Novel Polymeric Dispersants for Improved Dispersion of Polycyclic Pigments

Anthony Gilbert

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Agenda

- Defining “Polycyclic” pigments
- Introduction to dispersant design
- Types of water borne dispersants
  - Anchoring mechanisms and interactions
- Novel dispersant for “polycyclic” pigments
- Perylene black case study
- Perylene red case study
- Indanthrone blue case study
- High jetness carbon black case study

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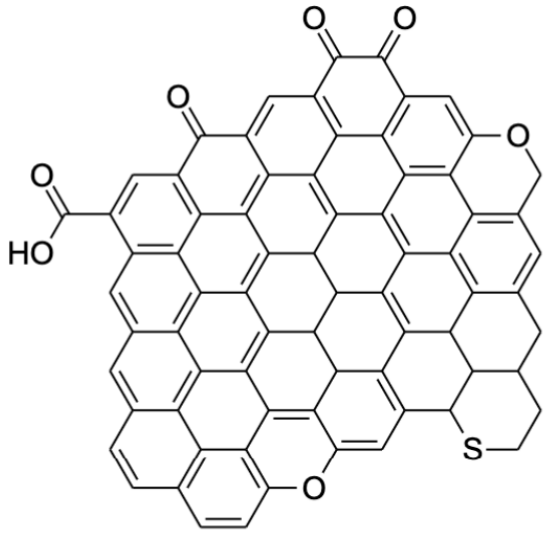
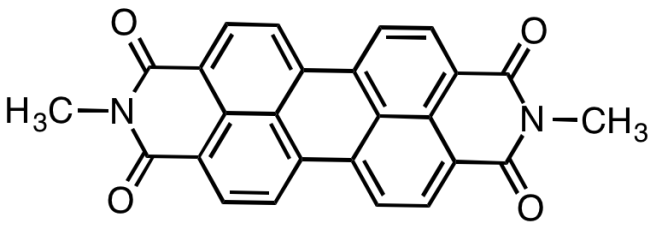
“Polycyclic” Pigments

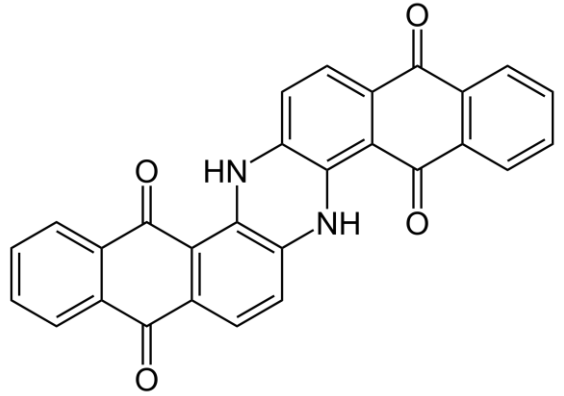
- High degree of aromaticity in the form of conjugated ring structures
  - Carbon black, perylenes (black, red), indanthrone, quinacridone, graphite, etc.



Carbon Black (PBk.7)



Perylene Red (PR.179)



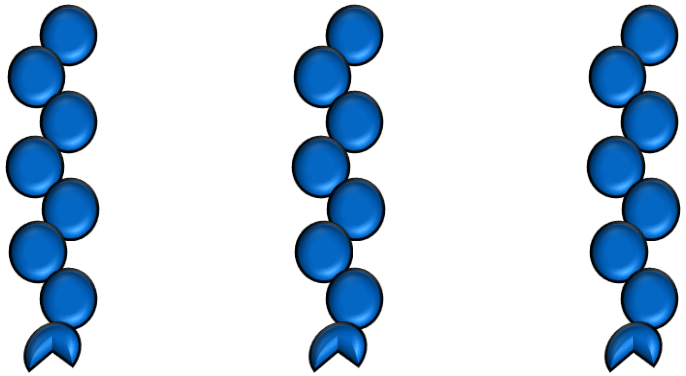
Indanthrone Blue (PB.60)

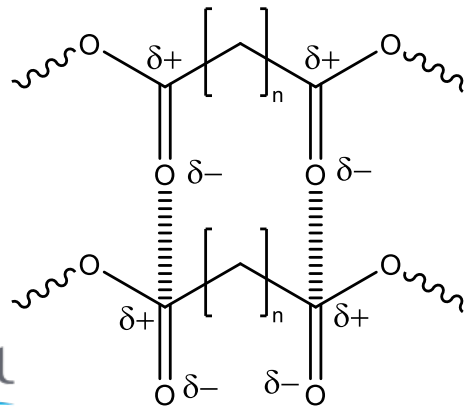
Polymeric Dispersant Design Considerations

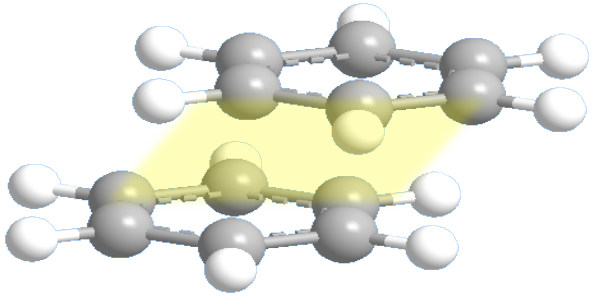
Stabilizing Chains
Provide steric barrier to prevent flocculation, must be soluble in continuous phase

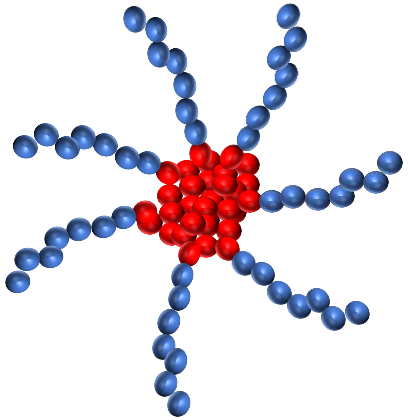
Anchor Groups
Adsorb to the pigment surface
- Hydrogen bonding
- Dipole interactions
- Van der Waals/hydrophobicity

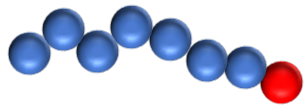
Molecular Weight
- Mobility
- Flow and physical form
- Stability











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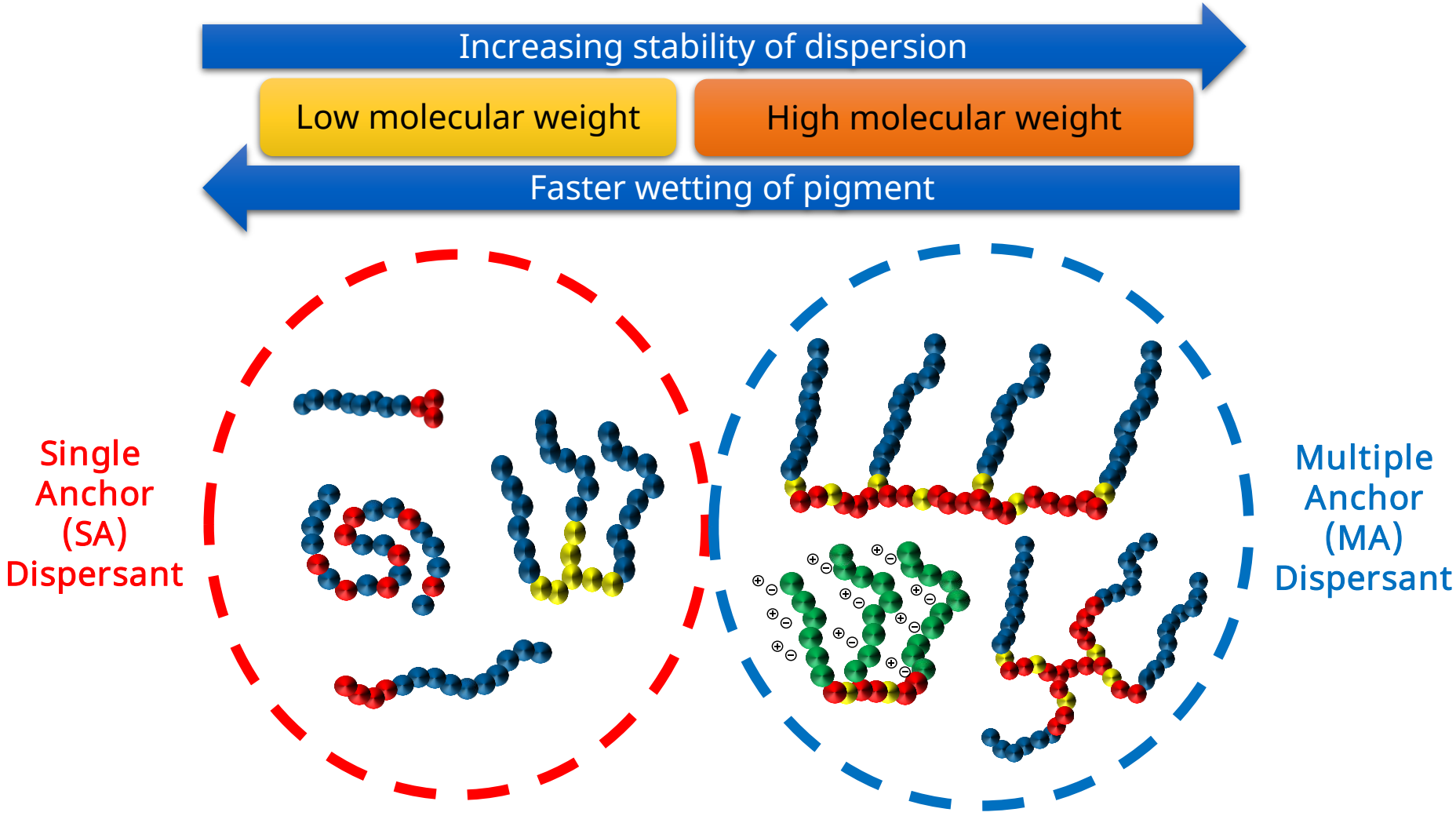
Classes of Polymeric Dispersants



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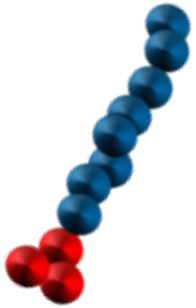
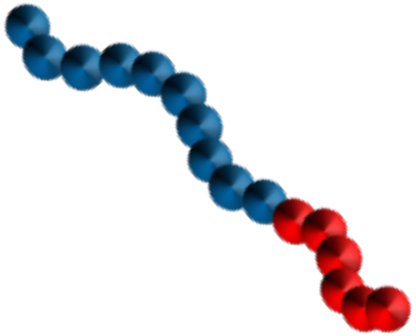
Common Water Borne Dispersant Types



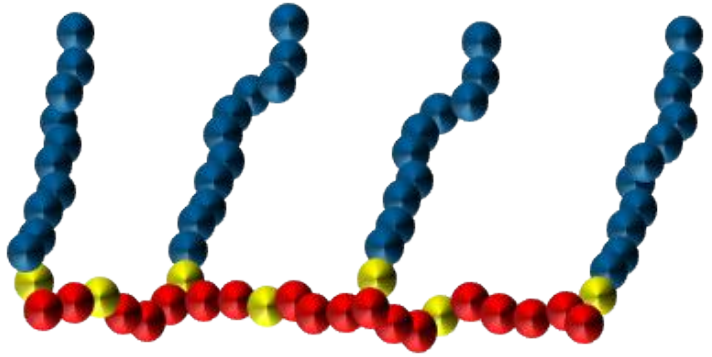
Single anchor, single chain
Commonly acids
(carboxy, phosphate)

Hydrogen and polar interactions with particles



Block copolymers
Commonly acrylics
(acrylic acid, hydrophobic acrylates)

Hydrogen and polar interactions with some van der Waals when using hydrophobic components



Comb copolymers
Variety of chemistries
(multifunctional, polyacids)

Hydrogen and polar interactions with van der Waals on some portions of backbone

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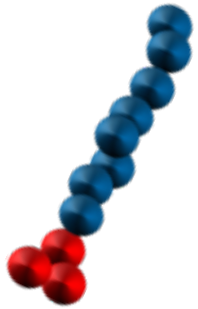
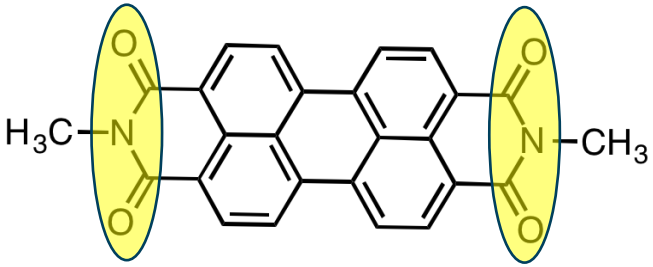
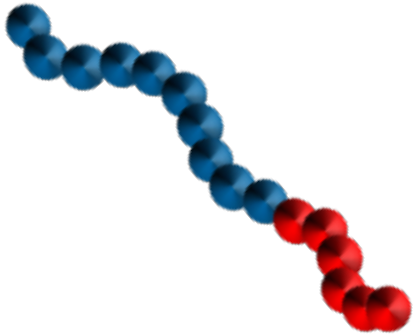
Common Water Borne Dispersant Types



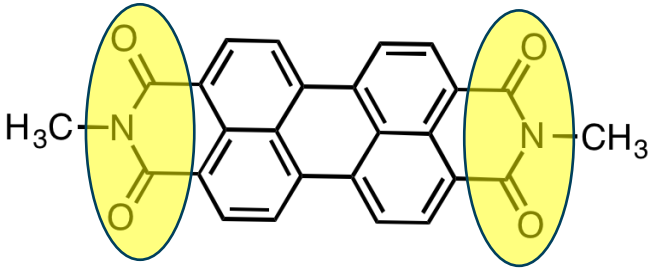
Single anchor, single chain



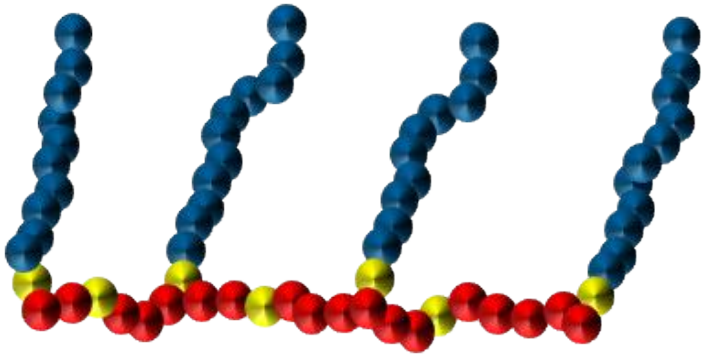
Interaction with pigment:
Acid functionality



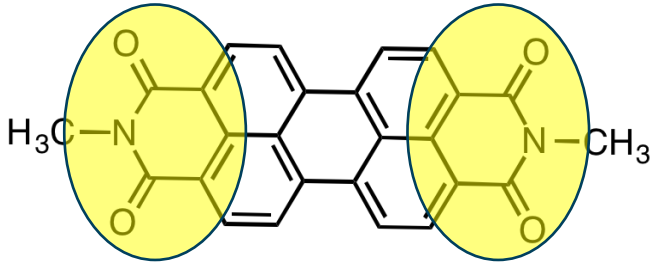
Block copolymers



Interaction with pigment:
poly-acid with some hydrophobicity



Comb copolymers



Interaction with pigment:
poly-acid with some hydrophobicity
or other mixed groups

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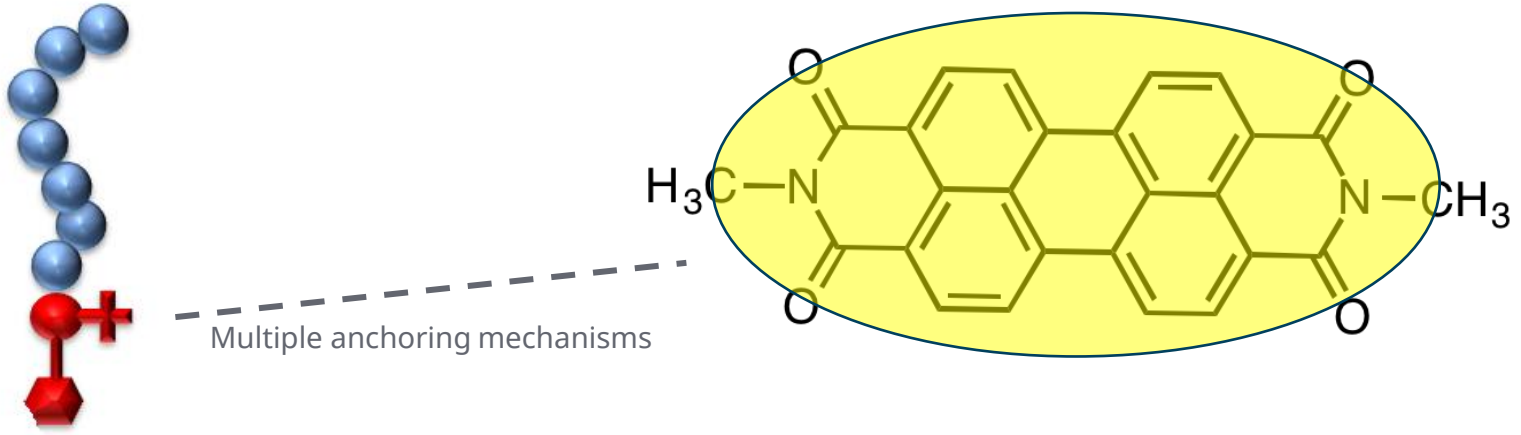
Novel Polymeric Dispersant for “Polycyclic” Pigments

- Novel “multi-anchor, single-chain” dispersant chemistry
  - Designed for stronger interaction with “polycyclic” pigments
  - More permanent attachment provides stability of multi-anchor, multi-chain dispersant without sacrificing wetting and efficiency properties
  - Significantly improved performance in perylenes, indanthrones, carbon blacks



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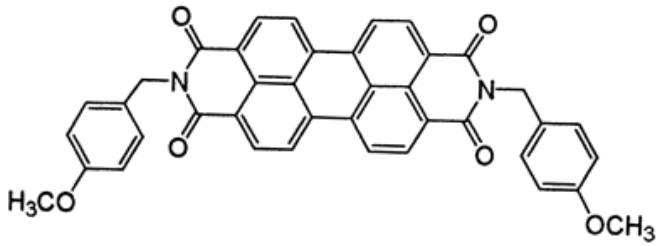
Perylene Black (P.Bk. 32)



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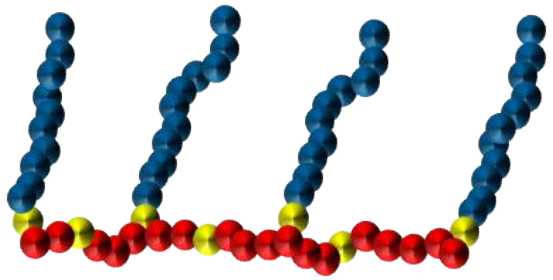
Dispersion Formulas



Material	Commercial Benchmark 1 (40% active)	Novel Dispersant (100% active)
Water	51.9	56.7
Dispersant	8.0	3.2
Defoamer	0.1	0.1
Perylene Black 32	40.0	40.0
D:P Ratio	8.0%	8.0%
Pigment Loading	40.0%	40.0%

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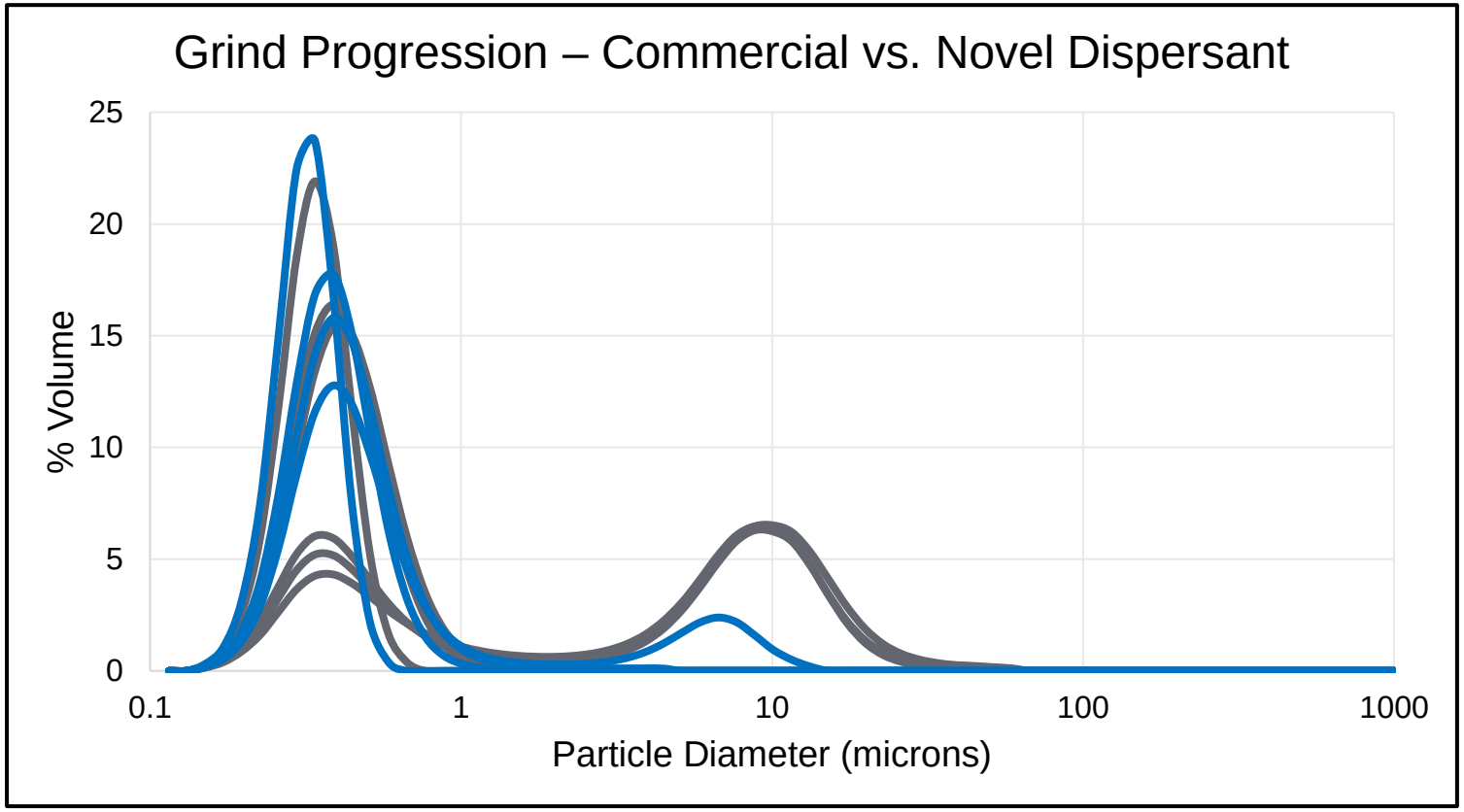
Perylene Black - Grind Efficiency of Novel Dispersant

- Agglomerate peak gone within 10 minutes on HSD with NO media milling
- 15 minute media mill with Novel Dispersant = 45 minute media mill with commercial dispersant



D90 Particle Diameter		
Grind Conditions	Commercial Dispersant	Novel Dispersant
5 Minute HSD	14.26 microns	5.10 microns
10 Minute HSD	13.19 microns	0.64 microns
15 Minute HSD	12.67 microns	0.53 microns
15 Minute Media mill	0.63 microns	0.39 microns
30 Minute Media Mill	0.57 microns	
60 Minute Media Mill	0.43 microns	

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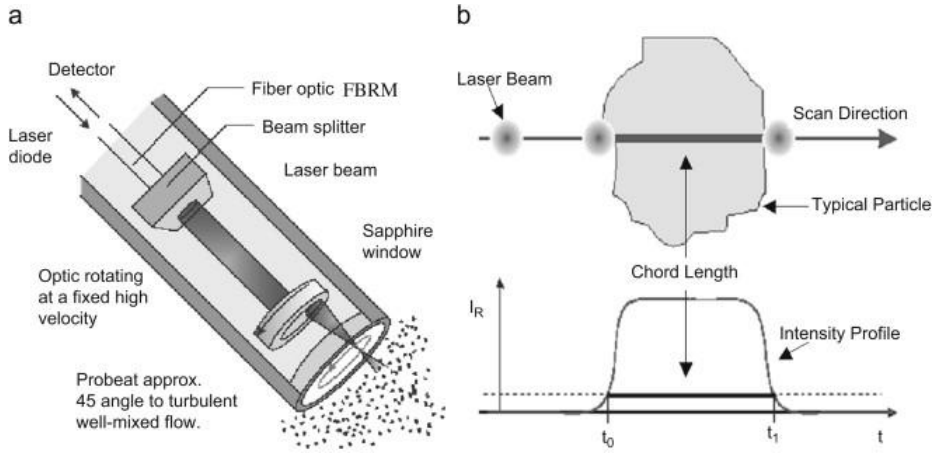
In-Situ Particle Size Analysis with Focused Beam Reflectance Measurement (FBRM)

- Real-time particle size distributions in highly concentrated and active systems
- Particle size measured at 40% weight pigment (perylene) while dispersing with HSD



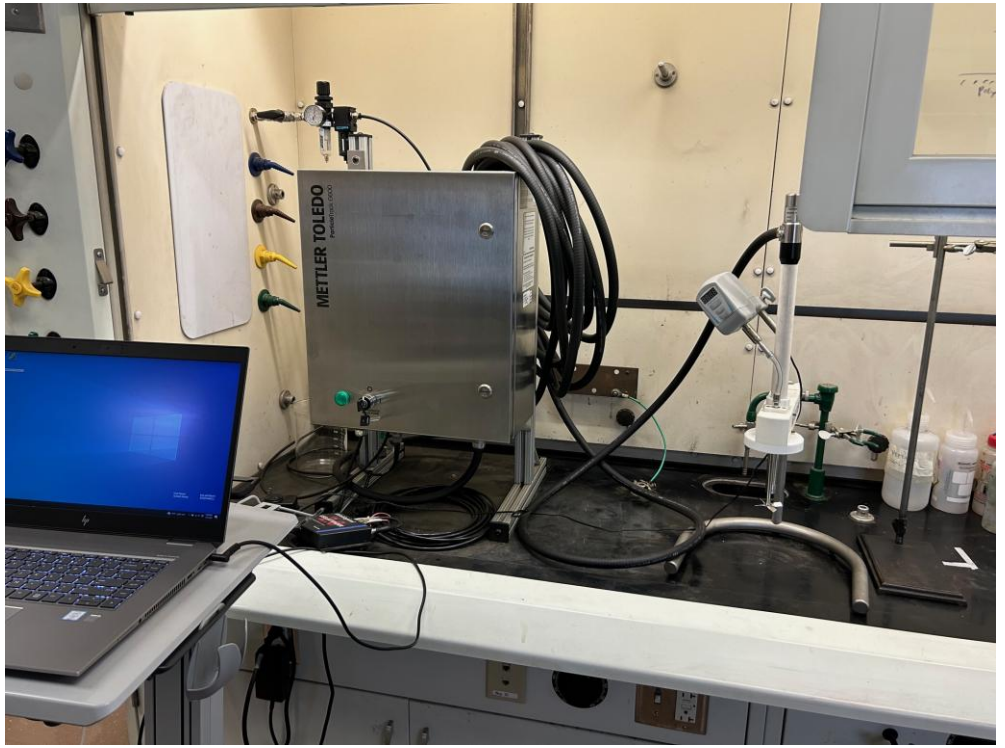
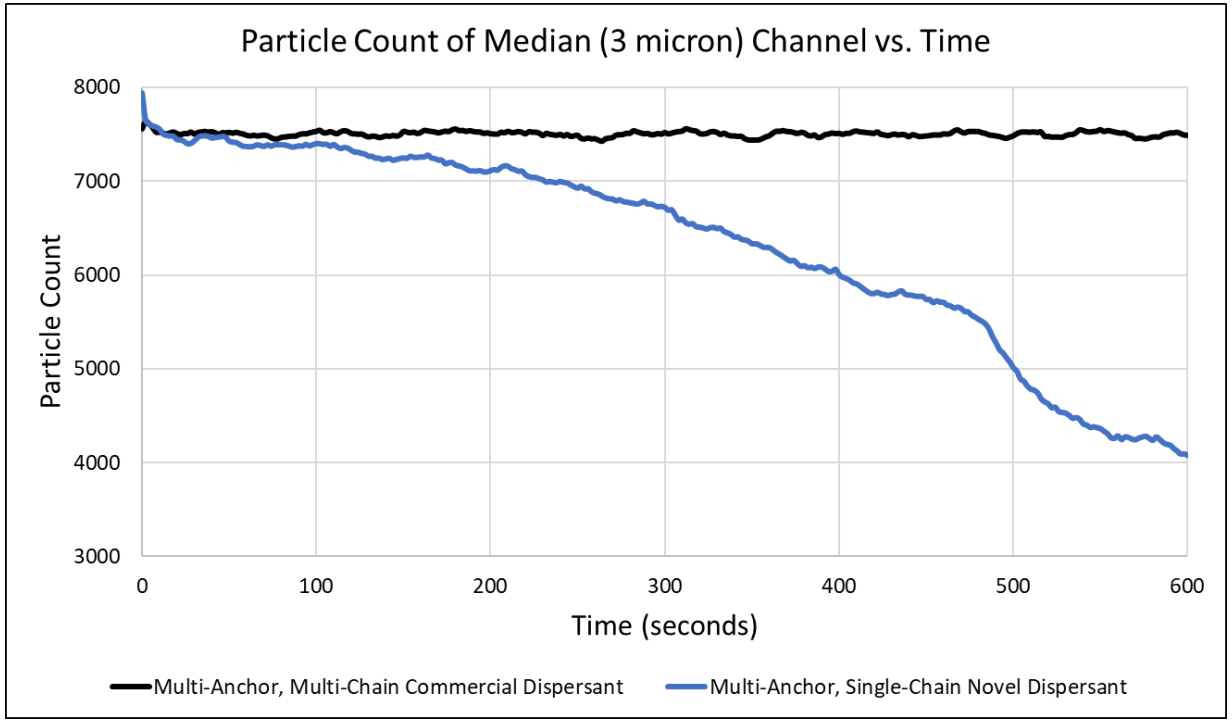
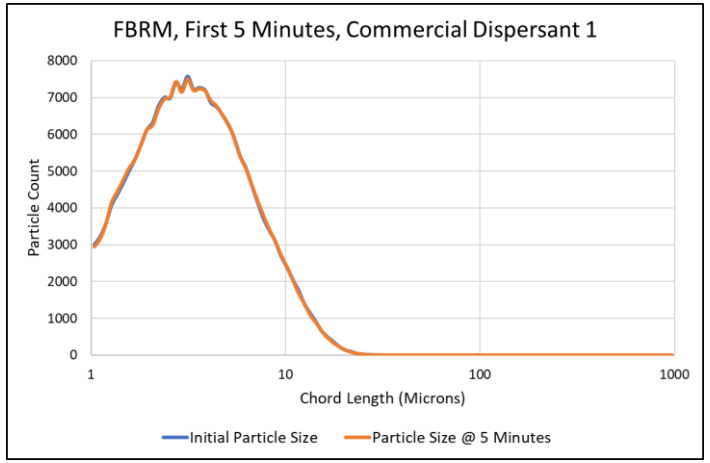


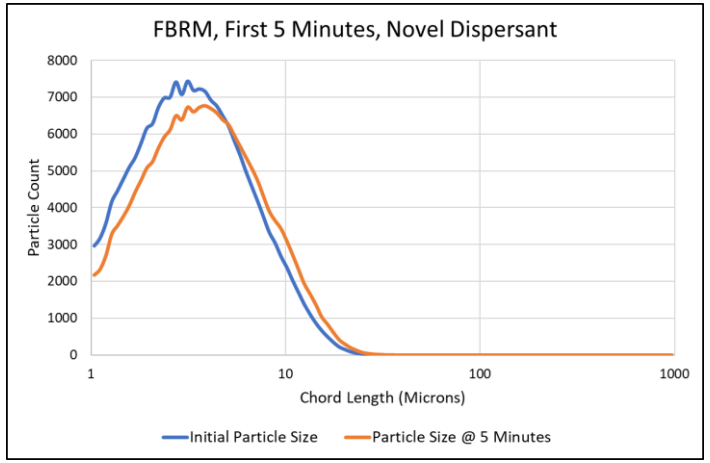
Diagram Credit: Greaves, D.; Boxall, J.; Mulligan, J. C.; Montesi, A.; Creek, J. L.; E. Dendy Sloan; Koh, C. A. Measuring the Particle Size of a Known Distribution Using the Focused Beam Reflectance Measurement Technique. *Chemical Engineering Science* 2008, *63* (22), 5410–5419. https://doi.org/10.1016/j.ces.2008.07.023.

In-Situ Particle Size Analysis with Focused Beam Reflectance Measurement (FBRM)

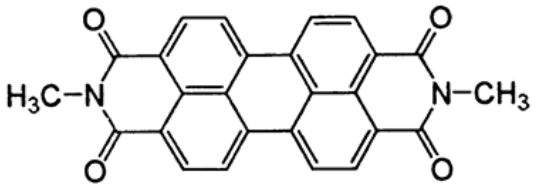
- Novel dispersant shows significant reduction in count of large particles over time







Perylene Red (P.R. 179)



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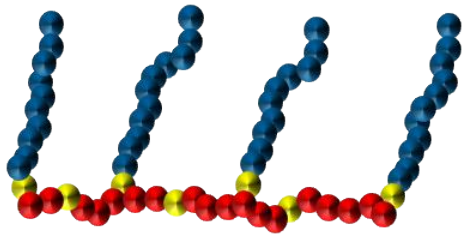
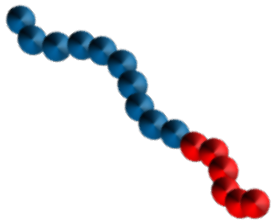
Perylene Red in Traditional Grind Process

- HSD followed by media milling with 1.0mm ceramic media





Material	Commercial Benchmark 1 (40% active)	Commercial Benchmark 2 (50% active)	Novel Dispersant (100% active)
Water	69.9	71.9	75.9
Dispersant	10.0	8.0	4.0
Defoamer	0.1	0.1	0.1
Perylene Red 179	20.0	20.0	20.0
D:P Ratio	20.0%	20.0%	20.0%
Pigment Loading	20.0%	20.0%	20.0%
Final Viscosity (10 s^{-1})	535 cP	Gelled	28 cP

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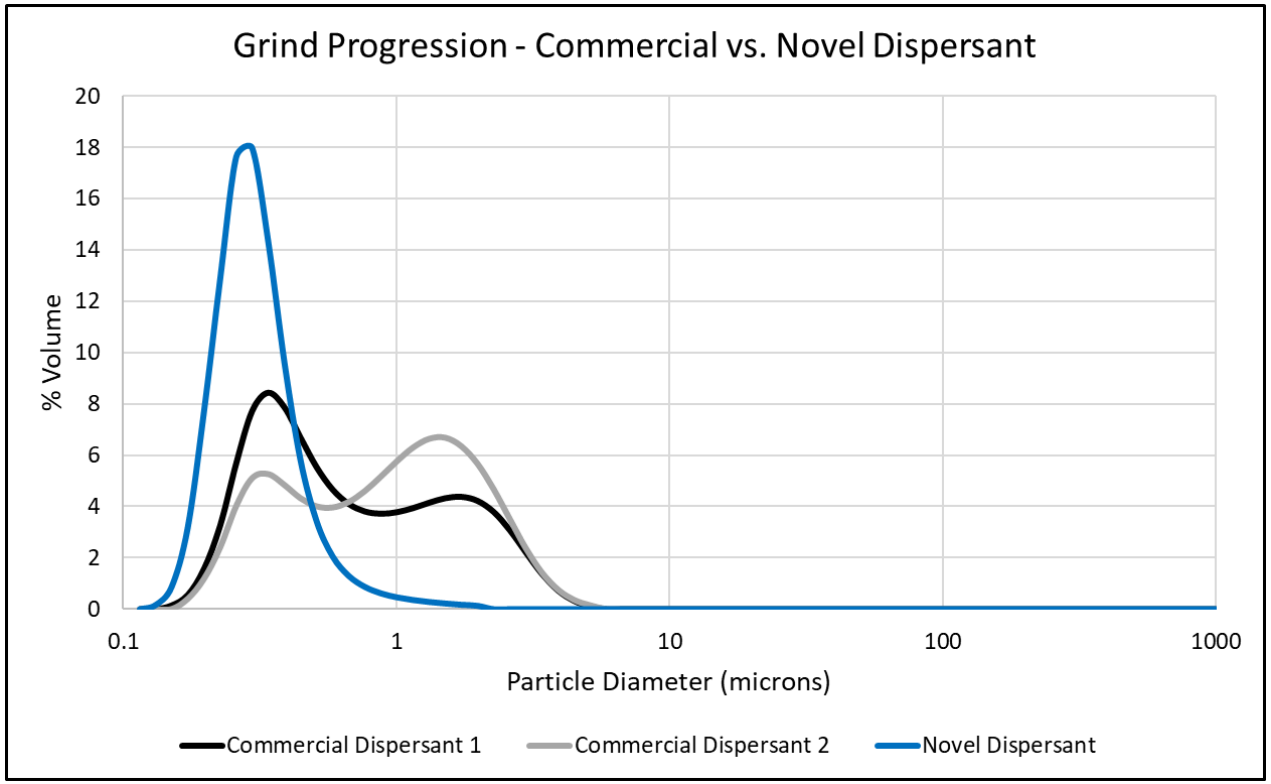
Perylene Red – Grind Progression

- Commercial dispersants still had significant volumes of agglomerated particles present after 6 hours of milling
- Novel dispersant achieved monomodal, sub -micron distribution in 6 hours



D90 Particle Diameter			
Grind Conditions	Commercial Dispersant 1	Commercial Dispersant 2	Novel Dispersant
15 Minute HSD	26.90 microns	23.5 microns	27.8 microns
1 Hour Media Mill	5.70 microns	4.60 microns	5.20 microns
2 Hour Media Mill	4.00 microns	4.00 microns	4.00 microns
4 Hour Media Mill	2.48 microns	2.17 microns	2.61 microns
6 Hour Media Mill	2.10 microns	Gelled, 2.47 µm	0.44 microns

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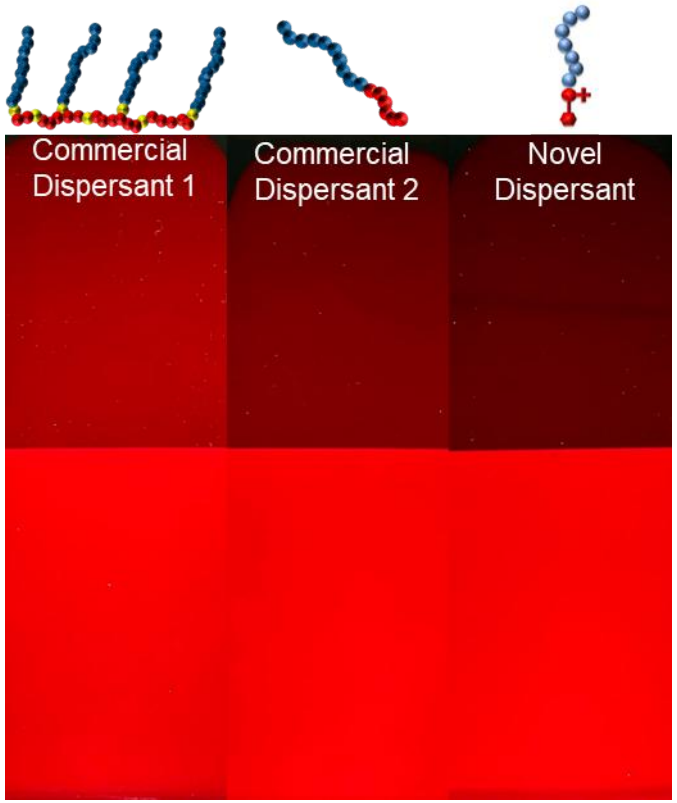
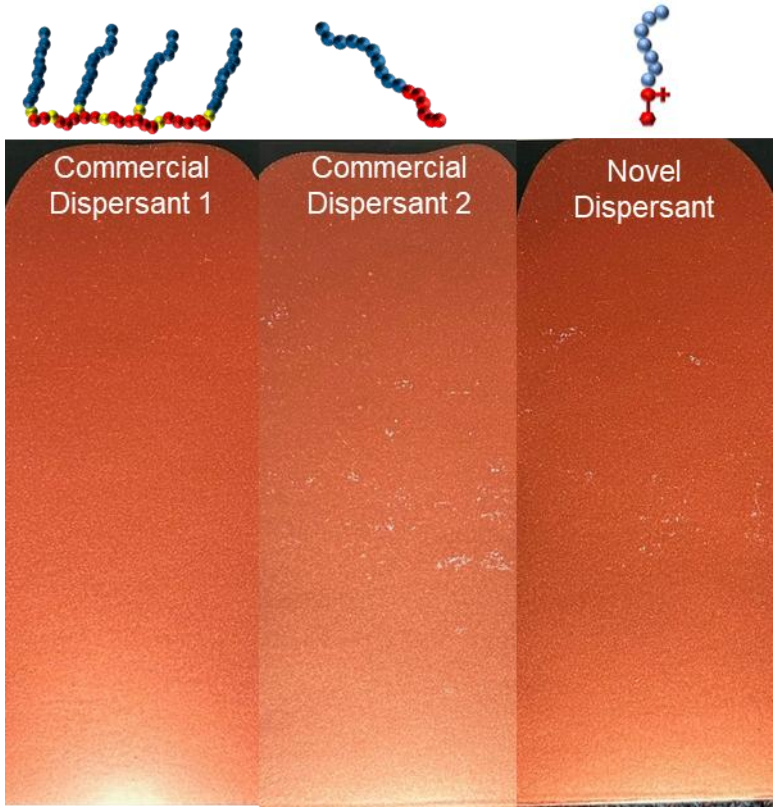
Transparency and Color Strength





Haze, on clear mylar:

P:B Ratio	Commercial Dispersant 1	Commercial Dispersant 2	Novel Dispersant
2.5% P:B	48.12	41.74	22.70
5.0% P:B	67.42	75.5	36.53

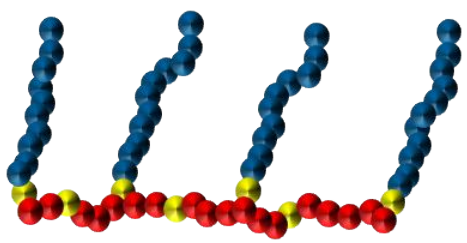
Color strength, 45º in metallic letdown:

Pigment Ratio	Commercial Dispersant 1	Commercial Dispersant 2	Novel Dispersant
80/20 Al:R.179	137%	100% (ref.)	147%

Perylene Red 179 Nano Dispersions

- 2-stage process
- 4 hours w/ 1.0mm ceramic
- 8 hours w/ 0.1mm ceramic

- Novel dispersant reaches significantly smaller particle size at a reduced viscosity



Material	Commercial Benchmark 1 (40% active)	Novel Dispersant (100% active)
Water	47.4	69.9
Dispersant	37.5	15.0
Defoamer	0.1	0.1
Perylene Red 179	15.0	15.0
D:P Ratio	100.0%	100.0%
Pigment Loading	15.0%	15.0%
Final Viscosity (10 $^{s-1}$)	517 cP	19 cP
Z-Average Diameter	127 nm	60 nm

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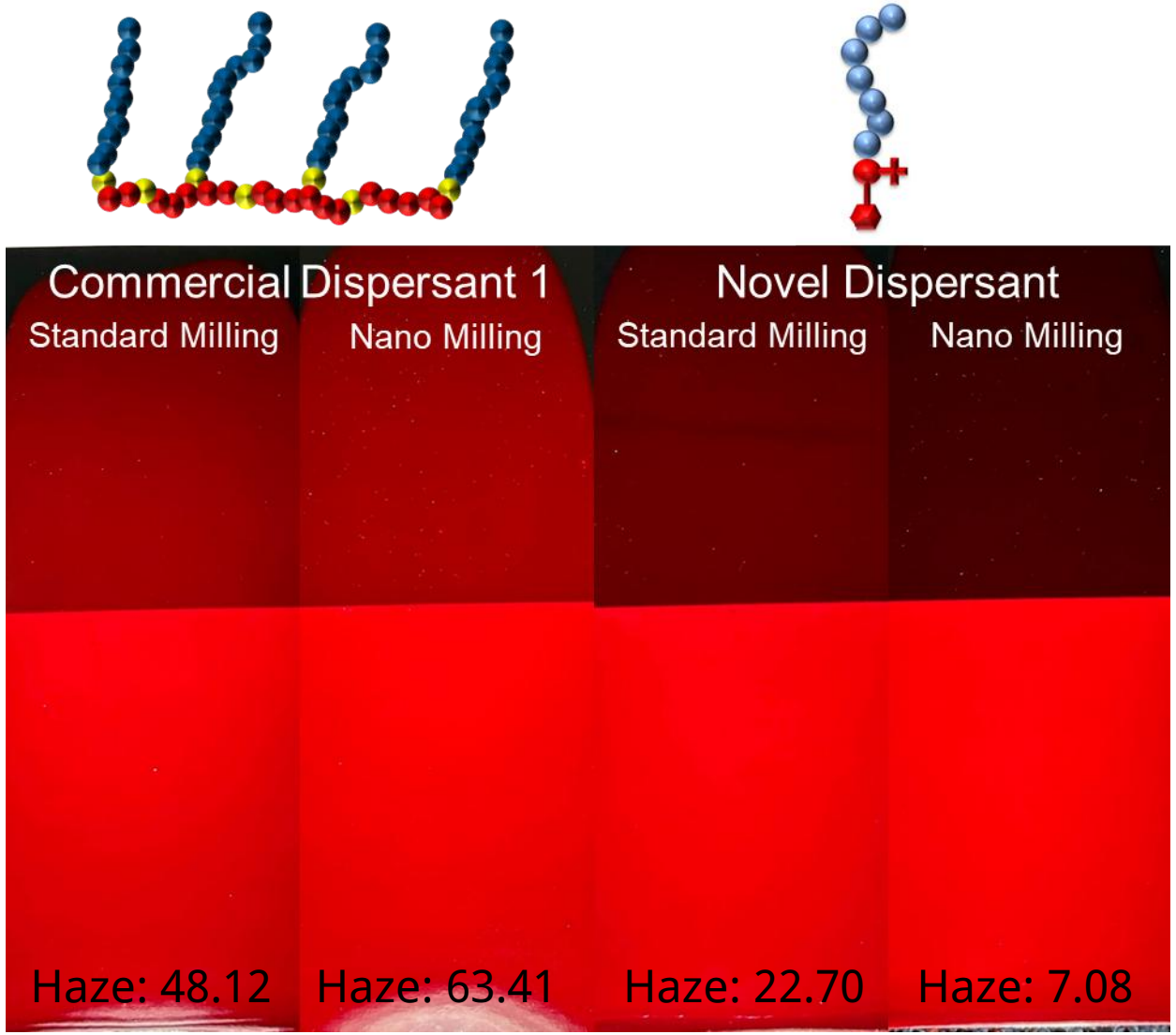
Transparency in Nano Dispersions

- Novel dispersant significantly outperforms commercial dispersant 1 in both standard and nano milling processes
- Commercial dispersant performs worse in nano process than standard process



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Other Pigments, Indanthrone (P.B 60) and Carbon Black (P.Bk 7)

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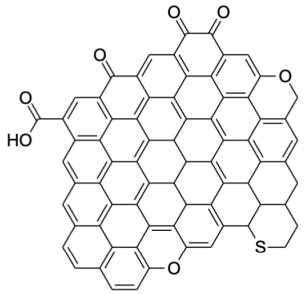
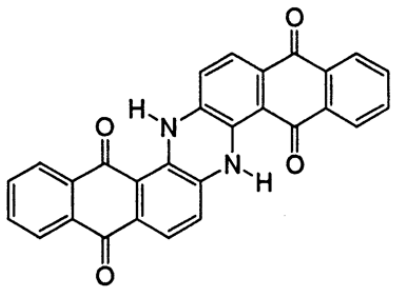
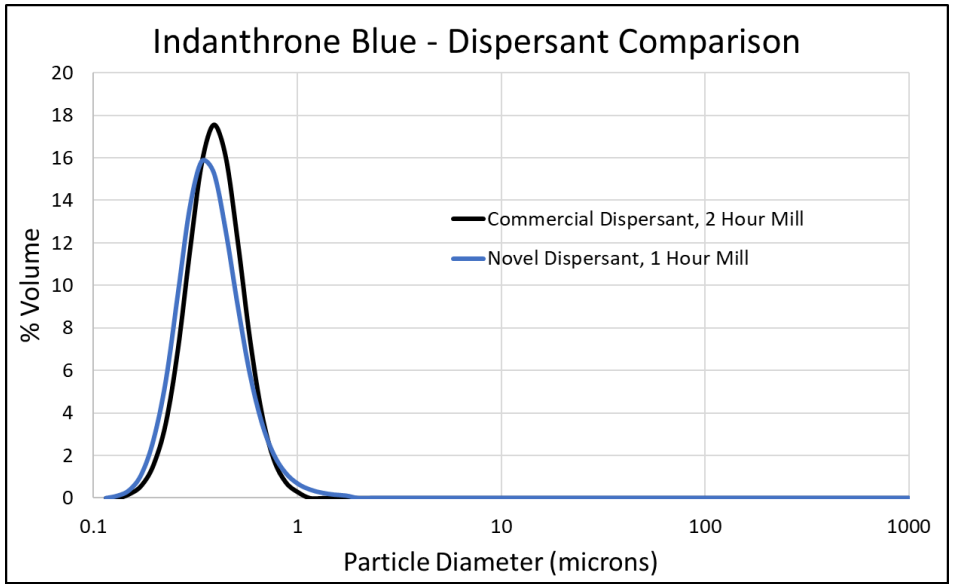
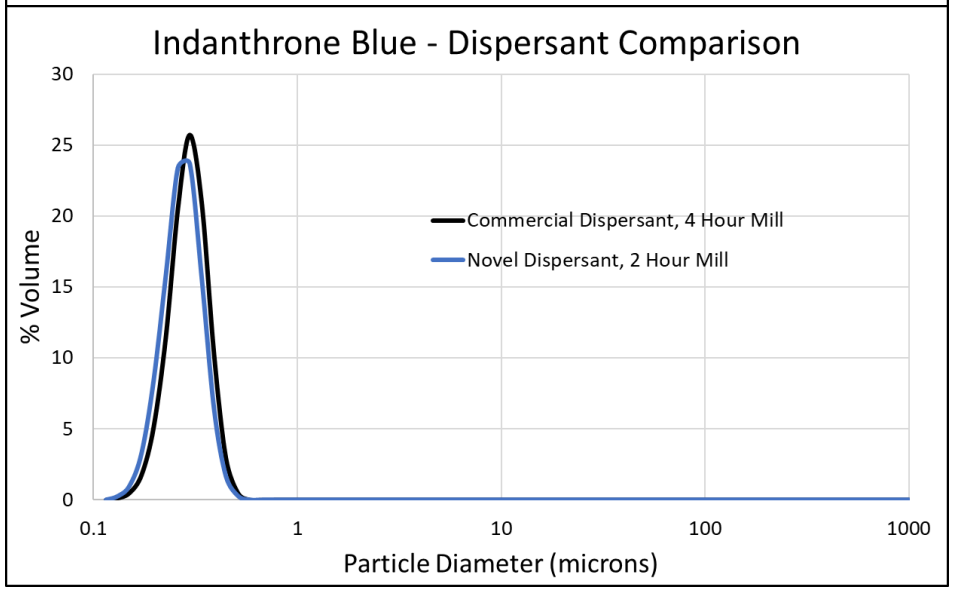




- 50% less time needed to reach same dispersion quality (particle size)

Material	Commercial Benchmark 1	Novel Dispersant
Water	54.9	63.9
Dispersant	15.0	6.0
Defoamer	0.1	0.1
Pigment Blue 60	30.0	30.0
D:P Ratio	20.0%	20.0%
Pigment Loading	30.0%	30.0%
Final Viscosity (10 $^{s-1}$)	23 cP	32 cP





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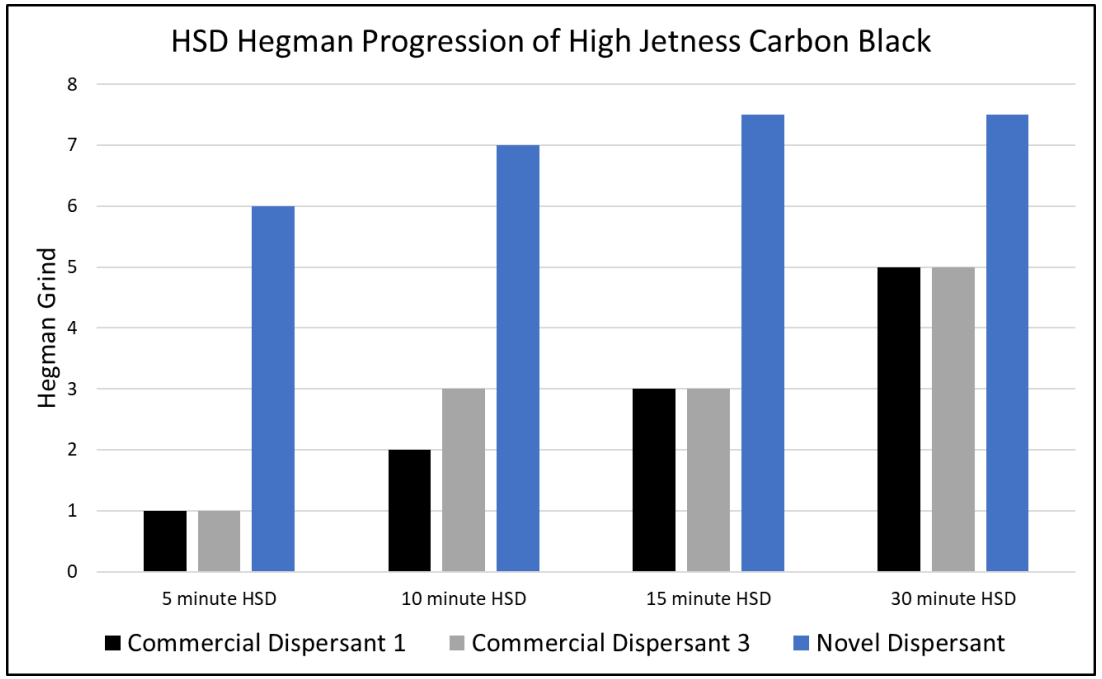
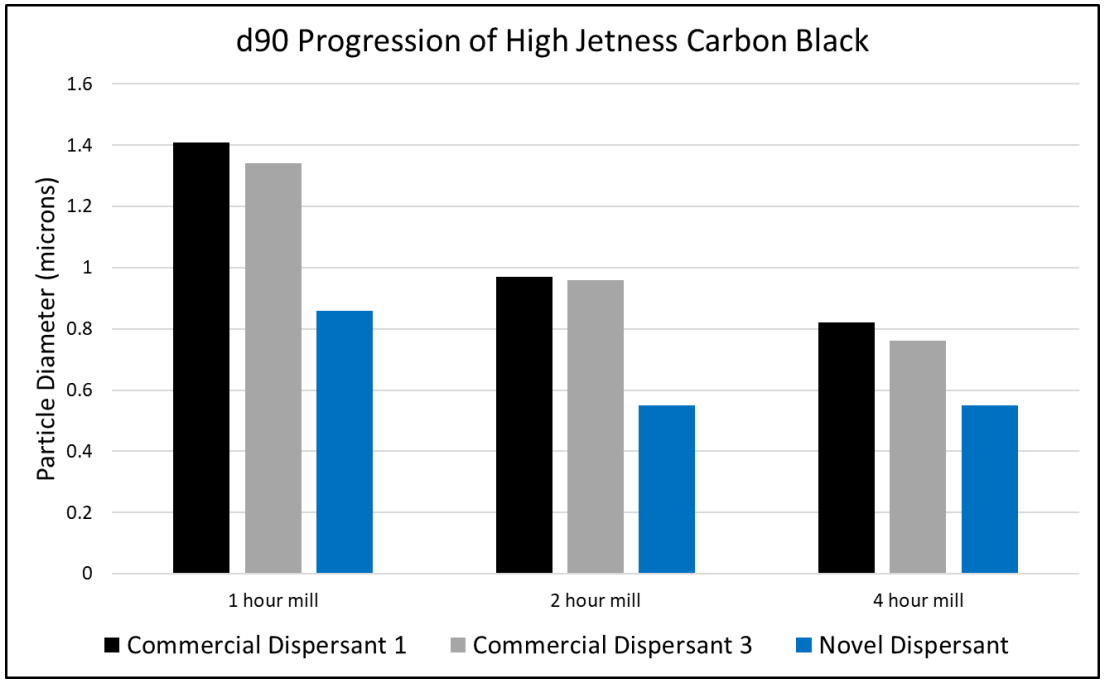
Carbon Black Particle Size Reduction

- Novel Dispersant drastically improves efficiency of grind with HSD
  - Hegman 7.5 in 15 minutes
- Novel dispersant achieves significantly finer d90 in media milling, indicating improved breakup of aggregated particles





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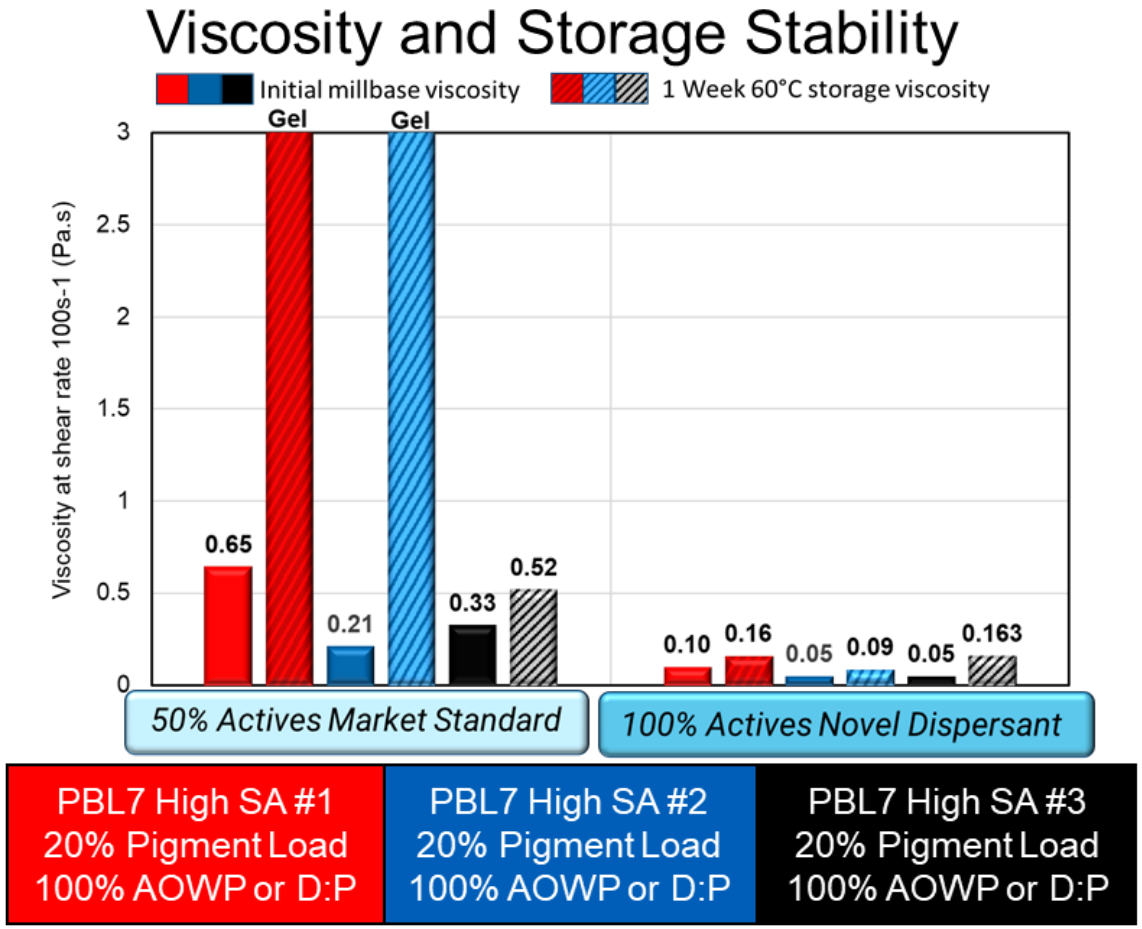
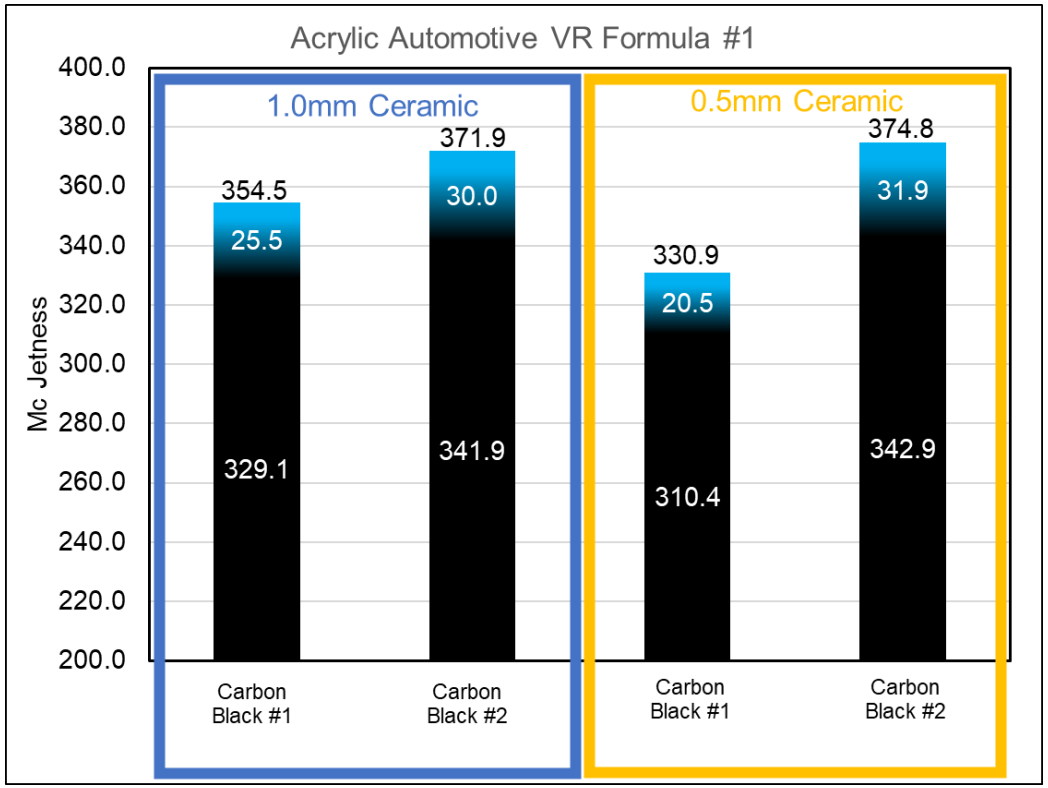
Carbon Black Viscosity and Stability

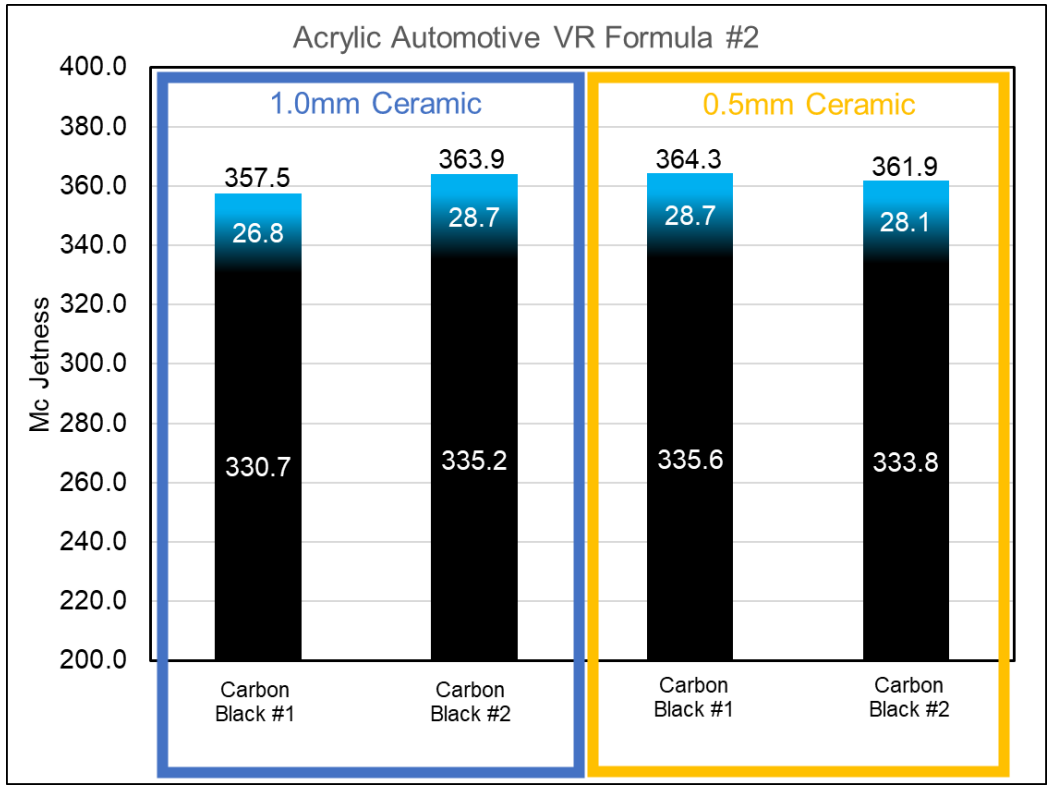
- Novel dispersant allows for significantly stronger viscosity reduction in all 3 major jet black pigments
- No significant viscosity increase after 1 week accelerated aging in oven
- Newtonian viscosity still present at 20% pigment loading



Carbon Black Jetness

- Able to achieve ~375 Mc jetness with Carbon Black #2 in Auto VR Formula #1
- Able to achieve strongest color properties with just 1.0mm ceramic media





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- Alison Drasdo
- Matt Dunn
- Andy Shooter

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