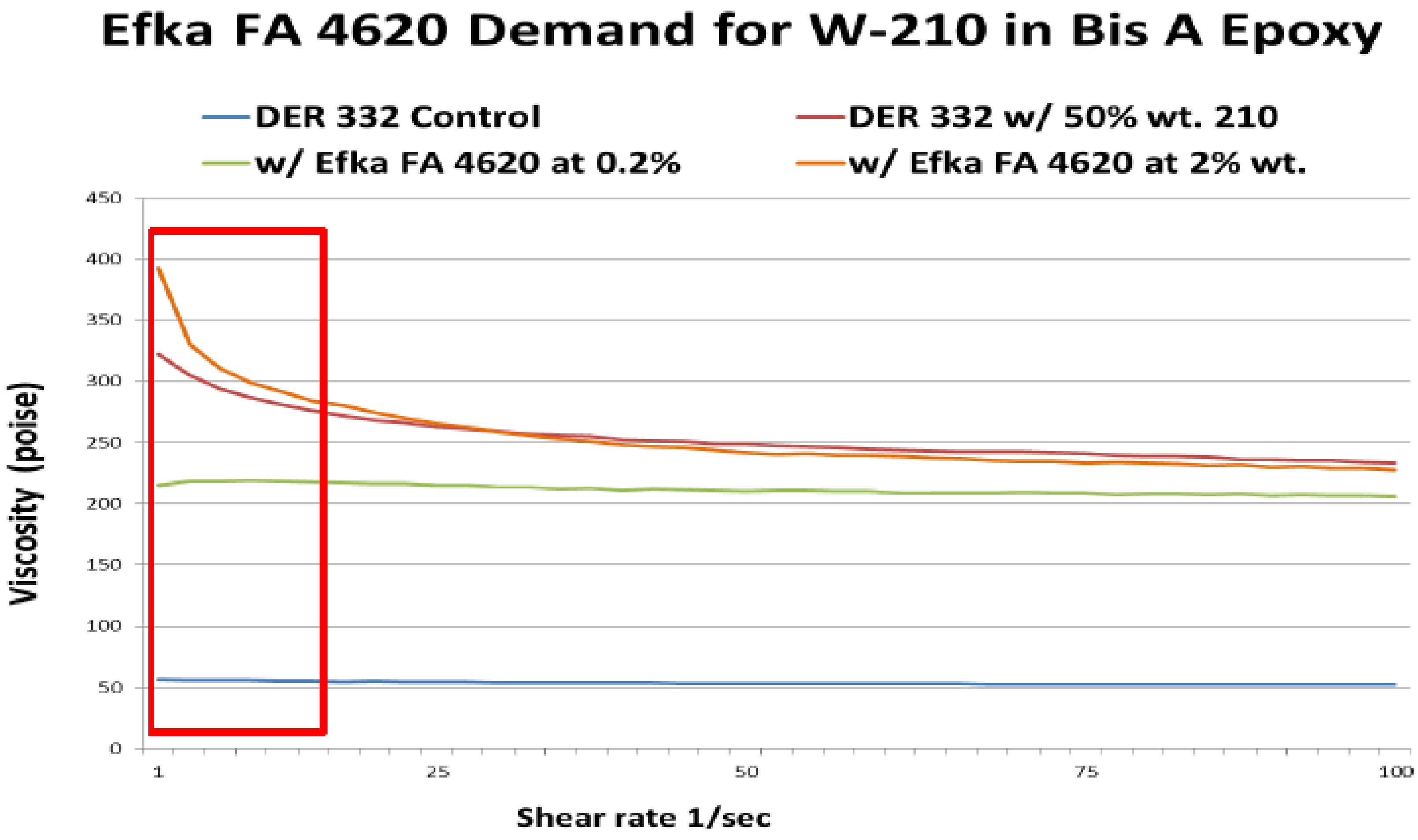
1. Determine grind/processing requirements based on pigment type
   - For easy to grind pigments a simple high shear mixing operation is sufficient
   - For hard to grind pigments a premix followed by milling is required
2. Add liquid ingredients first*
3. Add solids (pigments) slowly
   - Allow time to fully wet pigment
4. *May need to hold back some solvent/water to increase solids/viscosity
   - Increase energy of mixing to help break pigment down to primary size
5. Pull samples during grind to track property (color, degree of grind, visc.) as a function of grind time
6. Add back liquid hold out as a letdown to create final dispersion

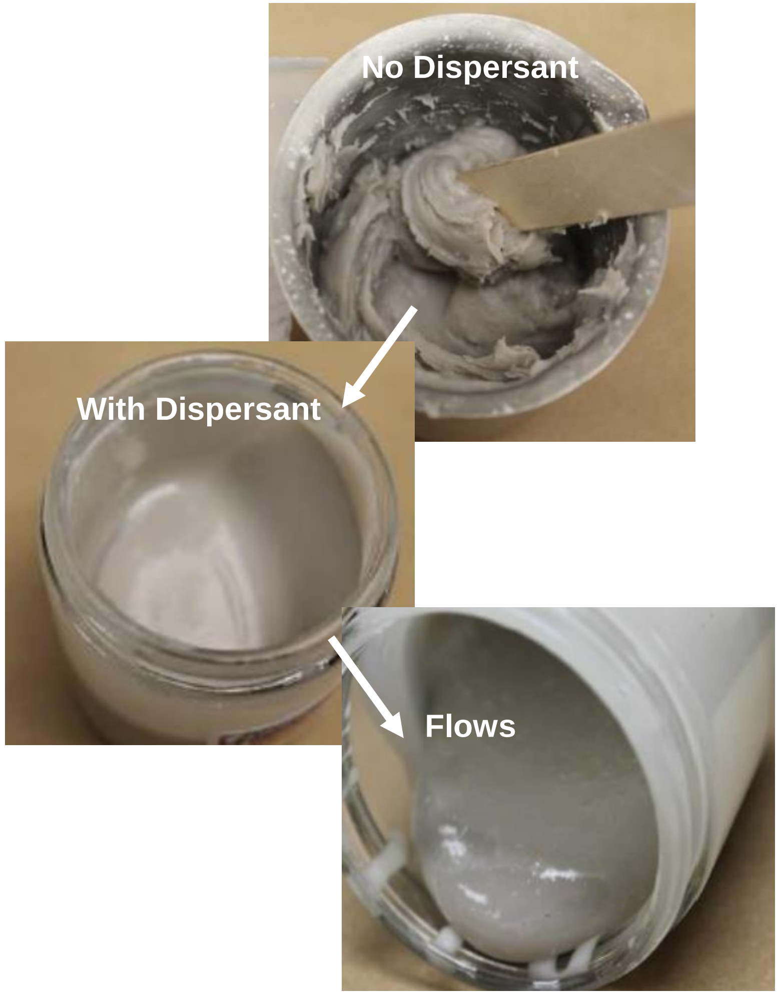


Notes:
* Latex emulsions are typically not shear stable
These would be added as a post add

Case Examples of Applications

Case Example: W-210 Microspheres with Efka® FA 4620





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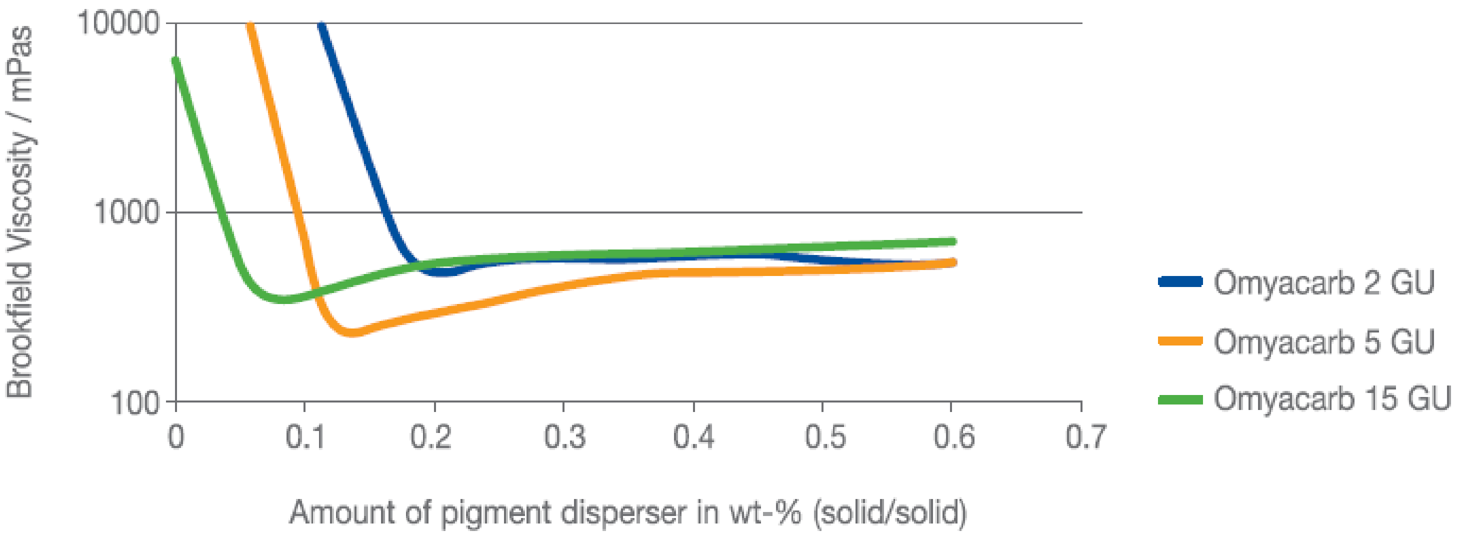
Case Example 2: Dispex ® AA 4135

Product	Dispex® AA 4135
Performance Highlights	• Offers reduced odor due to sodium hydroxide neutralization
Sustainability Highlights	• Low VOC • Low odor • Non-APEO • Excellent cost performance balance
Applications (Construction Market Focus)	• Recommended for flooring adhesives, sealants, construction adhesives, for ceramic tile adhesives, flexible roof coatings and for primers/bonding aids
Properties	• Solids(%): 35 • VOC content (%): <0.1

Dispersant effect on different grades of $CaCO_3$ Filler



- Dispex® 4135 provides a strong viscosity reduction
- Optimal dispersant levels depend on the filler grade

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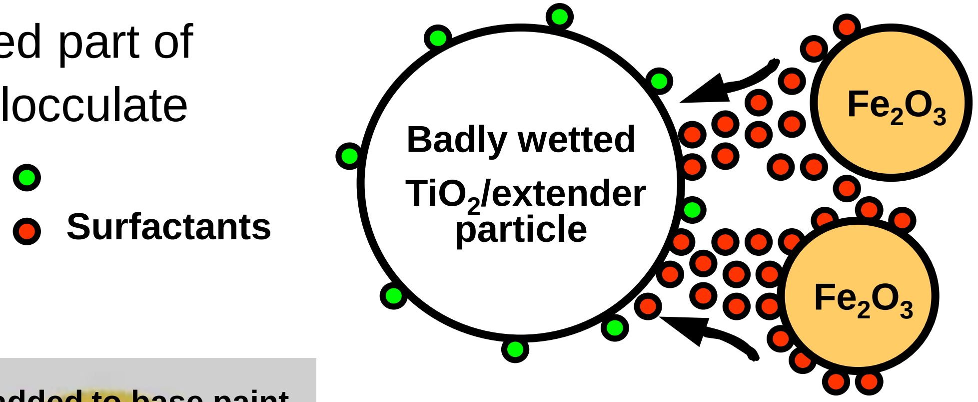
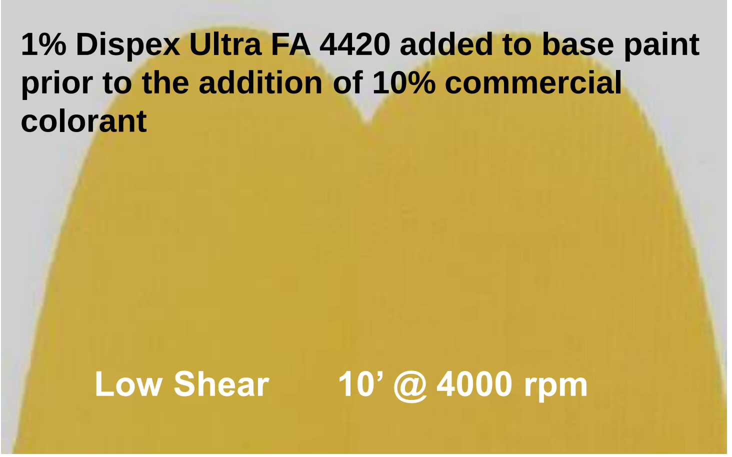
Case Example 3a: Color Acceptance with Dispex Ultra FA 4420

- Dispersant in the colorant is adsorbed by the poorly wetted part of the TiO_2/ extender in the paint, causing the iron oxide to flocculate
  - ➢ Color strength decreases over time



Decrease in color strength after high shear incorporation of colorant



No change in color strength after high shear incorporation of colorant

High shear incorporation of colorant mimics what happens over time

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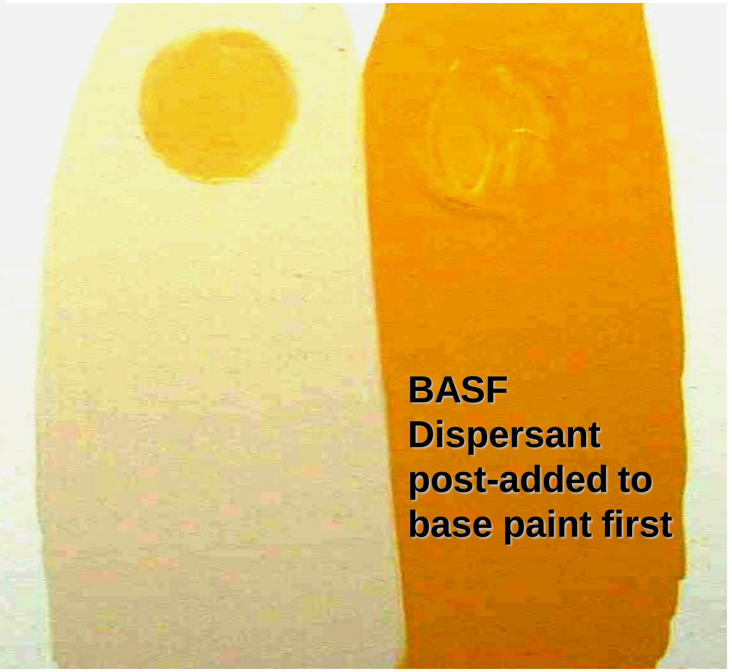
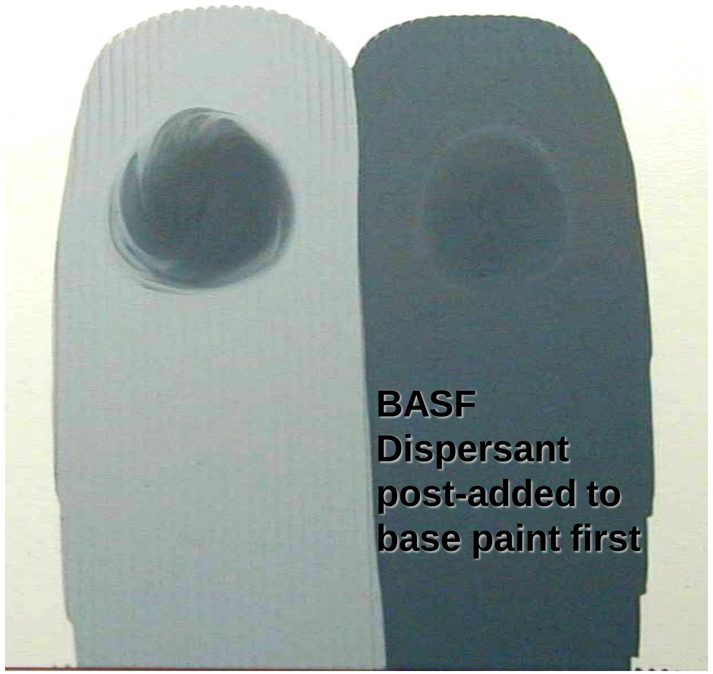
Case Example 3b: Color Acceptance with Dispex Ultra FA 4420

Commercial colorant 1
Mixed in same base paint



Commercial colorant 2
Mixed in same base paint

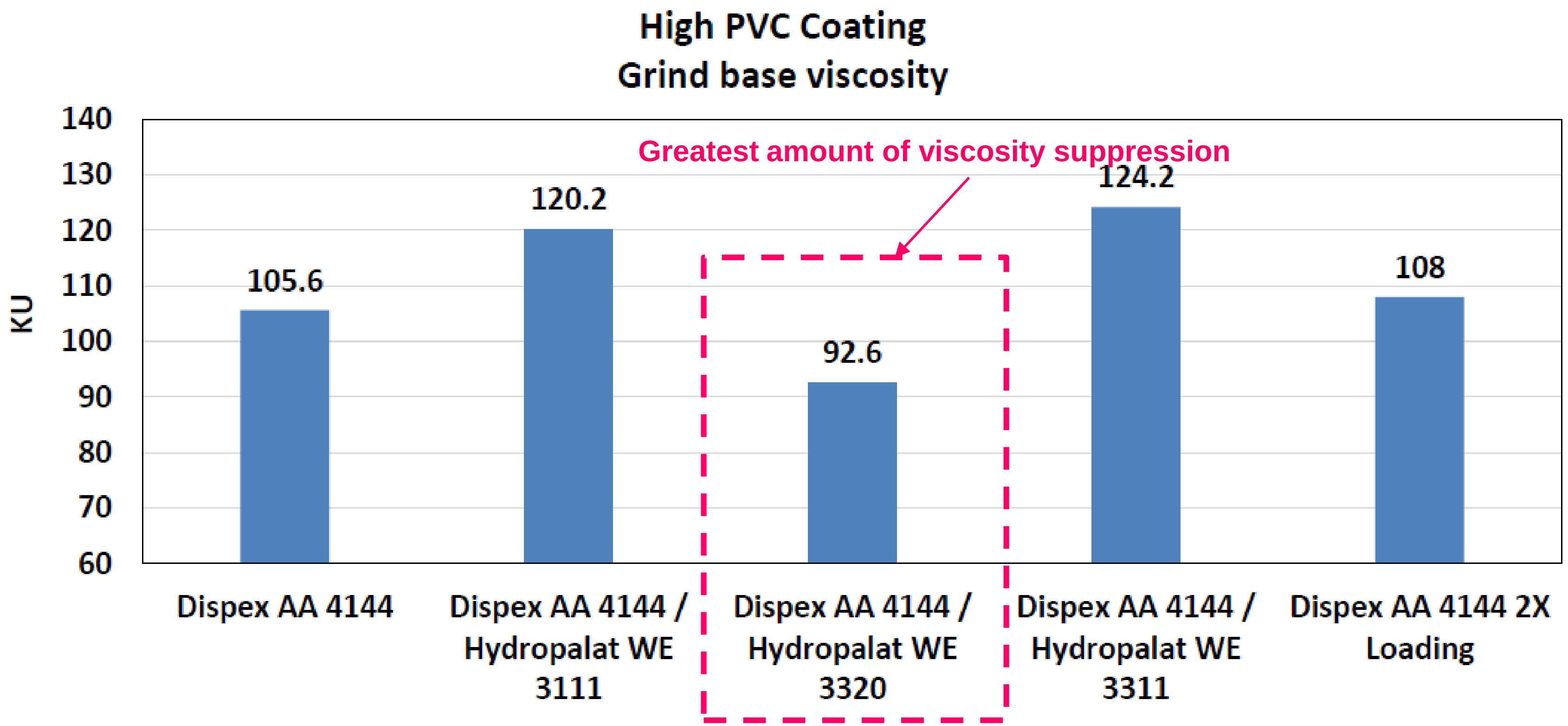


In the example the compatibilizing effect is achieved by addition of the Dispex Ultra FA 4420.

This effectively “tunes” the polarity of the base paint and improves compatibility towards the tested colorants

- **Dispex Ultra FA 4420** (Efka 6220) added to a base paint can significantly improve the performance of the colorants in the paint.

Case 4a: Surfactants as Co-Dispersants for High PVC Arch Coating



- Evaluated surfactants as co-dispersants.
  - ▶ Hydropalat WE 3320 was most efficient of items tested.
- Increased dosing of Dispex AA 4144 did not show any further benefit.

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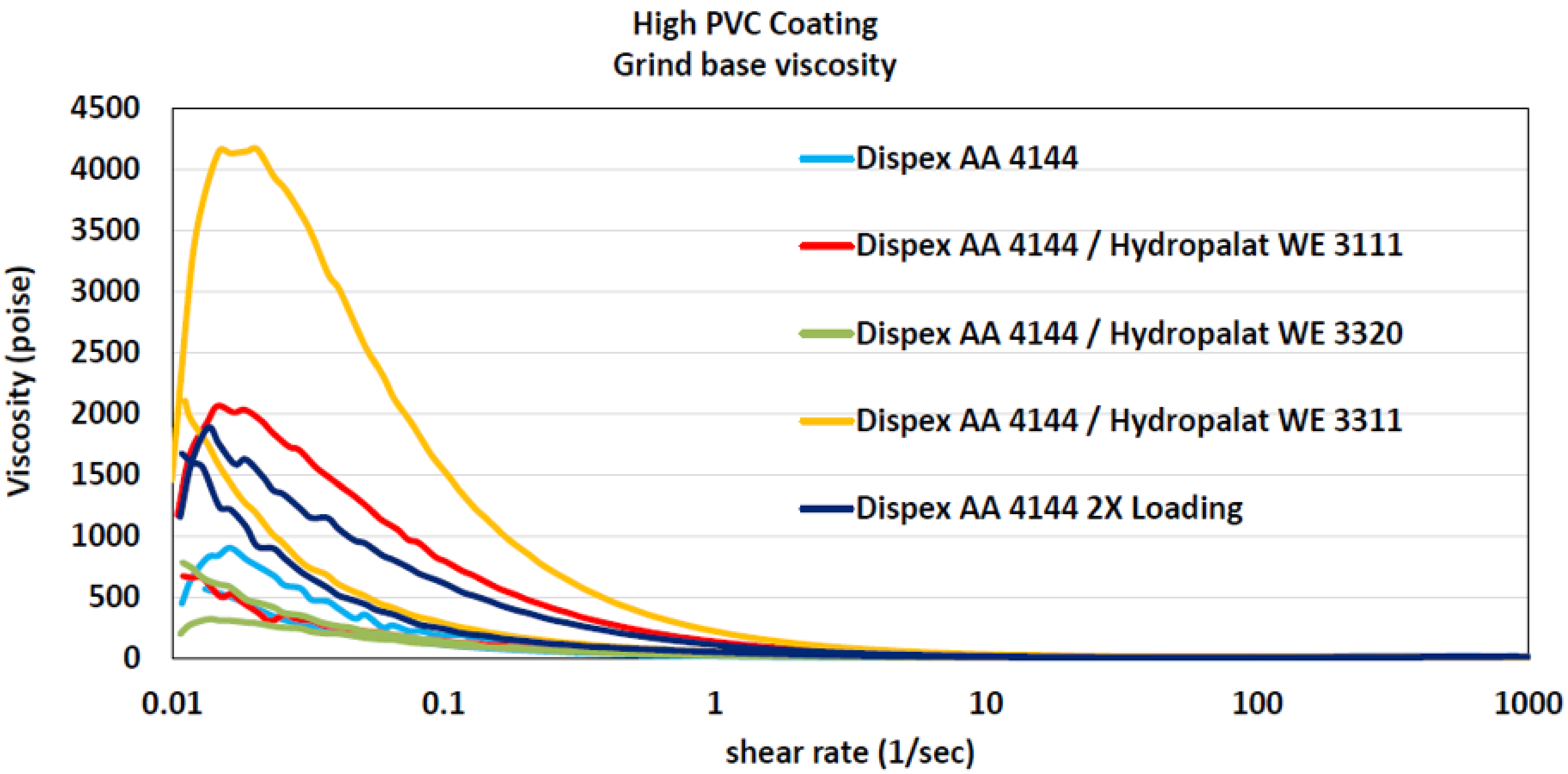
Case 4b: Surfactants as Co-Dispersants for High PVC Arch Coating



- Differences exist in low shear region of viscosity curve.
- Hydropalat WE 3320 most effective keeping viscosity low.

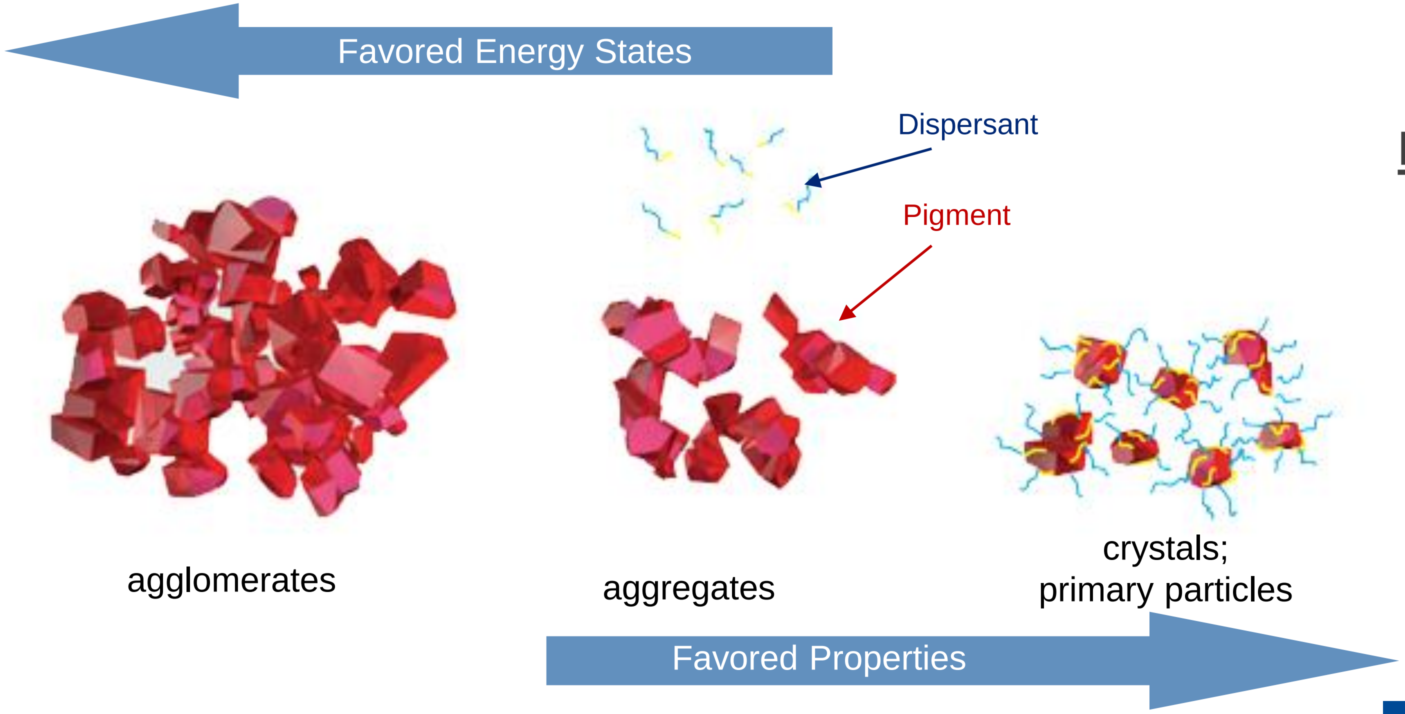
Addressing settling

Pigment Physical Phenomena and Thermodynamics

- Viscosity
  - Pigment surface interactions cause resistance to flow
  - Dispersants minimize pigment interactions → results in lower viscosity
  - Pros: Obtain desired film properties from pigment and lower handling viscosity for productivity and increased formulation latitude

Undesired Properties

- Less color saturation
- Higher handling viscosity
- Inefficient/inconsistent pigment coverage in coatings
- Separation and settling in coatings and storage conditions



Desired Properties

- Optimal color characteristics
- Lower handling viscosity
- Efficient/consistent pigment coverage in coatings
- Enhanced dispersion stability

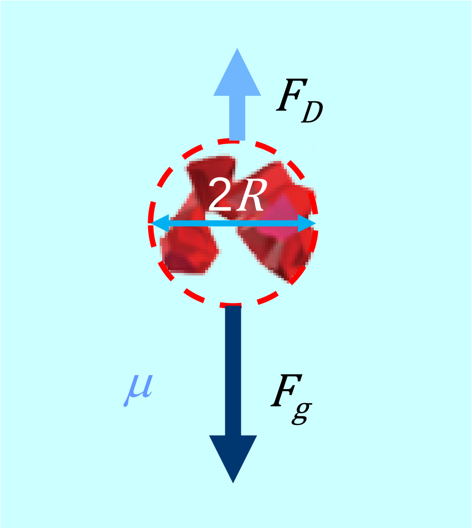
Pigment Physical Phenomena and Thermodynamics

- Settling
  - Function of a variety of aspects: gravity, density of pigment and fluid, fluid viscosity, and pigment size (Stoke's Equation)
  - Dispersants minimize pigment interactions → hence smaller effective particle size
  - In low viscosity regimes, the effect of dispersants may not be enough to mitigate settling

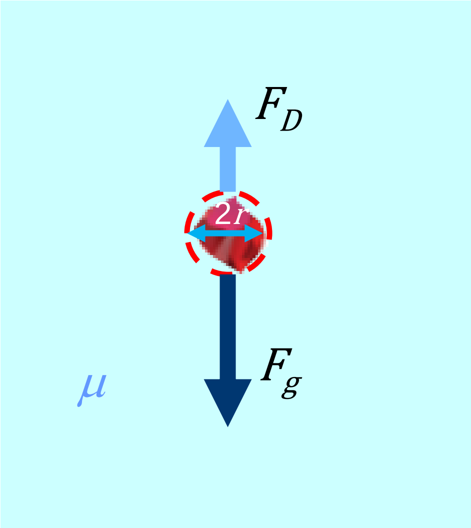
Stoke's Equation for Settling

$$v = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g R^2$$

v – settling viscosity
ρ_p – particle density
ρ_f – fluid density
μ – fluid (dynamic) viscosity
g – gravitational constant
R – particle radius



Undispersed



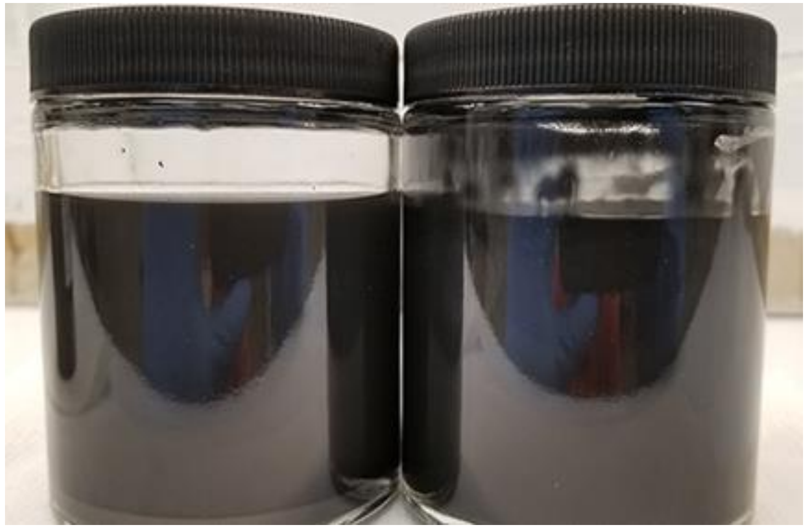
Dispersed
(smaller effective diameter)

F_D – Drag force,
function of particle diameter,
viscosity, density differences

F_g – Gravitational force,
function of particle diameter,
viscosity, density differences

Use of Rheology Modifier to address settling

Dispex Ultra FA 4416 with 0.7% Rheovis AS 1188



Settling No Settling

Higher Pigment Loading to address settling

High Pigment Loading – Efka PX 4585

Sep/Set

Sep/Set

47.4% DOP
15% Pigment

47.5% DOP
30% Pigment

High Pigment/Dispersant Loading – Dispex Ultra FA 4480

Sep/Set

10.4% DOP
30.3% Pigment

25.9% DOP
30.3% Pigment

35.6% DOP
30.3% Pigment

Questions?

BASF Solution Finder Tool for Formulation Additives

Check out our **Solution Finder Tool on www.basf.com/formulation-additives**

- This tool provides you the best additive solution for your challenging formulation task :
  - From dispersing agents, wetting agents and surface modifiers, to defoamers, rheology modifiers and film-forming agents

- Explore the BASF formulation additives portfolio for the paints and coatings industry, by :
  - Receiving recommendations for your formulation challenges
  - Understanding the main benefits of our products by application and get technical information
  - Ordering samples or contacting us for more detailed consultations

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