Dispersant Technology Fundamentals

Tony Moy
Sr. Technical Specialist
BASF Formulation Additives

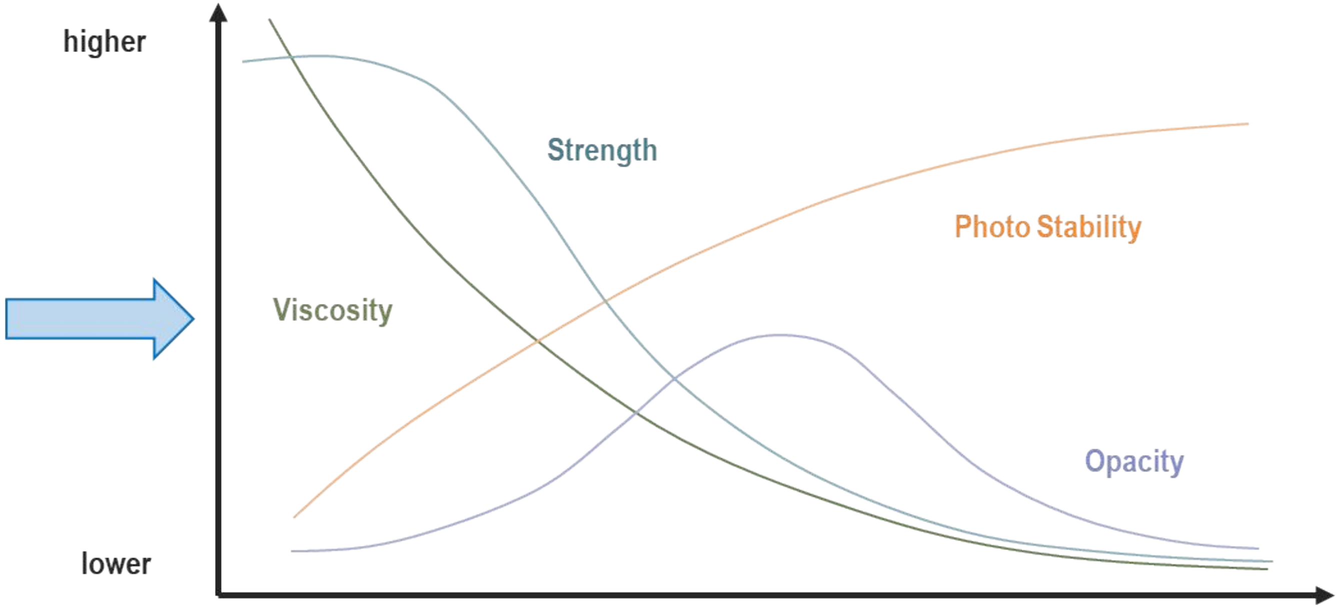
Agenda

- What, Why, and How
- Dispersant types, associated pigment applications, and considerations for selection
- Optimizing dispersant concentration/level in a formulation
- Process considerations
- Case Studies plus Bonus Topic
- Questions?

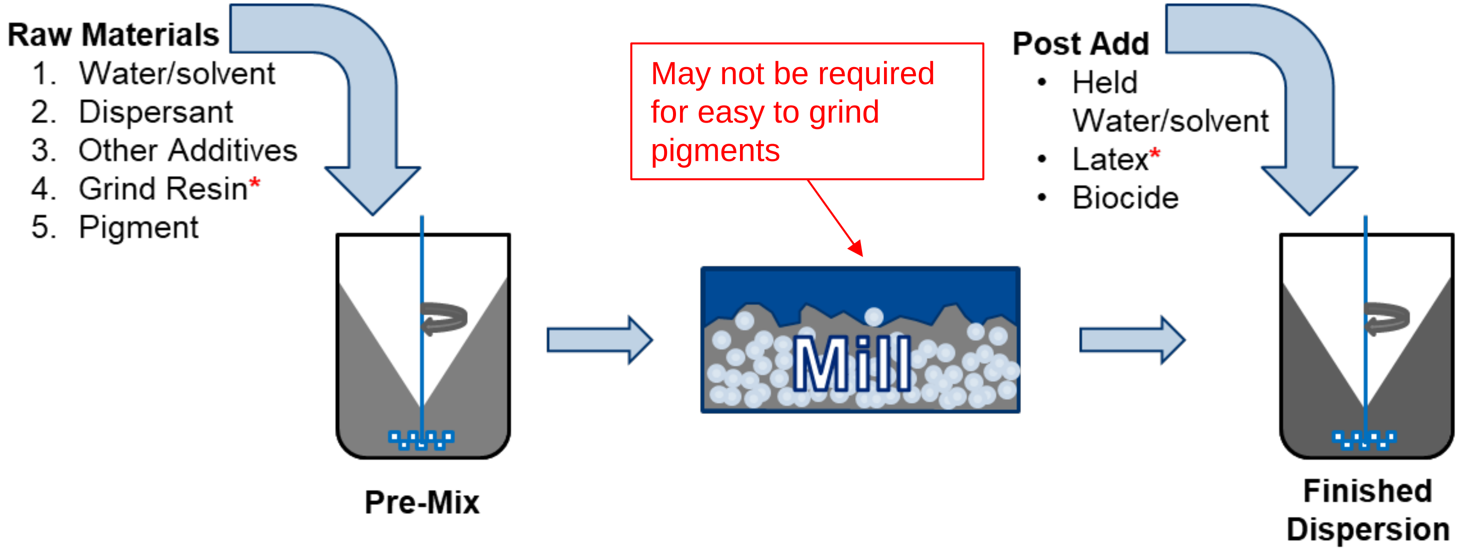
Coatings Trends & Technologies SUMMIT

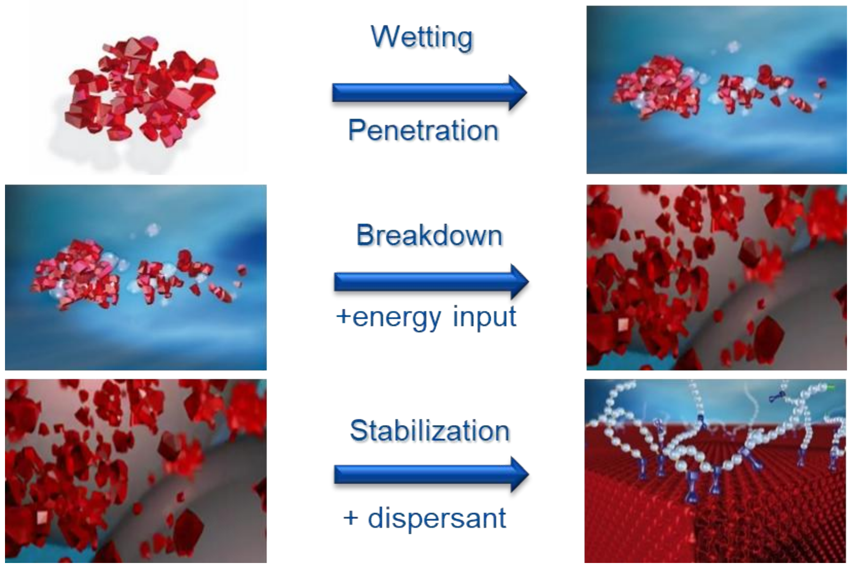
What are Dispersants?

- 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

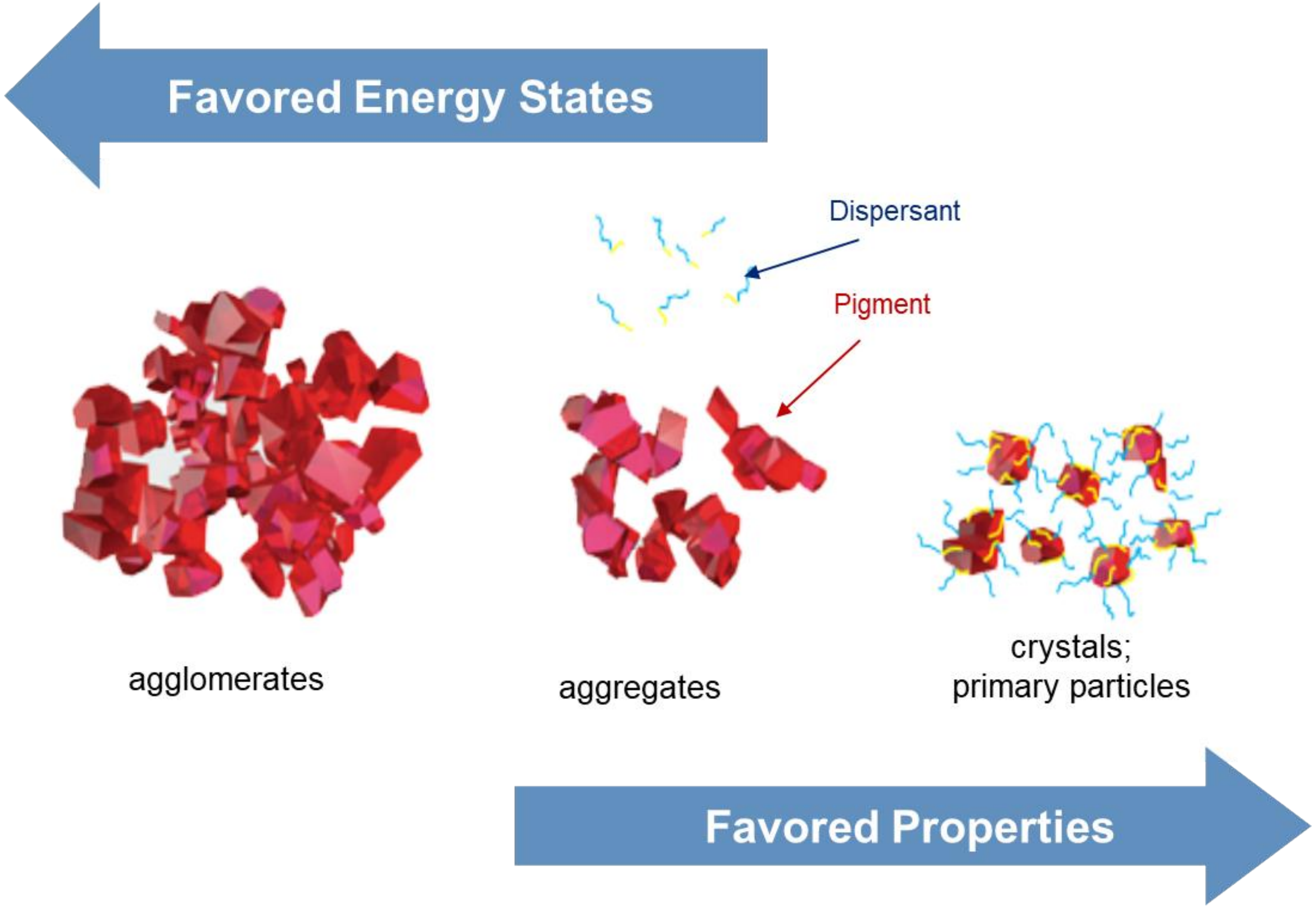


Dispersing Process





Why use Dispersants?
Why they are needed



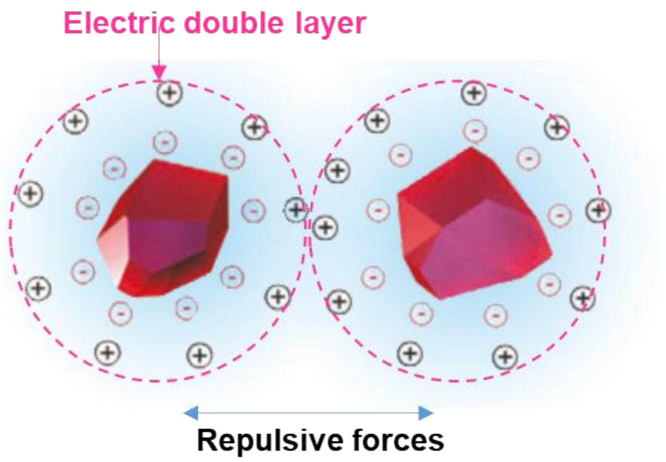
Dispersants enable favored properties of pigments

Why use Dispersants?
Value of Dispersants

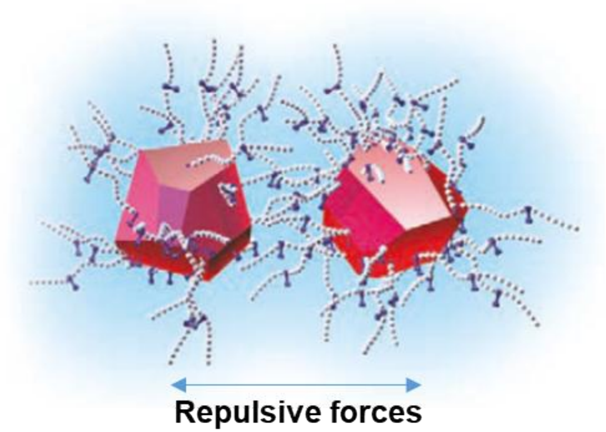
- Minimize interaction of pigments
  - Reduce viscosity
  - Enhance stability of pigment and dispersion
  - Reduced settling and kick out
  - Maximize performance contribution of pigments (color, protection, etc.)
  - Minimize the amount of pigment required to do the job
- More formulation latitude: 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

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

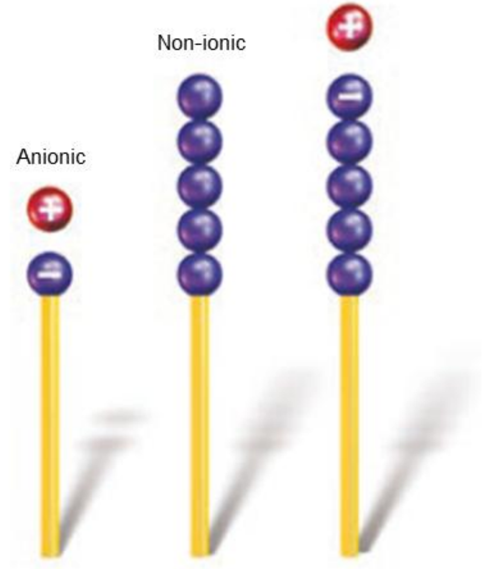


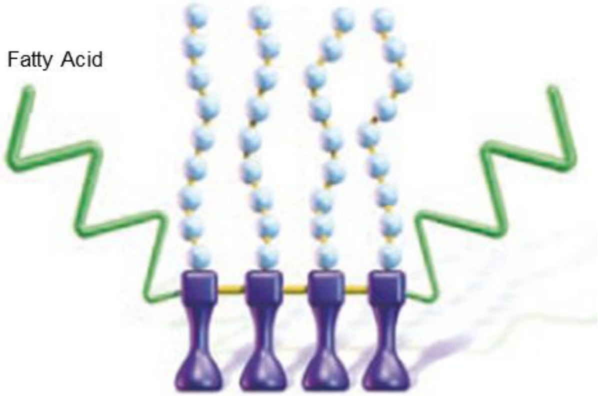
- Electrosteric
  - A combination of both

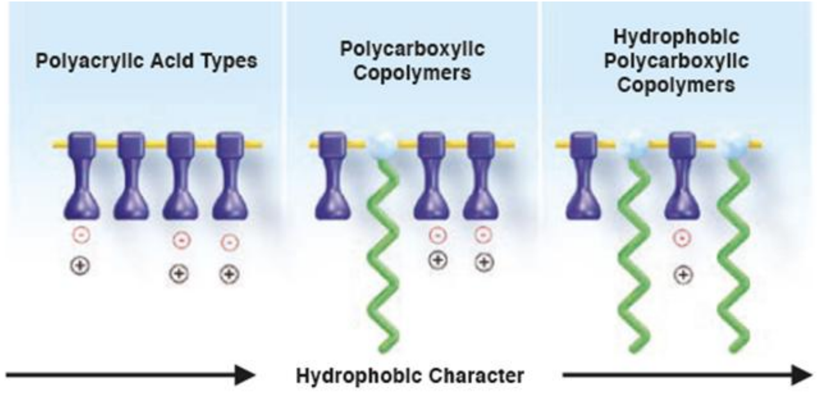
Ultimately force of repulsion created by dispersant must overcome attractive forces of pigment particles to realize a stable state

Coatings Trends & Technologies SUMMIT

Types of Dispersants








Polyacrylate


Polyurethane

Low Molecular Weight

Surfactant Types

- Ionic and Non-ionic

MW < 1000

Oligomeric (FAME) Types

- Fatty Acid Modified Esters

MW: 1000 - ~5000

Examples:

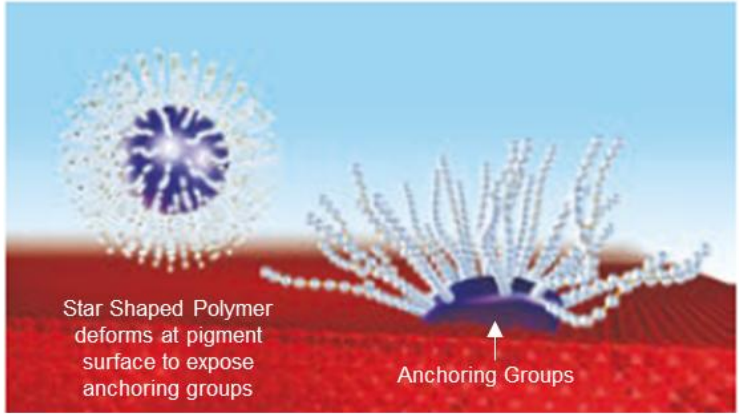
- Sulfates/sulfonates
- Phosphate esters
- Fatty acids
- Quaternary ammonium/Imidazolium salts

High Molecular Weight

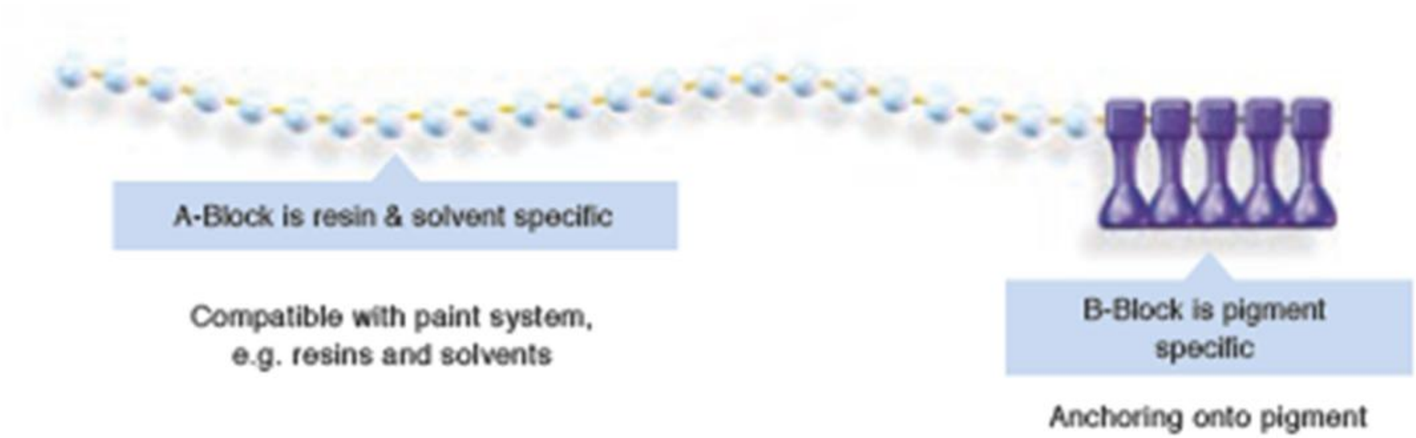
- Polyacrylic Acid (Anionic)
- Polycarboxylic Copolymers (Anionic)
- Polyacrylates
- Polyurethanes

MW > ~5000

Types of Dispersants



Star Shaped Polymer



Block Copolymer (CFRP)

Advanced High Molecular Weight

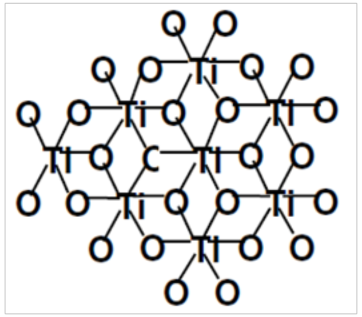
- Star Shaped Polymers
- Block Copolymers via Controlled Free Radical Polymerization (CFRP)

MW > ~5000

Stabilizing Inorganic Pigment

Inorganic pigments

- Polar surface: broken bonds leave charges (positive, negative, mostly heterogenous) on surface
- Large particle size, low specific area
- Easy to disperse
- Easy & stable anchoring, less tendency to re-agglomerate

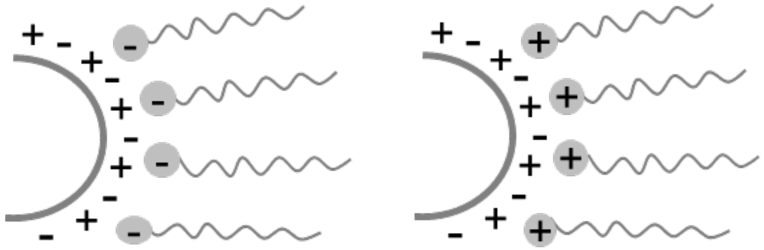


Broken bonds at TiO2 surface

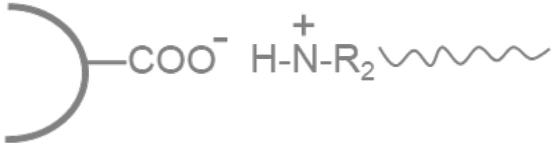
Anchoring group

- carboxylic, sulfonic and phosphoric acid groups and their salts
- amines; ammonium

Anchoring via ionic interaction



Anchoring via acidic/basic interaction



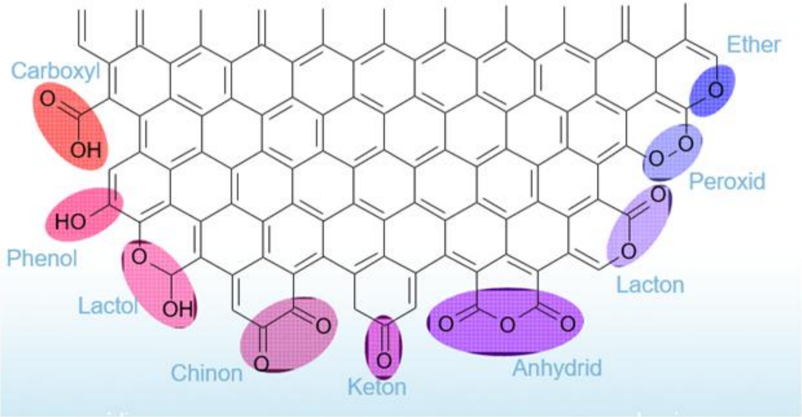
Dispersant selection

- LMW dispersant: good viscosity reduction
- HMW dispersant: recommended for color pigment dispersing

Stabilizing Carbon Black and Organic Pigment

Organic pigment

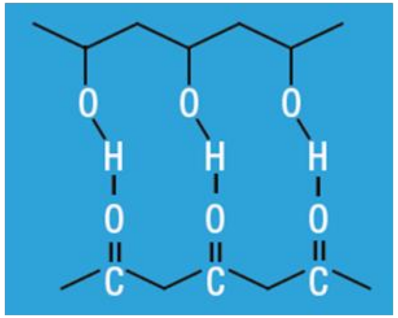
- Non polar surface: no surface charge, contains nitrogen derivatives, aromatic ring, ester, ketone and ether no surface charge
- Smaller particle size high specific area
- Difficult to disperse
- Difficult & unstable anchoring, tendency to re-agglomerate



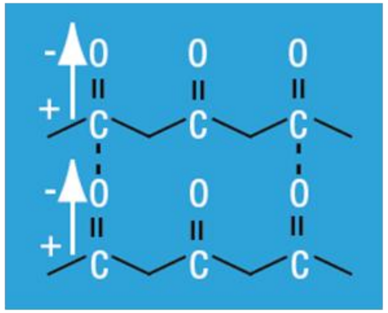
CB surface

Anchoring group

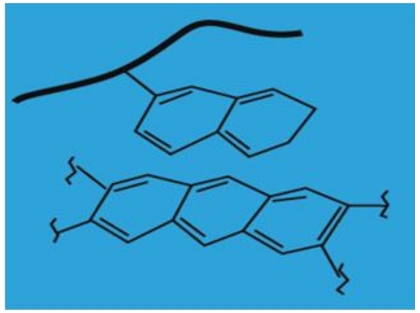
- Amine, cyclic ring



Hydrogen bonding



Dipole-dipole interaction



π-π interaction

Dispersant selection

HMW for good dispersing and stabilization

Selecting a Dispersant

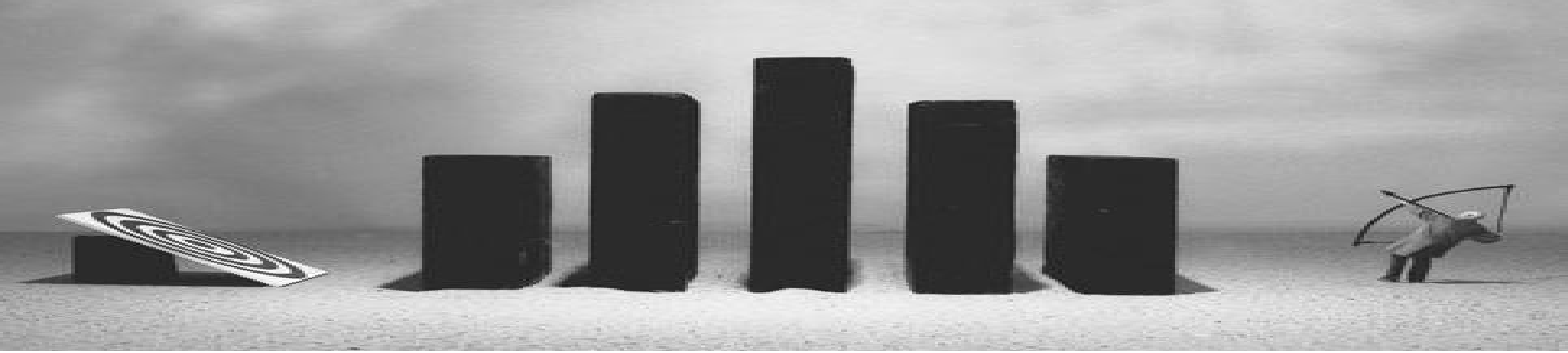
- Key Questions to consider when selecting/using dispersants

1. What is being dispersed? Pigment typically dictates the dispersant type
2. What is it dispersed in? Dispersant must be compatible with the media
3. How is it dispersed? More difficult to disperse pigments require higher energy mixing
4. What is the objective? There will typically be a compromise in performance targets

Dispersant(s) to trial

Coatings Trends & Technologies SUMMIT

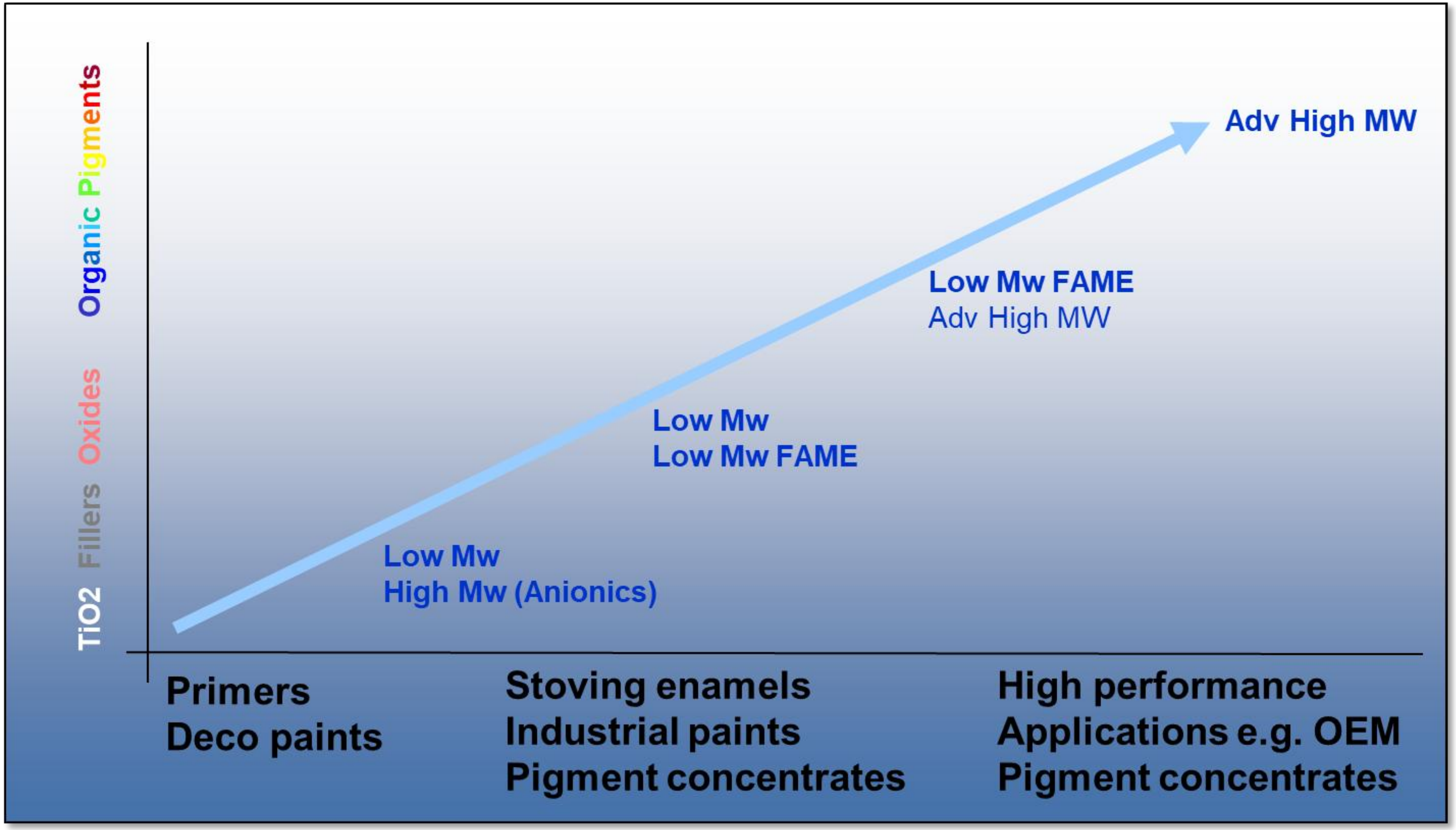
Selecting a Dispersant: General Guidelines – Pigments & Benefits



- **LMW dispersants:**
  - Fillers, extenders, TiO2
  - Economic solutions with less demand for performance
  - Good viscosity suppression
  - Combined with resin or HMWD
  - Solvent and water borne
- **Oligomeric (FAME) dispersants:**
  - Broadest compatibility
  - Universal application
  - Good viscosity suppression
  - In some cases, can provide controlled flocculation for improved stability
- **HMW dispersants:**
  - For organic and inorganic pigments (Universal)
  - Lowest viscosities
  - Highest color strength
  - Highest gloss
  - Best stability

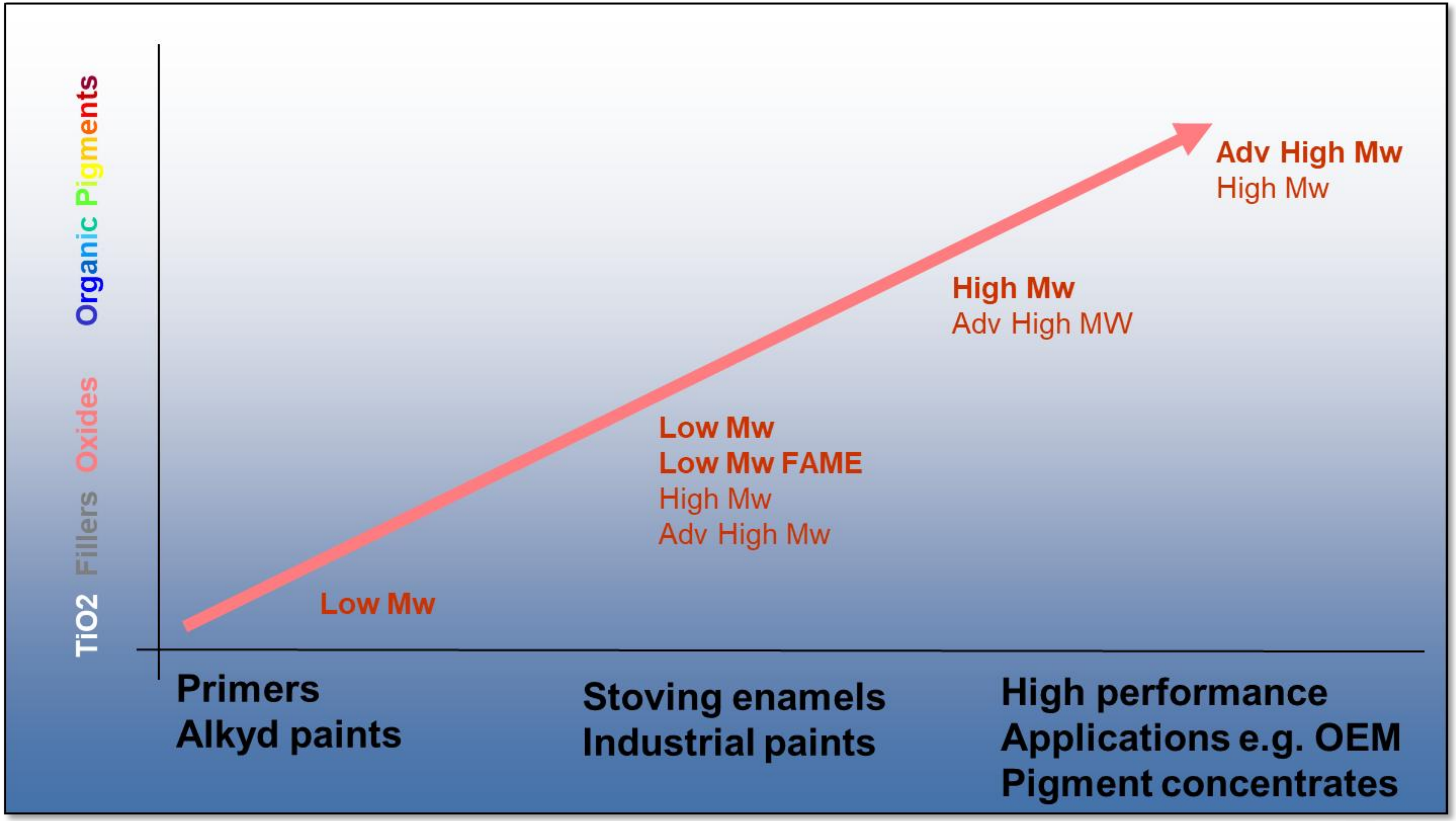
Dispersants – Pigments – Applications

Water-based



Dispersants – Pigments – Applications

Solvent-based



Coatings Trends & Technologies SUMMIT

Pigment Grinding Reference

Pigment Type	Grind	Grind Equipment	Media	Media Size (If applicable)
White	Easy	HSD or Sandmill	Glass	2.0 mm
Inorganic Fillers	Easy	HSD	N/A	N/A
Aluminum, Pearls (Mica) – Effect Pigments	Don't grind	Paddle mixer	N/A	N/A
Black (Organic)	Difficult	HSD Premix + High Energy Mill	Zirconia or Yitria Treated Zirconia (YTZ)	0.4-0.8 mm
Blue (Phthalo)	Difficult	HSD Premix + High Energy Mill	Zirconia	0.4-0.8 mm
Violet (Quinacridone)	Difficult	HSD Premix + High Energy Mill	Zirconia	0.4-0.8 mm
Red (DPP)	Difficult	HSD Premix + High Energy Mill	Zirconia	0.4-0.8 mm
Red (Quinacridone)	Moderate to Difficult	HSD Premix + High Energy Mill	Zirconia	0.4-0.8 mm
Green (Phthalo)	Difficult		Zirconia	0.4-0.8 mm
Yellow (Isoindoline) (Benzimidazalone) (Bizmuth Vanadate)	Moderate	Sandmill	Glass	2.0-4.0 mm
Trans Iron Oxide (Red, Yellow)	Moderate to Difficult	HSD Premix + High Energy Mill	Zirconia	0.4-0.8 mm

Coatings Trends & Technologies SUMMIT

Optimizing the use of Dispersants

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

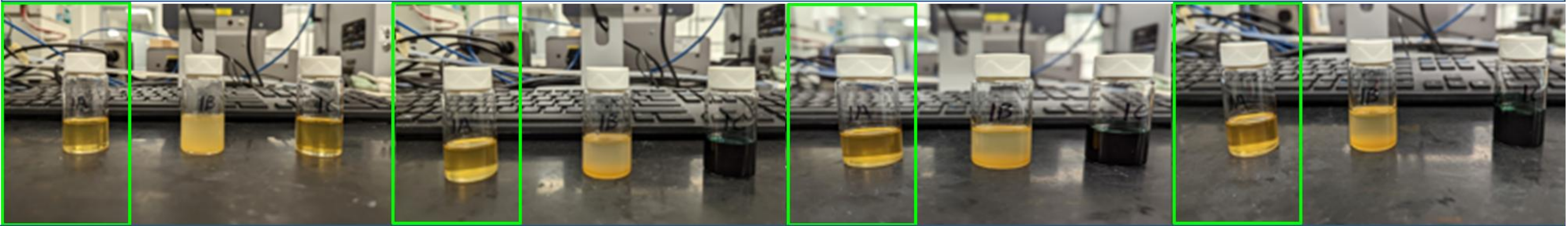
Example of Compatibility Check for Dispersants

Various dispersant/resin combinations exposed to 100 °C over 72 hour duration

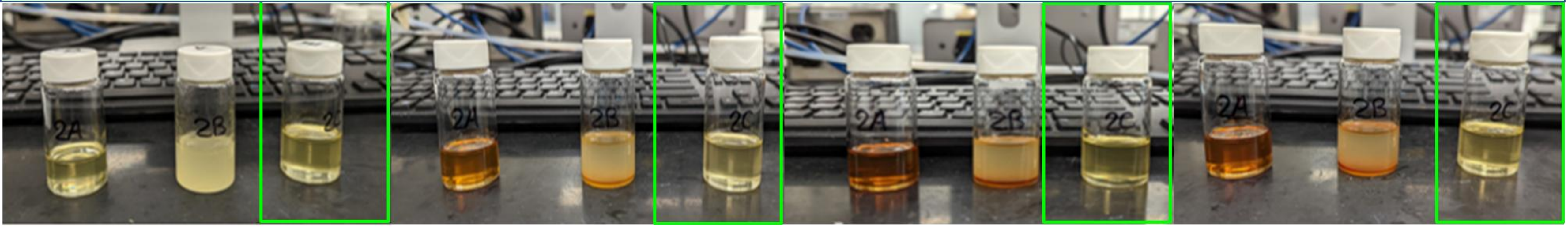
- Assess for initial compatibility
- Assess for thermal stability over time

Initial			24 Hours			48 Hours			72 Hours		
Ester Resin	Polyol Resin	Epoxy Resin	Ester Resin	Polyol Resin	Epoxy Resin	Ester Resin	Polyol Resin	Epoxy Resin	Ester Resin	Polyol Resin	Epoxy Resin

Dispersant A



Dispersant B



Best resin for compatibility / stability for given dispersant

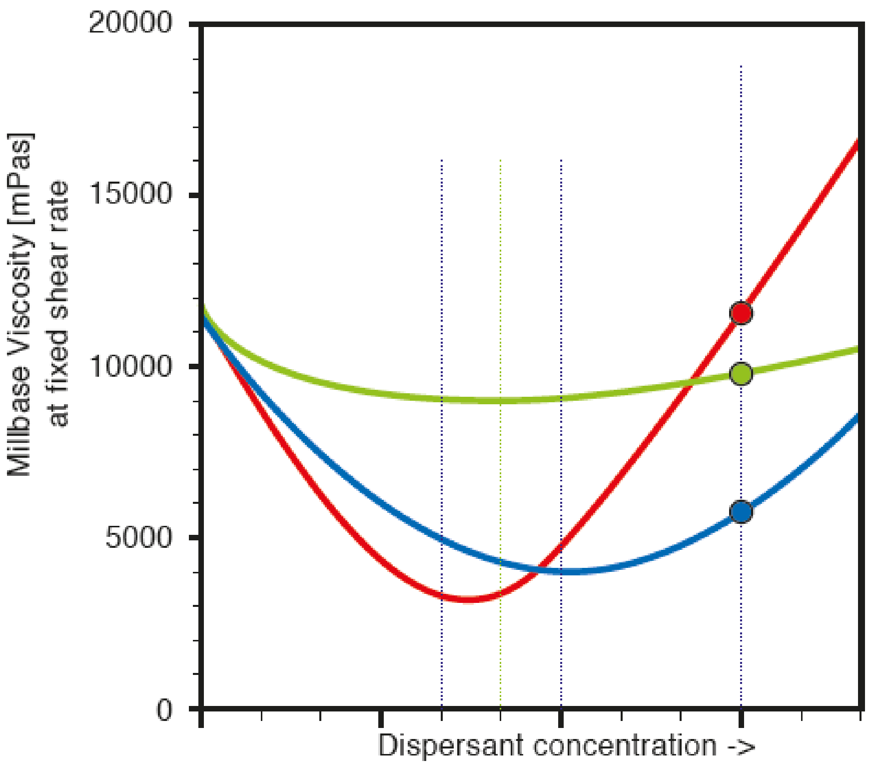
Dispersant Demand Curve Viscosity Example

- 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

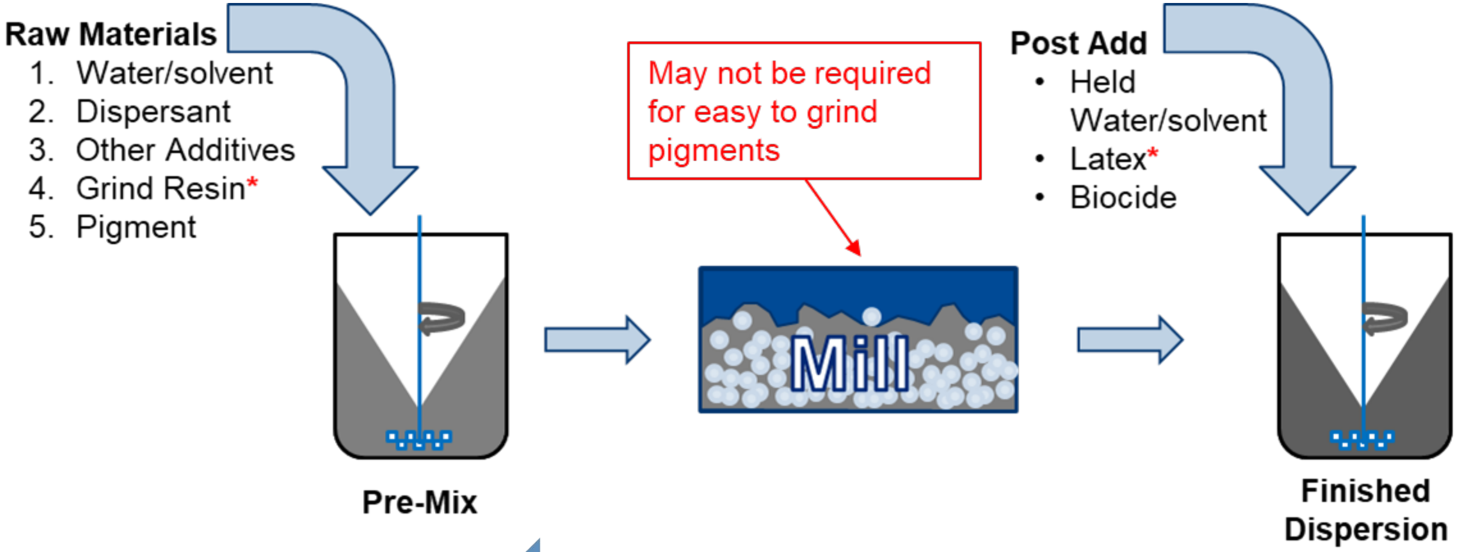
determined with ladder study

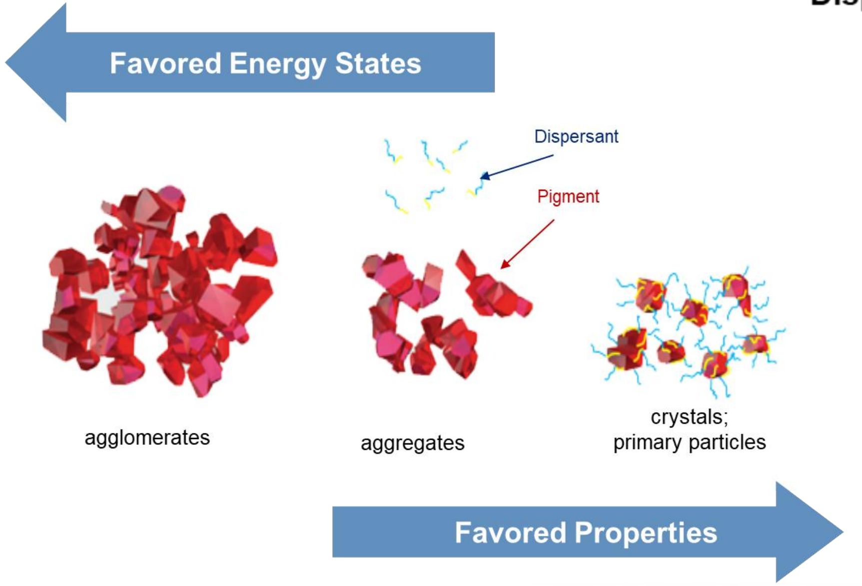
Running one point study can lead to incorrect conclusion!

Coatings Trends & Technologies SUMMIT

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





Coatings Trends & Technologies SUMMIT

Processing makes a difference

Dispermat (HSD)

- Carbon Black Pigment
- Oligomeric FAME Dispersant 22.5% DOP
- 1.0% Wetting Agent

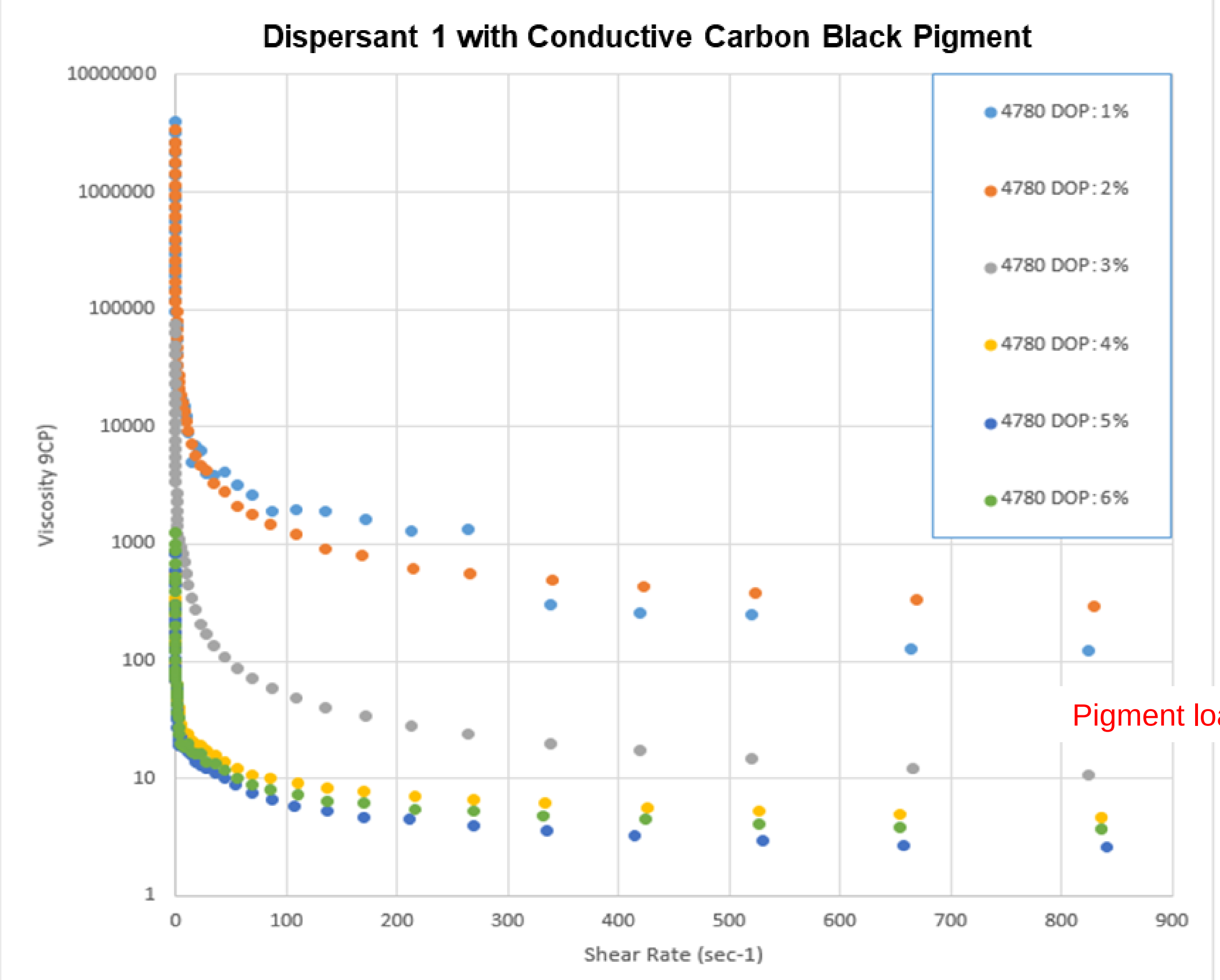
Shaker Grind 0.6-0.8 mm Zr

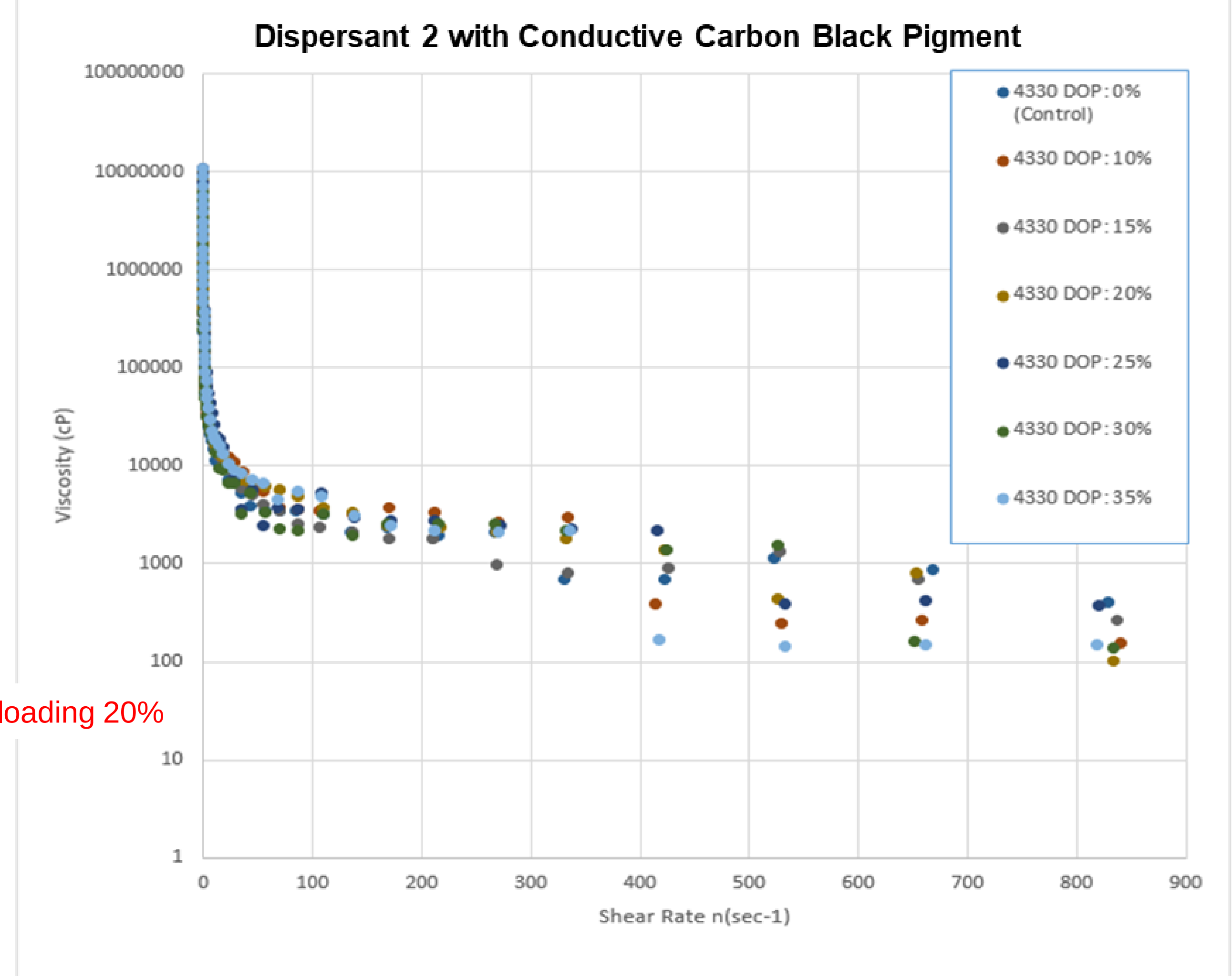
- Carbon Black Pigment
- Advanced High MW (CFRP) Dispersant 37.5% DOP

Processing is important – even with more advanced dispersants

Coatings Trends & Technologies SUMMIT

Case Study 1: Dispersing Conductive Carbon Black pigment





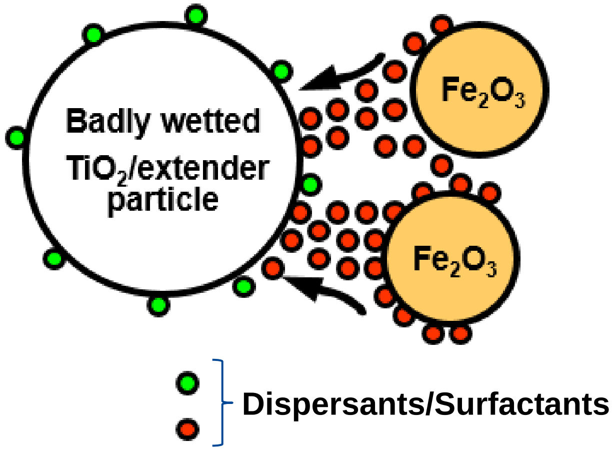
Pigment loading 20%

The right dispersant can make a big difference!

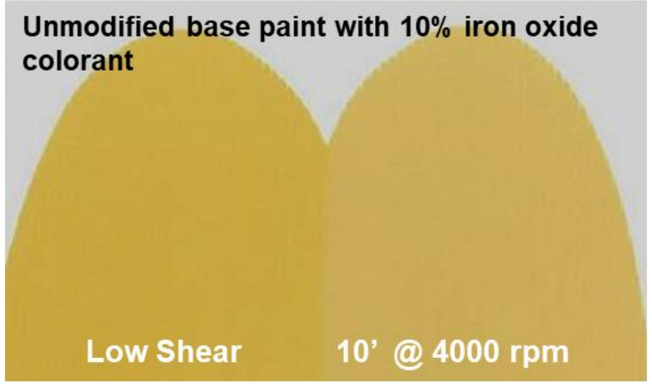
Case Study 2: Addressing Color Acceptance Issues

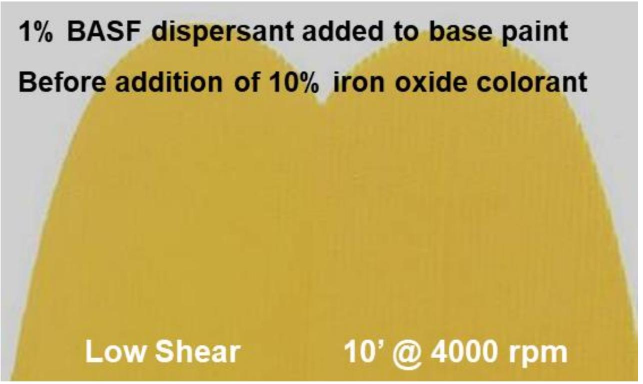
Problem:

- Dispersant leached from colorant by poorly wetted TiO2/ extender
  - Colorant flocculates over time
  - Color strength decreases over time



Dispersant X significantly improves color acceptance



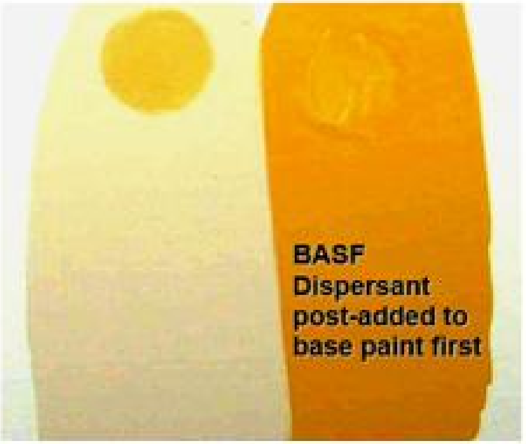


High shear incorporation of colorant mimics what happens over time

Decrease in color strength after high shear incorporation of colorant

No change in color strength after high shear incorporation of colorant

Commercial colorant 1
Mixed in same base paint



Commercial colorant 2
Mixed in same base paint

Addressing Settling

Pigment Physical Phenomena and Thermodynamics

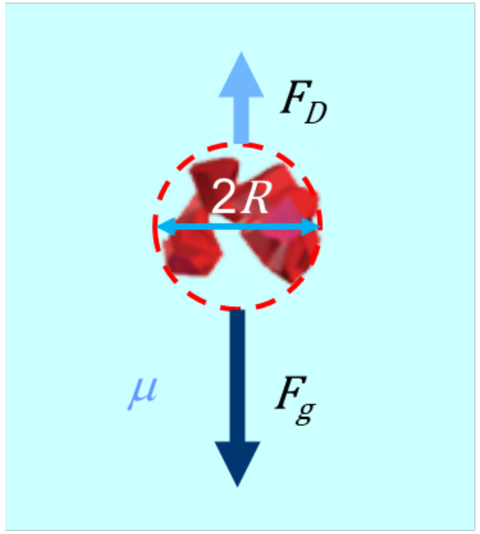
BONUS TOPIC

- 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

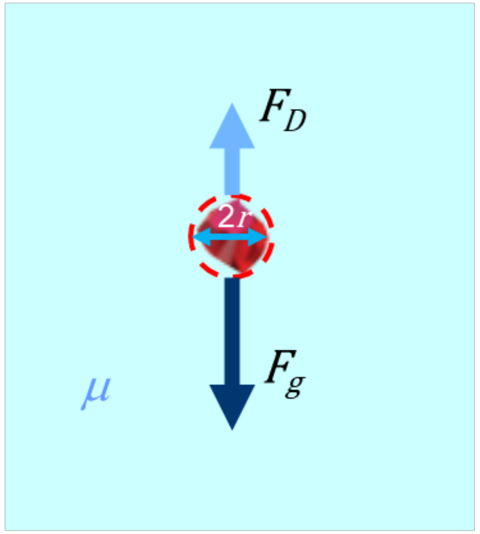
Stoke's Equation for Settling

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

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

Addressing Settling Dispersant with Rheology Modifier

No Rheology Modifier | With Rheology Modifier

No Rheology Modifier | With Rheology Modifier

Settling | No Settling

Coatings Trends & Technologies SUMMIT

Tony Moy

Sr. Technical Specialist

Anthony.moy@basf.com

Website: basf.us/dpsolutions

Email: formulation-additives-nafta@basf.com