INDUSTRY INSIDER

Functional Pigments

INSIDE: PG 5 Hydrophobic Pigments • PG 7 Nanoparticles: When Smaller is Better • PG 9 Titanium Dioxide: An Introduction • PG 12 Efficient Use of TiO₂ Pigment • PG 14 Resources
**FUNCTIONAL PIGMENTS**

With a variety of applications, formulators use functional pigments to extend function and improve performance. Marc Hirsch provides an overview. By Marc Hirsch

Functional Pigments (FP) is a somewhat confusing term in the coatings industry, since it can be interpreted to include hiding (prime), anti-corrosive, conductive and special effect pigments as well as extenders (inert). In addition, nanopigments are functional pigments, as each type performs one or multiple functions in a coating. All play a vital role in the formulation of coatings.

**FUNCTION: PRIME**

Prime pigments, also called hiding pigments, can be organic or inorganic. Typically, organic pigments are cleaner and brighter and far more expensive than inorganic pigments. Some organic pigments are synthesized due to a lack of adequate supply of naturally-occurring pigments, or due to their toxicity.

For white and pastel colors, titanium dioxide, and specifically rutile, affords the best opacity/hiding. The greater the difference between a pigment and refractive index (RI) of air (1.00 RI), the greater is the hiding of the pigment. Titanium dioxide (TiO₂) is produced with an optimal particle size for hiding, and is surface-treated to provide additional benefits. On the other hand, nanoscale TiO₂ is a highly-effective ultraviolet-absorber, replacing the much-maligned benzophenone and other banned organic UV-filters.

<table>
<thead>
<tr>
<th>CAS 13463-67-7</th>
<th>RUTILE</th>
<th>ANATASE</th>
<th>BROOKITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>2.73</td>
<td>2.55</td>
<td>2.58</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>4.23</td>
<td>3.78</td>
<td>4.11</td>
</tr>
</tbody>
</table>

*TABLE 1. Forms of titanium dioxide*
**FUNCTION: ANTI-CORROSION**

Corrosion Inhibitive Pigments (CIP) help prevent or reduce corrosion which is primarily caused by electrochemical deterioration of a metal due to the reaction with its environment to transform the metal into its lowest energy state.

Corrosion is normally accelerated by the presence of water, oxygen and salts (particularly of strong acids). The type of metal and the environmental conditions, particularly what gases that are in contact with the metal, determine the form and rate of deterioration. Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode). CIPs are effective by several methods which include passivation, barrier and sacrifice.

**FUNCTION: CONDUCTION**

Conductive pigments (CP) are pigments that enable energy to be transported through a coating.

- **Thermally-conductive pigments** increase the rate at which heat transfers through a coating and has utilization in cooling systems where an increase in heat loss through air conditioning fins and coils greatly reduces energy costs to run the equipment.
- **Electrically-conductive pigments** allow electricity to be passed through or dissipated as in static-dissipative materials.

The types of pigments included in both applications include: silver, nickel, silver-coated nickel, nickel-coated carbon fiber, carbon black, carbon fiber, multi-walled and single-walled carbon nanotubes, as well as other materials.

Some of these can be utilized to formulate coatings with EMI-shielding. **Electromagnetic shielding** is the practice of reducing the electromagnetic field in a space by blocking the field with barriers made of conductive or magnetic materials. This is utilized with sensitive analytical instrumentation as well as protection of detection by radar.
FUNCTION: SPECIAL EFFECTS
Special Effect Pigments (SEP) are pigments that provide an infinite array of colors and effects that enable unlimited design possibilities for coatings. These effects include the illusion of flickering lights, metallic reflection, interference sparkle and color variation and luster that changes with the viewing angle and light source. In an article in the Prospector Knowledge Center, Ron Lewarchik thoroughly presents this topic. The pigments reviewed are metallic flakes, thermochromic, photochromic, luminescent and phosphorescent pigments.

FUNCTION: EXTENSION
Extenders (inert) Pigments don't sound very glitzy or important but are. They are used to provide many functions, including improvement in hiding, stain blocking, single-coat priming and painting and increased scrub resistance to name a few. The use of small particle silicates spaces the larger particles of titanium dioxide (TiO2) to improve the efficiency of the hiding pigment. Micaceous pigments are used in printing to provide better clarity of inks as they won't penetrate the paper substrate as much. In corrosion-inhibitive paints, micaceous iron oxide creates a "tortuous path" for water to migrate through the film, imparting improved protection.

NANOPARTICLE | APPLICATION
--- | ---
Alumina | Coagulant and detackifier
Alumina | Antireflective coatings
Boehmite | Scratch resistance
Zirconium Oxide | Hardness, catalyst and catalyst carrier
Cerium Oxide | UV Absorber
Zinc Oxide | UV Absorber
Titanium Dioxide | UV Absorber
Silver | Antimicrobial
Silica | Hardness

TABLE 2. Examples of nanoparticles and their applications

Nanoparticles are normally defined as those particles that have a dimension of between 1 and 100 nm. The use of nanoparticles in coatings has provided a means to further improve performance such as scratch resistance, hardness, antistatic properties and UV resistance. These performance attributes are derived from the property profiles of nanoparticles.

In the following articles, you will gain a deeper understanding of how some of these functional pigments perform, and how you can optimize your formulation efforts with them. Be sure to visit the Knowledge Center for additional formulation insights.

REFERENCES:
1. Rahman, S., Saidur, R., & Hossain, Md. (2011). A review on the performance of nanoparticles suspended with refrigerants and lubricating oils in refrigeration systems. Renewable and Sustainable Energy Reviews. 15, 310-323. 10.1016/j.rser.2010.08.018. Fig. 5.
Avoiding Defects

Dispersing and wetting hydrophobic pigments and fillers in water-based paints to avoid pigment flooding and floating

By Ron Lewarchik

A critical part of any coatings formulation is ensuring that the coating will be free of inherent defects, including pigment flooding and floating. Waterborne formulations represent some unique challenges due to multiple factors, including the high surface tension and polarity of water that does not contribute to the wetting of most pigment and filler particles. In this article, I'll define some important considerations in formulating waterborne paints to avoid pigment flooding and floating.

FLOODING, FLOATING, SURFACE TENSION, BERNARD CELLS, FLOCCULATION AND AGGLOMERATION

FLOATING describes a mottled, splotchy appearance on the surface of a paint film. It is most apparent in coatings colored with two or more pigments and is a result of the horizontal separation of different pigments. Flooding is the phenomena observed when the surface color of an applied film is uniform but is darker or lighter than it should be. This is attributed to a vertical separation of different pigments in the film.

SURFACE TENSION results when the force that occurs in a liquid at the interface differs from the forces within the liquid. Thus, surface tension is caused from the surface molecules having a higher free energy than those molecules in the bulk of the liquid.

Surface tension differential can cause a convection current resulting in a regular hexagonal surface pattern called Benard Cells. A hexagonal Benard Cell pattern results in smaller, more mobile pigment particles (smaller, less dense) being deposited on the perimeter and the less mobile particles (larger, more dense) remaining away from the perimeter.

FLOCCULATION is the recombination of dispersed pigment particles that were not properly stabilized in the pigment dispersion. Flocculation is undesirable as it detracts from hiding and color development. Flocculation is reversible by applying a low degree of shear. In figure 2, the phthalocyanine blue pigment is flocculated. Upon rubbing with a finger, the deeper blue color returns.

PIGMENT AGGLOMERATION is defined as pigment particles that are clumped together without sufficient vehicle or wetting agents present between pigment particles. When agglomeration occurs, extensive shear and attrition forces are usually necessary to reinstate a stabilized pigment dispersion.

REMEDIAL ACTIONS TO OVERCOME FLOATING AND FLOODING IN WATERBORNE PAINTS

Pigment dispersion in aqueous media uses the same principles as in organic solvent media such as proper wetting, pigment dispersion and stabilization. However, the surface tension
of water and high polarity make it more problematic in wetting low polarity pigments. In many cases, water interacts aggressively with the surface of the pigment, destabilizing the dispersant on the pigment surface. Overcoming flooding and floating starts with selecting pigments that are free of fines. Also, many pigment manufacturers supply surface treated pigments to avoid flooding and floating.

Secondly, ensure that the pigment dispersion is uniform and stabilized (elimination of pigment flocculation of one pigment, with the exclusion of other pigments).

Thirdly, the use of suitable wetting agents/surfactants help to ameliorate differences in polarity and surface tension between pigments that contribute to flooding and floating. Inorganic pigments such as iron oxides, titanium dioxide, calcium carbonate and many other filler pigments have a polar surface and are easily wet by water. However, water alone normally does not stabilize the pigment dispersion against flocculation, so they require a surfactant to wet and stabilize the dispersion. Also, many pigment manufacturers supply surface treated pigments to avoid flooding and floating. For some organic pigments that have a surface with low polarity, many manufacturers modify the surface with a layer of inorganic oxide to provide increased polarity to improve wetting in aqueous-based systems.

Fourthly, the use of an appropriate thixotrope helps to build sufficient viscosity and a network structure that discourages pigment separation. However, one must be sure that there is acceptable compatibility between the thixatrobe and dispersant.

Overcoming flooding and floating in solvent-borne paints primarily involves utilizing a suitable pigment dispersant and the elimination of Benard Cell formation with the addition of a surface control agent.

A final consideration affecting the stability of an aqueous paint pigment is the pH of the pigments. For example, if a low pH carbon black pigment is used in the pigment dispersion without the use of a suitable wetting agent in an anodic aqueous based paint (pH normally > 8), longer term instability can result as the neutralizing amine on the resin backbone can migrate to the acidic pigment.

Care must be taken while reducing a latex paint with water because floating can occur (slow addition of water with proper mixing and ensure against over reduction). This is due to a shift in the equilibrium between the dispersed pigment particles and water, resulting in a decrease in the amount of stabilizing dispersant on the pigment.

There are numerous suppliers listed in UL’s Prospector website with a wide variety of wetting agents, pigment dispersants, surfactants, thixotropes and pigments to meet your requirements in both solvent and waterborne coatings.
Nanoparticles: When Smaller is Better

Scratch resistance, hardness, UV resistance ... all can be improved on a nanoscale level
By Ron Lewarchik

Nanoparticles are normally defined as those particles that have a dimension of between 1 and 100 nm. The use of nanoparticles in coatings has provided a means to further improve performance such as scratch resistance, hardness, antistatic properties and UV resistance. These performance attributes are derived from the property profiles of nanoparticles.

Nanoparticles provide the inherent properties of the material they are derived from. For example, nano alumina maintains the properties of alumina, such as hardness and scratch resistance, but only on a nanoscale. Likewise, nano silica provides hardness, nano titanium dioxide provides a high refractive index and UV stabilization, and nano zinc oxide remains a UV light absorber, even if the zinc oxide particles are nano-sized. The benefits of these materials are imparted to the coatings that they are used in.

The most pronounced property that is influenced by the particle size is the change in light scattering. For example, nano-sized particles may produce transparent coatings as light-scattering decreases with decreasing particle size. Most objects are visible due to light scattering from their surfaces. Scattering of light depends on the wavelength or frequency of the light being scattered as well as the size, shape and type of particle.

Since visible light has a wavelength on the order of micrometers, most particles much smaller than this, such as nano particles, are mostly transparent as their ability to scatter light diminishes with their size. However, light scattering is also dependent on the Refractive Index (RI) and the difference in RI between the interface of the particle and the surrounding medium. For example, if the surrounding medium has an RI similar to that of the RI of the particle, then the mixture of the two materials will be...
more transparent. To illustrate, silica has an RI of about 1.5 and polymethylmethacrylate has an RI of about 1.5, so a coating comprised of nano silica and an pMMA will be nearly transparent. The properties of nanoparticles based on their dimension can be quite dramatic.

FIG. 1. Nanoparticles and light transparency

Ultrafine zinc oxide and ultra fine titanium dioxide as a nanomaterial are engineered to have primary particles less than 100 nm are more transparent to visible light (400 – 700 nm), but are effective UV absorbers and thus used in coatings and in sunscreens. The relationship between nanoparticle composition, coupled with their optical properties as delineated above, provide an avenue to impart unique features and performance to coatings which to a large degree have yet to be fully exploited. For example, nanoparticles can be used to provide the surface performance characteristics of a material such as scratch and abrasion resistance without a major influence on gloss or color.

As the dimension of a particle decreases, the ratio of surface area to volume increases quite dramatically. Higher surface area produces greater interaction of particles and higher attractive forces. The high attractive forces of unstabilized nanoparticles produce large agglomerates that are microsize (> 100 nm) in dimension and thus defeat any advantage that nanoparticles provide to enhance performance.

FIG. 2. Nanoparticles and agglomeration

Accordingly, the advantages of nanoparticles for use in coatings requires that the particles be used in a stabilized deagglomerated state. There are multiple ways that stabilization can be accomplished, as each type of nanoparticle is different from a compositional standpoint, the supplier should be consulted on the best means to achieve a stabilized particle.

TABLE 2. Examples of nanoparticles and their applications

<table>
<thead>
<tr>
<th>NANOPARTICLE</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Coagulant and detackifier</td>
</tr>
<tr>
<td>Alumina</td>
<td>Antireflective coatings</td>
</tr>
<tr>
<td>Boehmite</td>
<td>Scratch resistance</td>
</tr>
<tr>
<td>Zirconium Oxide</td>
<td>Hardness, catalyst and catalyst carrier</td>
</tr>
<tr>
<td>Cerium Oxide</td>
<td>UV Absorber</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>UV Absorber</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>UV Absorber</td>
</tr>
<tr>
<td>Silver</td>
<td>Antimicrobial</td>
</tr>
<tr>
<td>Silica</td>
<td>Hardness</td>
</tr>
</tbody>
</table>

As illustrated in Table 2, the proper use of nanoparticles in coatings can impart multiple beneficial properties. Stabilization of dispersed nanoparticles is essential to ensure that the full benefits of these materials are realized. Secondly, formulations utilizing nanoparticles must be tailored to provide proper acceptance rather than as a drop-in to achieve a desired property. In summary, properly formulated coatings utilizing nanoparticle technology can achieve performance attributes heretofore not obtainable by other means.
Titanium Dioxide: An Introduction

With a variety of applications across industries, TiO₂ is most widely used in paints for its opacity effects.

By Marc Hirsch

Titanium dioxide, also known as titanium (IV), is an oxide of titanium that occurs naturally. Its chemical formula is TiO₂ and its pigment color index is CI 77891. It has many uses outside of paint, which include food, paper coatings, plastics, cosmetics and others. It is primarily obtained from ilmenite, rutile and anatase, but also occurs as brookite. Additionally, titanium dioxide can occur in high-pressure conditions as a monoclinic baddeleyite-like form and an orthorhombic α-PbO₂-like form.

SOURCE
Titanium is mainly sourced from ilmenite ore, which is the most widespread form of titanium dioxide-bearing ore around the world. Rutile is the next most abundant and contains around 98 percent titanium dioxide in the ore. The metastable anatase and brookite phases convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range of 600 to 800°C (1,112 to 1,472°F).

PROCESSING
There are two main processes for TiO₂: In 1916, the Titanium Pigment Corporation of Niagara Falls, New York, and the Titan Company A/S, of Norway simultaneously began commercial TiO₂ production with the sulfate process. In 1951 DuPont introduced the chloride process.

SULFATE PROCESS
FeTiO₃ + H₂SO₄ = TiO₂ + FeSO₄ + H₂O
2.5t ilmenite + 3.5t H₂SO₄ (100%)
1t TiO₂ + 4t FeSO₄·7H₂O + 7t « spent acid » (21%)

CHLORIDE PROCESS
2 FeTiO₃ + 7 Cl₂ + 6 C = 2 TiCl₄ + 2 FeCl₃ + 6 CO
TiCl₄ + O₂ = TiO₂ + 2 Cl₂
1.2t titanium slag + 0.4t petcoke + 0.3t chlorine
1t TiO₂ + 1.2t FeCl₃ + 0.1 HCl + 0.25t metal chlorides

FIG. 1. Material balances for sulfate and chloride processes

As per Figure 2 and Figure 3, the chloride process has been the predominant production method but has decreased over the past 25 years due to the influx of Chinese sulfate-grade TiO₂. However, the chloride process still dominates the global market.
In addition to the raw processing, the pigment is treated in various ways for specific uses. Some organic treatments are provided to improve dispersibility or the reduction of degradation by ultraviolet light. Inorganic treatments consist of other metal oxides that also provide protection from UV. The pigments are ground to a specific particle size (median and distribution) for optimal opacity as well. Dependent upon the treatment and particle size, TiO\textsubscript{2} can range from a yellow to a blue undertone, which has to be considered by formulators of base paints for customized colors.

**APPLICATIONS**

As stated previously, there are many applications of TiO\textsubscript{2}, but paint is by far the largest (Figure 4). Of all white-hiding pigments, titanium dioxide, and specifically rutile, affords the best opacity/hiding (Figure 5).

TiO\textsubscript{2} does possess the highest opacity of paint pigments, but it is not an inexpensive pigment, nor does it work alone for optimal usage. Extender pigments such as silica, silicates and carbonates are used as "spacers" in a paint, so that the TiO\textsubscript{2} pigment particles are less agglomerated and are more readily amenable to optimum hiding. This is more easily achieved in higher PVC (pigment volume concentration) paints, as opposed to gloss paints, because the extenders can have a deleterious effect on gloss. The extender pigments may also be functional, providing improvement to touch-up and burnishing, scrub resistance and cleanability.
In the past 15 years, nanomaterials have found greater utilization in many applications. This has been true also for TiO₂, where the very small particles are very useful in cosmetics as well as catalytic self-cleaning. In cosmetics, the move away from organic ultraviolet absorbers has led to the use of nano-sized zinc oxide (ZnO) and TiO₂. Both are highly effective in absorbing UV sunlight.

Nano-TiO₂ has also found utilization in the remediation of pollutants and deposited materials on skyscraper windows and other structures not easily accessed. The schematic in Figure 7 represent what occurs.

REFERENCES:
Pigment Volume Concentration 3 February 2012. Master Painter's Institute; [accessed August 2016].
Titanium dioxide (TiO₂) is a white pigment used to give whiteness and hiding power to a coating. The pigment is considered as being expensive, especially when volume prices of systems are used. The high volume price is caused by the high density of TiO₂.

**SCATTERING BY SOLID PARTICLES**

Particles in a matrix, like a binder system in a coating, can change the direction of light when the particles and the medium have a different refractive index (n). This phenomenon, called **scattering**, results in both the white color and hiding power of the coating. Scattering efficiency is governed by a few properties:

- **Scattering is strong** when the difference in refractive index of particle and matrix, \( \Delta n = n_p - n_m \), is big.
- **For a specific wavelength of light**, \( \lambda \), there is an optimum with respect to particle size.

\[
d_{optimal} \approx 0.5 - \lambda
\]

**FIG. 1** Scattering of light by particles in a coating.

---

**Discover several measures that can help maximize processes for using titanium dioxide.**

By Jochum Beetsma

---

**Scattering:**
A phenomenon that results in both white color and hiding power of a coating.
The refractive index of binders used in coatings is around 1.6. TiO₂ is preferably used as scattering source because the pigment has a high refractive index, depending upon the crystal structure of the pigment:

<table>
<thead>
<tr>
<th>CRYSTAL STRUCTURE</th>
<th>RUTILE</th>
<th>ANATASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>4.25</td>
<td>3.90</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.70</td>
<td>2.55</td>
</tr>
<tr>
<td>d-50 (nm)</td>
<td>≈300</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE. 2 Key properties of the most common types of TiO₂ pigment.**

TiO₂ particles having a diameter of around 300 nm scatter visible light, λ = 400 – 800 nm, most effectively.

**OPTIMIZING SCATTERING EFFICIENCY OF TiO₂**
Several measures can be taken in order to maximize the efficiency of expensive TiO₂ pigment:

- Select rutile TiO₂ with average primary particle diameter, called d-50, of around 300 nm. Both crystal structure and particle size can be found in the technical documentation of the pigment supplier.
- Separate the primary particles as much as possible during the dispersion process and stabilize the particles with dispersant to prevent flocculation.

- Assure that the TiO₂ particles are distributed uniformly over the complete system. This is called spacing. An approach to prevent crowding, the opposite of spacing, is to use a suitable filler. The filler particles, filling the spaces between the TiO₂ particles, act as spacers.

Often a lot of money can be saved, especially by improving the separation process and/or by changing the type or amount of dispersant.
THOUSANDS OF COATINGS MATERIALS AT YOUR FINGERTIPS!

Ready to research for your next coatings project? The Prospector® material and ingredient search engine has listings for thousands of products from global suppliers. Register today to find technical data, order samples and more.

REGISTER NOW!
ulprospector.com/register

ABOUT PROSPECTOR FROM UL
Prospector is a specialized material and ingredient search engine for product developers offered by UL, the world leader in product safety. Offering accurate, reliable technical information for hundreds of thousands of products and the ability to connect with suppliers from around the world, Prospector helps product developers, designers and engineers find materials faster. For more information visit: ulprospector.com.

DISCLAIMER
The views, opinions and technical analyses presented here are those of the authors, and are not necessarily those of UL, ULProspector.com or Knowledge. ULProspector.com. While UL makes every effort to verify the accuracy of its content, we assume no responsibility for errors made by the authors or editorial staff. All content is subject to copyright and may not be reproduced without prior authorization from Prospector.