WHITE PAPER

An efficient approach to dispersing pigments

**Nikolina Milanovic and Brian O. Casey,
Evonik Resource Efficiency**

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ABSTRACT

As problems related to pigment dispersions become more frequent and as requirements regarding color reproducibility become increasingly rigorous, new demands for pigment wetting agents and dispersants are required to resolve these pigment stabilization issues. Over the past 20 years, advances in polymeric dispersants have made significant improvements in the process of wetting and stabilizing pigments. As a result, many dispersant technologies that better stabilize small pigment particles and that better prevent flocculation are emerging in the marketplace. This paper will explain pigment and dispersant interfaces and how harmonizing and optimizing these interactions will lead to a better pigment dispersion.

INTRODUCTION

Until the development of synthetic pigments, pigments of natural origin – materials such as clay, earth colors, and minerals – were used to color paints. Vegetable oils with high lecithin content were used to wet out natural pigments. Since then, technology has progressed immensely.

Dispersing pigments is sometimes viewed as an art instead of a technical process. This is mainly due to the multiple steps that occur during the dispersion process. These processes can seem confusing, but breaking the steps down into a structured manner makes them easier to understand and helps find solutions faster.

The following research explains the science behind dispersing pigments and fillers, in hopes to reach a better understanding of how to stabilize them more efficiently. This study discusses different types of wetting and dispersing additives that can be used to stabilize two notoriously difficult pigments.

PIGMENT AND ADDITIVE INTERACTIONS

Pigments are tiny solid particles that have the ability to refract light[1]. Pigments serve two main functions: an optical function, providing color, opacity, and gloss; and a protective function, for the surface beneath the coating.

Structures of pigments

Pigments come in three forms: primary particles, aggregates, and agglomerates. Primary particles are single, small particles that form during synthesis [2]. These are the smallest components in pigments and fillers, and they mostly consist of cuboid, rod, and spherical-shaped particles (Figures 1–2). During calcination, primary particles may form together to create larger particles through chemical bonding. These particles are called aggregates, and they are organized lattice regions connected from face to face of the primary particle. Alternatively, particles that form via physical bonds instead of chemical bonds are called agglomerates. These particles are connected by edges, resulting in a smaller surface area and more difficulty in wetting out the pigment.

Figures 1-2: Transmission electron microscope images of iron oxide pigments
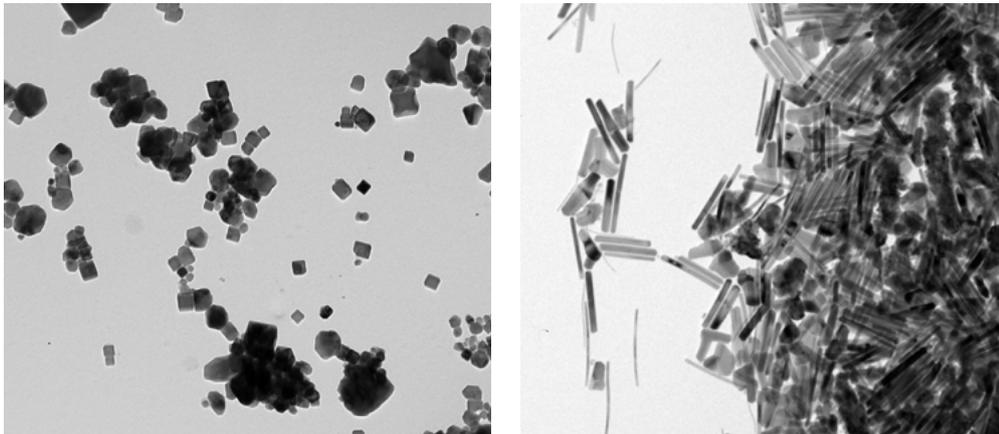
Organic and inorganic pigments

Pigments are widely classified as either organic or inorganic. Inorganic pigments are used for coloristic properties as well as other properties such as anti-static and anti-corrosion character- istics. Inorganic pigments normally have a high refractive index, meaning they have a greater ability to scatter light[3]. Therefore, these pigments are very good at "hiding" the surface under the coating layer. Oxide compounds such as titanium dioxide and iron oxides are typical examples of inorganic pigments. Carbon blacks are technically classified as inorganic pigments, but they require a different anchor group to adsorb onto the pigment surface[4].

Organic pigments are intensely colored, therefore they are incorporated solely for their coloristic properties. Organic pigments are classified as azopigments, polycyclic pigments, and anthraqui- none pigments[4]. They tend to have a smaller particle size than inorganic pigments, thus making them more transparent. They have a tendency to dissolve when moisture is present, which causes them to migrate and chalk to the surface. Because of their smaller particle size, organic pigments are normally more difficult to disperse compared to inorganic pigments. Because most inorganic pigments have polar surfaces, they are much easier to wet out.

Dispersing technology

In order to understand wetting and dispersing agents, a fundamental knowledge of the dispersing process is required. Dispersing agents stabilize deflocculated pigment particles. For stabilization of these particles to occur, the dispersant must be able to overcome van der Waals attractions that are constantly moving pigment particles back together[2]. The pigment dispersion process can be broken down into three steps: wetting, de-agglomeration, and stabilization.

Step one: Wetting

The first step of the dispersion process consists of wetting the pigments by a liquid. The liquid spreads over the pigment surface and fills the voids and pores of the pigment, displacing any remaining air pockets[2]. For a pigment to be wetted by a liquid, the surface tension of the liquid must be lower than the surface energy of the pigment[1]. This interaction between pigment and liquid is described below by the Young equation. A liquid with a low surface tension typically wets pigments better than one with a higher surface tension.

Equation 1

Step two: De-agglomeration

After the pigments are wetted, they are broken down to achieve small particle sizes with a large surface area. This yields a higher color strength, which is more cost-efficient for paint manufacturers.

In order to grind down to smaller particle sizes, more energy is required. To break up agglomerates and increase the surface area (ΔA), an increased energy input (ΔW) is required (Equation 2)[1]. This energy is proportional to the surface tension (Y) of the dispersion. The smaller the surface tension, the greater the surface area will be for a certain amount of energy[3].

$$\Delta W = Y \bullet \Delta A \qquad \text{Equation 2}$$

When dispersing, agglomerates are broken down into primary particles and small aggregates. When breaking down agglomerates, only physical bonds are being interrupted.

Figure 3: **Typical ranges of energy contents of one mole (6.0231×10^{23}) associated with the different types of chemical and physical bonds[4]**
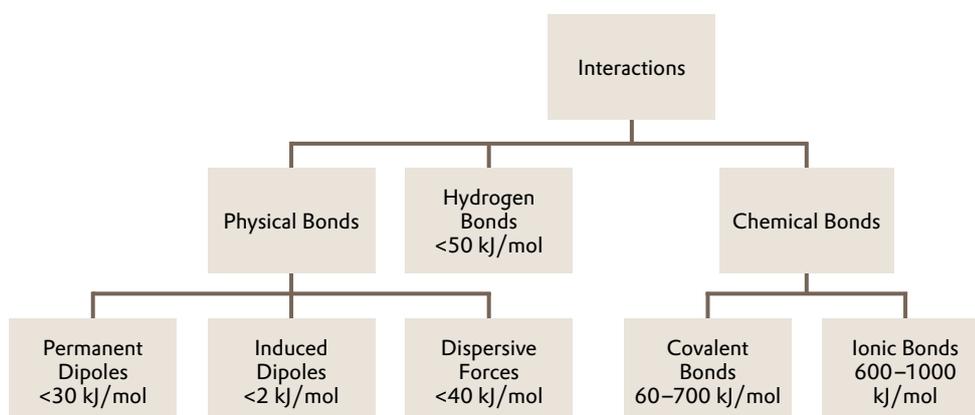

These energies range from 40–50 kJ/mol, meaning 40,000 to 50,000 joules are required to break these physical bonds[4]. If aggregates are milled, then approximately 600 to 1000 kJ/mol are required to break these chemical bonds[4]. This is about ten times the energy it takes to grind agglomerates.

Step three: Stabilization

Consequently, when there are large surface areas and small pigment particles, the energy is very high and thermodynamically unstable. Solid particles will always gravitate towards each other in Brownian motion to minimize their surface area and return to a lower energy state that is more stable[2] (Figure 4).

Figure 4: Stability of pigment dispersions
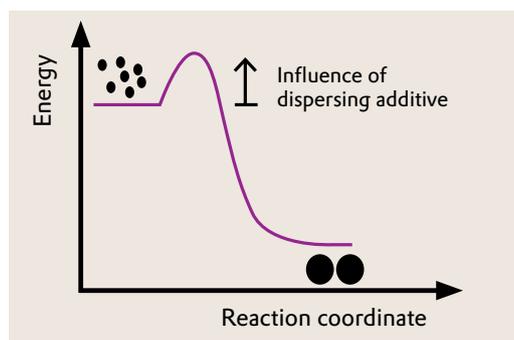
If these particles are not well stabilized, then they will flocculate back together. To achieve good pigment stabilization, the dispersing agent must be able to adsorb onto the surface of the pigment. Therefore, the additive must have anchor groups with high affinity for the pigment surface.

The stabilization of pigments can be achieved by electrostatic, steric, or electrosteric stabilization (Figure 5).

Figure 5: Mechanisms of pigment stabilization[1]
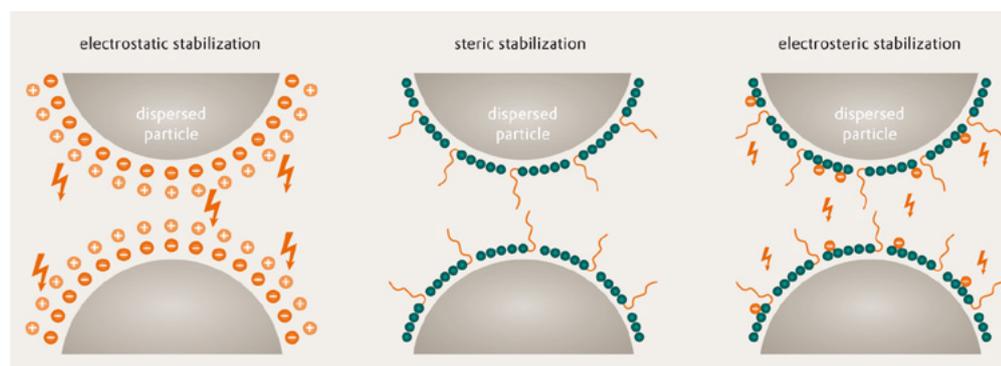
Electrostatic stabilization is most suitable for use in waterborne formulations with high dielectric charges. The dispersing additive adsorbs onto the pigment surface and dissociates into an anionic and cationic part. This creates an electric double layer that prevents pigments from flocculating together via an electrostatic repulsion of like-charges[3].

In contrast to electrostatic stabilization, steric stabilization uses polymeric side chains to keep pigment particles stable in a dispersion. When pigment particles come closer together, the polymeric side chains restrict their movement and decrease entropy[4]. The outcome is a repulsive force between the two particles. These interactions also restrict the movement of the particles that give rise to the viscosity.

In some cases, using only electrostatic or only steric stabilization is not enough. Pigment dispersions have complex demands, therefore it is sometimes necessary to combine the two stabilizations to create electrosteric stabilization.

WETTING AND DISPERSING AGENTS

The terms wetting agent, wetting additive, dispersant, or wetting and dispersing additive are often used without full understanding of their exact definitions. There are very important differences in the chemical structures and functions of each.

Wetting agents are low molecular weight, amphiphilic molecules with a hydrophilic and hydrophobic segment. They aid in reducing surface tension and wetting out surfaces, but most of the time, stabilization of pigments is not achieved. Dispersing agents are oligomers or polymers that aid in the stabilization of pigments and fillers. At the core of every dispersing agent, there must be a wetting agent in order to facilitate the first step in the dispersion process – wetting out the pigment. The major difference between these two technologies, is that dispersing agents utilize anchor groups and polymeric side chains to stabilize pigments.

Polymeric side chains

Polymeric side chains aid in the adsorption of the dispersing agent onto the pigment surface. The side chains must be soluble in the medium. If they are not soluble, they could collapse onto the pigment surface causing flocculation.

Additionally, polymers of medium molecular weight are optimal. If the mass is too low, in the case of wetting agents, then there might not be enough of an effect to stabilize pigments. On the other hand, if the mass is too large, then it could be incompatible and cause viscosity to rise.

Anchor groups

Anchor groups are placed at the end of the polymeric chains to attach to the surface of the pigment. Without these anchor groups, the polymeric side chains would not be useful. Specific chemical groups are used as anchors for certain pigment types.

Dispersants with aromatic rings have an affinity for surfaces of organic pigments. They adsorb onto the surface by van der Waals forces. Dispersants with hydroxyl-, carbonyl-, or carboxyl-groups have a high affinity for the surface of inorganic pigments. These adsorb onto the surface by hydrogen bonding or induced dipole interactions. Amine groups have high affinity for carbon black surfaces. Without nitrogen, there is not much suitability for carbon black.

EXPERIMENTAL DESIGN

For this study, two of the most difficult pigments were chosen to prepare pigment concentrates: yellow iron oxide and organic violet (Tables 1-2). Four 100%-active additives were chosen to be tested, ranging from 10% to 30% additive solids on pigment.

- **Additive A**: a low molecular weight alkoxylate
- **Additive B**: a medium-weight polyether with aromatic groups
- **Additive C**: a medium-weight polyether phosphate with acid groups
- **Additive D**: a high molecular weight polymer with hyper-branched polyester chains with aromatic and acid groups

All samples were made in 8-ounce glass jars with 100 grams of material to work with. Glass beads of size 2.4–2.9 mm were added as grinding media in a 1:1 ratio. The formulations were processed on a Skandex shaker for one hour. After dispersing was completed, samples were cooled to room temperature and filtered through a mesh cone filter.

Yellow iron oxide formulations

The yellow iron oxide formulations consist of 55% pigment loading, with 10% additive solid on pigment. Because of increasing environmental demands, an exempt solvent (Oxsol 100) was chosen for this study.

Table 1: Yellow iron oxide formulations

Products	Blank	Sample A	Sample B	Sample C	Sample D
Oxsol 100	20.0	20.0	20.0	20.0	20.0
Grinding Resin	25.0	19.5	19.5	19.5	19.5
Additive A	–	5.5	–	–	–
Additive B	–	–	5.5	–	–
Additive C	–	–	–	5.5	–
Additive D	–	–	–	–	5.5
PY42	55.0	55.0	55.0	55.0	55.0
TOTAL	100.0	100.0	100.0	100.0	100.0
ASOP	0	10%	10%	10%	10%

Pigment violet formulations

Price is a big driving factor in the pigment concentrate market. Because organic pigments are normally more expensive, titanium dioxide was coupled in this formulation to reduce price. The pigment loading for violet was 6% and titanium dioxide was 30%, with 30% additive solid on pigment.

Table 2: Pigment violet formulations

| Products	Blank	Sample A	Sample B	Sample C	Sample D
Water	43.0	32.2	32.2	32.2	32.2
Grinding Resin	20.0	20.0	20.0	20.0	20.0
Defoamer	1.0	1.0	1.0	1.0	1.0
Additive A	–	10.8	–	–	–
Additive B	–	–	10.8	–	–
Additive C	–	–	–	10.8	–
Additive D	–	–	–	–	10.8
PW6	30.0	30.0	30.0	30.0	30.0
PV23	6.0	6.0	6.0	6.0	6.0
TOTAL	100.0	100.0	100.0	100.0	100.0
ASOP	0	30%	30%	30%	30%

YELLOW IRON OXIDE RESULTS

Viscosity was measured on a Haake Rheostress 1 Rheometer equipped with PP35 Ti L03 089 plate and tested under a 0.20 mm gap at room temperature. Initial viscosity studies showed that the blank and Sample A had very shear thickening behavior, meaning their viscosities rose along with the shear rate. This is not ideal for pigment concentrates because it could clog the dosing machine when tinting white base paints. Sample B had a shear thinning viscosity until 1,000/s, where there was a rise in viscosity. This indicates that there was not enough dispersant to wet out the remaining pigment. Sample C and Sample D had shear thinning curves, with viscosity being the lowest overall for Sample D. This is attractive to pigment concentrate suppliers because a low viscosity means more pigment loading is possible. Viscosity will also be tested after a storage period at elevated temperatures to confirm the performance of the additives.

Figure 6: Initial room temperature viscosity for yellow iron oxide formulations
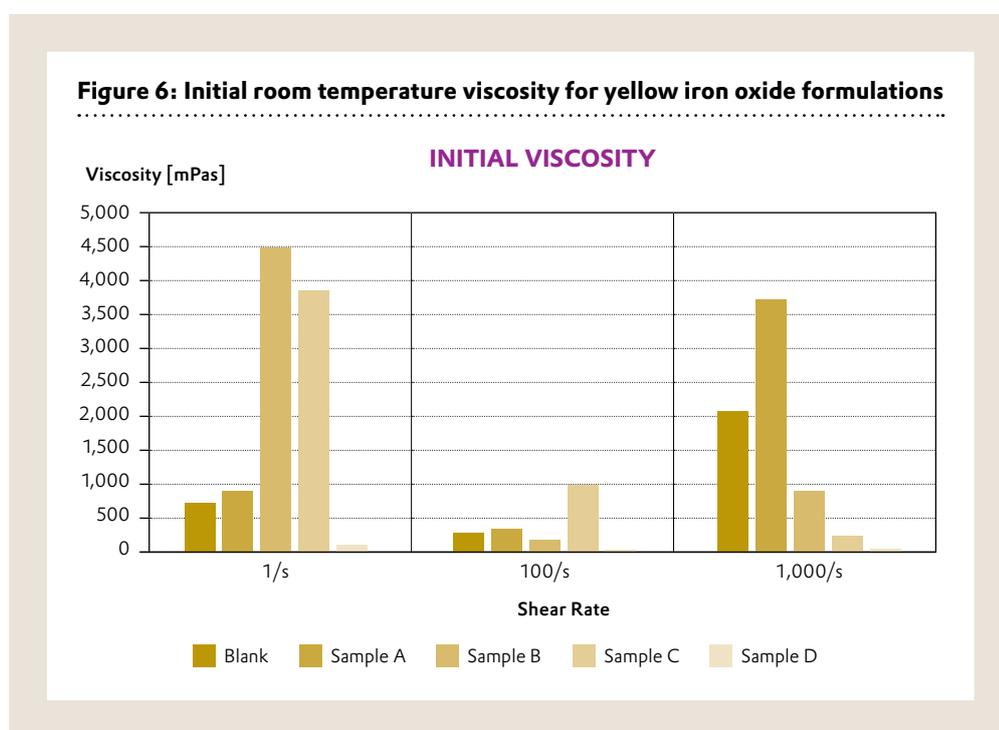
The blank, Sample A, and Sample B did not have a suitable grind after one hour of processing. A suitable grind for most pigment concentrate suppliers would be a 6 Hegman or above. Sample C and Sample D both had grinds over 7 on the Hegman scale. Sample C had a higher viscosity but good grind after one hour; this indicates that the dispersant loading was not optimized. Further work will continue to create an optimized formulation with this dispersant. For Sample D, there was a very low viscosity and high grind, indicating that this was a suitable dispersant loading for this formulation. Color acceptance and color strength research will be done additionally to confirm the performance of the additives.
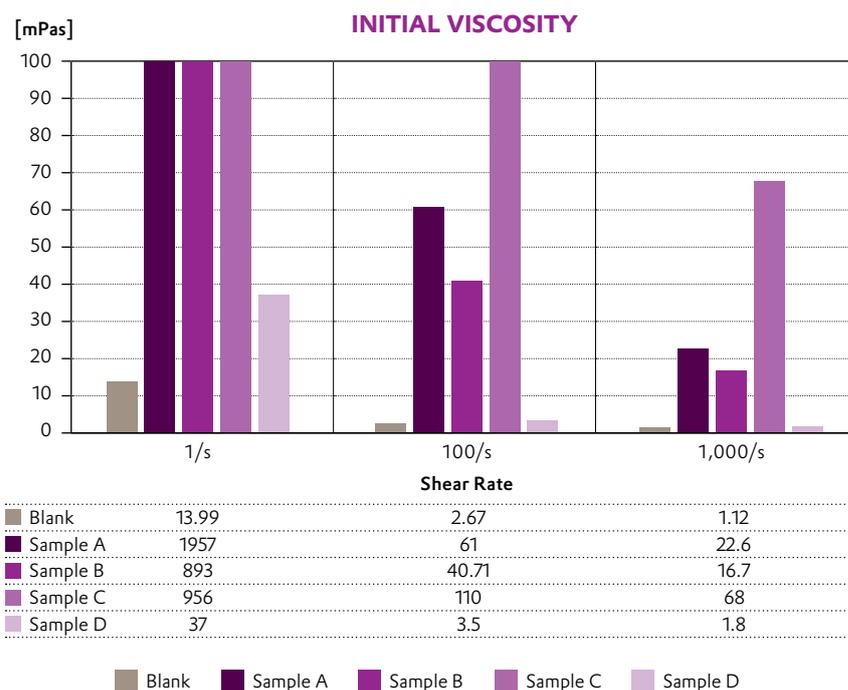
Figure 7: Hegman grind readings after 1 hour of processing for yellow iron oxide formulations

GRIND AFTER 1 HOUR PROCESSING
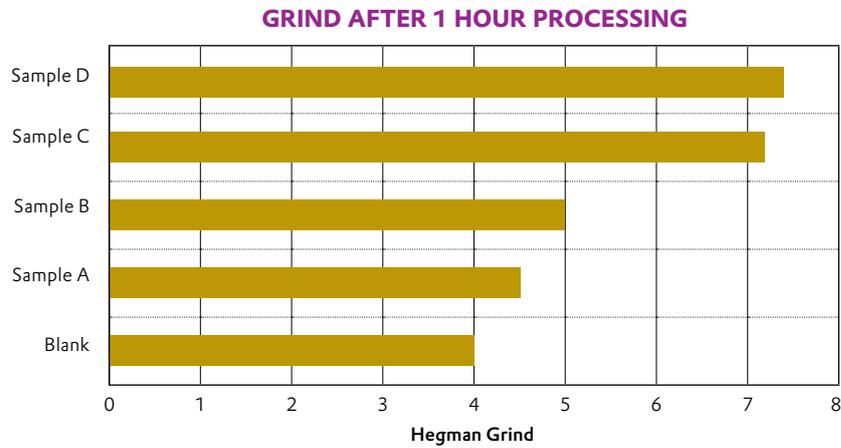

VIOLET-TITANIUM DIOXIDE RESULTSGEN

Viscosity parameters for the violet samples were the same as previously mentioned for the yellow iron oxide formulations. Initial viscosity was very low for the blank and Sample D. Sample A had a very high viscosity at a low shear rate, but as the shear rate increased, the viscosity lowered. Sample B and Sample C both had shear thinning curves.

Figure 8: Initial viscosities of violet-titanium dioxide formulations

INITIAL VISCOSITY

	1/s	100/s	1,000/s
Blank	13.99	2.67	1.12
Sample A	1957	61	22.6
Sample B	893	40.71	16.7
Sample C	956	110	68
Sample D	37	3.5	1.8

Samples were tested for particle size using a Beckman Coulter LS 13-320 Laser Diffraction Particle Size Analyzer. The blank, Sample B, and Sample C showed the lowest median particle size after one hour of grinding. However, the results are still too high for an organic pigment. (Recall: There is also titanium dioxide in this formulation. It is possible that this could be skewing the particle size measurements.) These formulations likely require more energy to break up the remaining agglomerates and aggregates. Additional measurements will be taken over longer periods of grind time to see if this will lower the particle size.

Figure 9: Median particle size of violet-titanium dioxide formulations
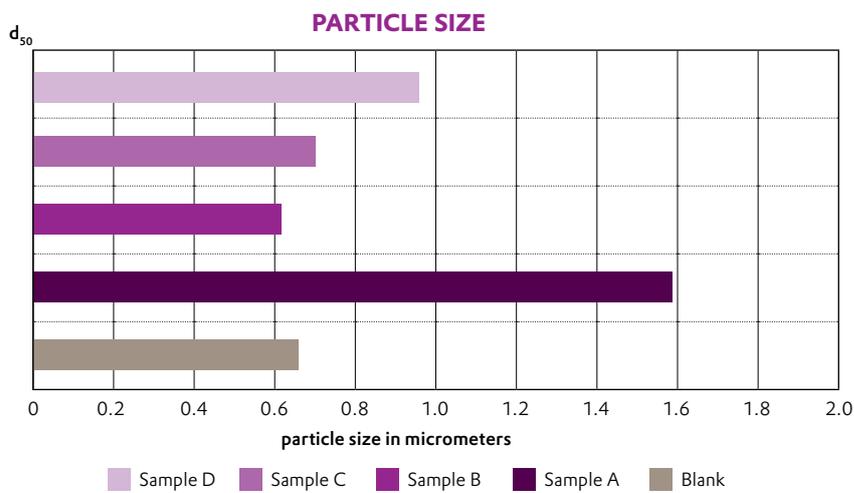
Pigment dispersions were evaluated for color acceptance and color strength using a commercial grade architectural paint at 4 % by volume. Drawdowns were made on Leneta 3B cards at 3 mils wet and allowed to air dry before color measurements were taken using an X-Rite 962 spectrophotometer.

Figure 10: Color strength values for violet-titanium dioxide formulations
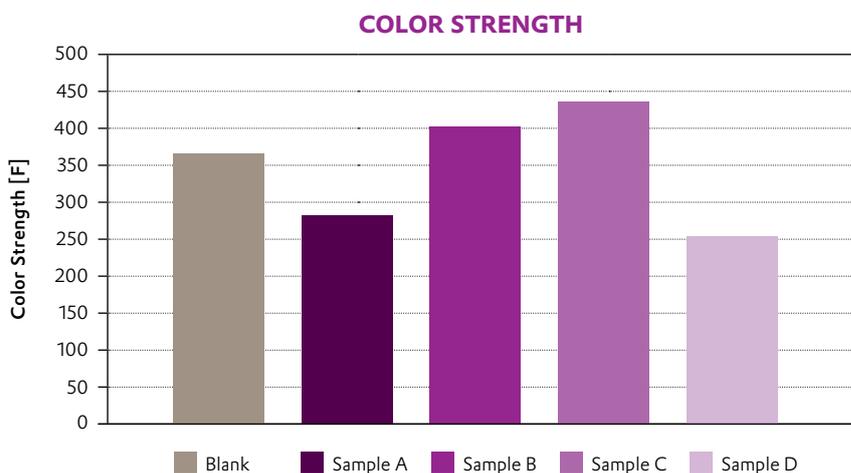
Figure 11: Color acceptance values for violet-titanium dioxide formulations
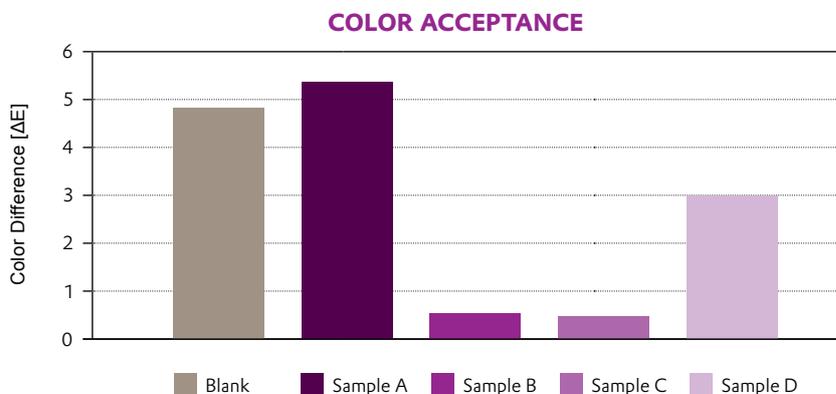
The blank has a high color strength but also a very high ΔE. This indicates that while the blank may look stable, after the pigment is disrupted, it falls out of stabilization. Sample A and Sample D both had lower color strengths and higher ΔE values. This would be unacceptable to paint manufacturers because not only would the pigment not be utilized for tint strength, it would also change color when applied. Sample B and Sample C had the highest color strength and a ΔE less than one. These would be the most stable and most attractive formulations in this case.

For this formulation, overall Sample B and Sample C had the best performance. More research will be done to optimize these formulations. Additionally, all dispersion samples will undergo elevated temperature testing for 1 week at 50 °C. Viscosity, particle size, color acceptance, and color strength will then again be tested for confirmation of each additive's performance.

CONCLUSION

The results for yellow iron oxide convey that Sample D was the best dispersant for that formulation. The higher molecular structure in combination with the hyper-branched polymeric chains was found to be especially useful with the viscosity of the formulation. This allows for a higher pigment loading to be achieved at a fraction of the grinding time. Less machine time, less energy consumption, and fewer labor costs drastically reduce the complexity of processing, simply by utilizing the most suitable additive. This contributes to a more cost-efficient way to formulate pigment concentrates and coatings.

On the other hand, Sample D did not perform well in the violet-titanium dioxide formulation. Most likely, the molecular weight was too high and the polymeric side chains were not soluble and caused incompatibilities with this system. Here, Sample B and Sample C performed well in regards to color strength and color acceptance, and they produced the most economic grinds by getting the most out of the pigment. These two additives kept the violet and titanium dioxide stable using a "controlled flocculation" matrix. This allowed for the two pigments to be bound together to prevent further flocculation by using the dispersant as the bridge between the two.

Figure 12: Controlled flocculation matrix between organic and inorganic pigment

organic pigment   inorganic pigment
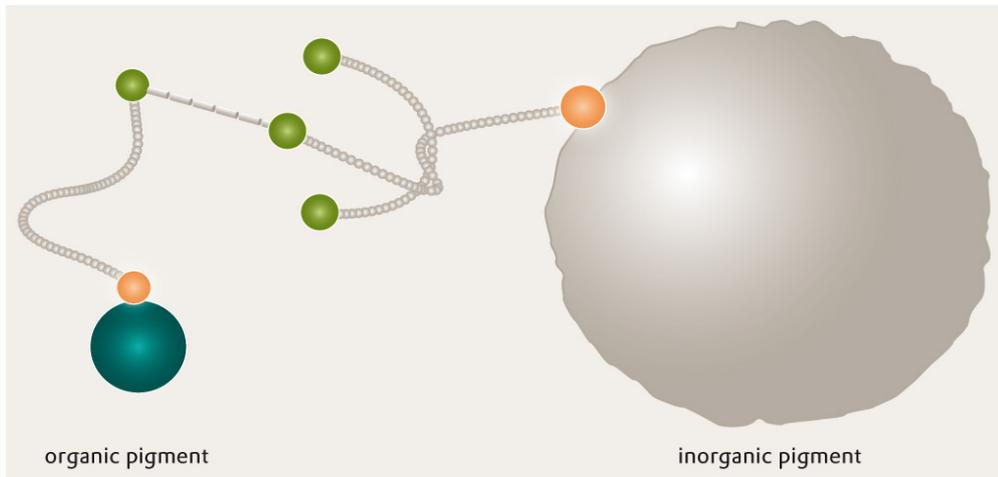
Pigment and additive interactions can be difficult to determine because there are so many variables at play. However, the ability to understand the dispersant and pigment structure and the forces acting on them leads to a better understanding of how to harmonize the two when developing paints and pigment concentrates.

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CONTACT

Brian O. Casey, Phone +1 804 727-0667
brian.casey@evonik.com

AEROSIL®/ACEMATT®
Evonik Resource Efficiency GmbH
Rodenbacher Chaussee 4
63457 Hanau
Germany
Phone +49 6181 59-12532
Fax +49 6181 59-7112532
ask-si@evonik.com

TEGO®
Evonik Resource Efficiency GmbH
Goldschmidtstraße 100
45127 Essen
Germany
Phone +49 201 173-2222
Fax +49 201 173-1939
coating-additives@evonik.com

SURFYNOL®/DYNOL™/ AIRASE®
Evonik Materials Netherlands BV
Kanaalweg 15
3502 GD Utrecht
Netherlands
Phone +31-30-2857100
apcse@evonik.com

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