Polymers, Light and the Science of TiO$_2$
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TITANIUM DIOXIDE — TiO$_2$ is a multifaceted material when used in polymer applications. It has been long established as the leading white pigment, and this is the application that people are most familiar with. However, titanium dioxide brings more to the polymer industry than just white, bright opacity. In a more basic sense, titanium dioxide is a photo-responsive material—it's value is in its interaction with light. For example, this interaction can be the familiar scattering that results in opacity or it could be the absorption of UV light energy, thereby protecting the polymer from UV degradation. Applications continue to develop, all based on the interaction of the titanium dioxide particle with light.
As other applications for titanium dioxide have developed, its pigmentary properties remain the most important. Titanium dioxide is the most important white pigment used in the polymer industry. It is widely used, because it efficiently scatters visible light, thereby imparting whiteness, brightness, and opacity when incorporated into a plastic product. It is chemically inert, insoluble in polymers, and heat stable under the harshest of processing conditions. Titanium dioxide is commercially available in two crystal forms—anatase and rutile. The rutile pigments are preferred over anatase pigments, because they scatter light more efficiently, are more stable, and are less likely to catalyze photodegradation.

Few, if any, commercial grades of titanium dioxide are pure TiO\textsubscript{2}. Most have inorganic and, in some cases, organic treatments deposited on the surfaces of the TiO\textsubscript{2} particles by precipitation, mechanical blending, or via other routes. These surface treatments provide improvements in one or more performance properties of the pigment, such as ease of dispersion, weatherability, or discoloration resistance. A single prescription for surface treatment does not produce a pigment having maximum value-in-use for all plastics applications, and it is a continuing research goal to develop titanium dioxide grades to meet the changing needs of the plastics industry.
Light-Scattering Properties
Titanium Dioxide Provides Opacity by Scattering Light

Unlike colored pigments that provide opacity by absorbing visible light, titanium dioxide and other white pigments provide opacity by scattering light. This scattering is possible because the white pigment can bend light. If there is enough pigment in a system, all light striking the surface, except for the small amount absorbed by the polymer or pigment, will be scattered outward, and the system will appear opaque and white. Light scattering is accomplished by refraction and diffraction of light as it passes through or near pigment particles.

Refraction

Refraction is depicted in Figure 1, where the sphere represents a TiO₂ particle suspended in a low refractive index polymer. As a ray of light falls on the TiO₂ particle, it is bent, because light travels more slowly through the high refractive index pigment than through the low refractive index polymer in which it is dispersed.

Figure 1
Refraction of light by particles

Figure 2 schematically depicts a cross-section of two white-pigmented films and how differences in pigment refractive index affect opacity. In the film containing a high refractive index pigment Figure 2a, left, light is bent more than in the film containing the low refractive index Figure 2a, right, with the result that light travels a shorter path in the film and does not penetrate as deeply. Both upper films appear opaque and white, because no absorbing particles are present, and practically all incident light is returned to the surface.

However, in a thinner film Figure 2b, the film containing the high refractive index pigment still appears opaque and white, whereas the film with the low refractive index pigment allows some of the light to pass completely through the film and be absorbed by the black background. This film is not completely opaque and appears gray compared with the white film.

Figure 2a
Path of Light in White Film (both films completely opaque)

Figure 2b
Path of Light in White Film (film on right not opaque)
**Refractive Index and Scattering Power**

To understand why titanium dioxide, especially the rutile form, offers such great advantages in hiding power, it is only necessary to compare the refractive index of rutile TiO₂ to the refractive indices of anatase TiO₂, other commercial white pigments, and polymer systems as shown in Table 1. In general, the greater the difference between the refractive index of the pigment and that of the polymer matrix in which it is dispersed, the greater the light scattering.

**Diffraction and Particle Size**

Diffraction, the other factor affecting the degree to which a pigment scatters light, is depicted schematically in Figure 3. Here, light passing near a pigment particle is bent. This phenomenon accounts for a pigment's ability to scatter light in an adjacent area several times larger than the cross-sectional area of the pigment itself. For the most effective light scattering, the pigment diameter should be slightly less than one-half the wavelength of light to be scattered. Because the eye is most sensitive to yellow-green light (about 0.55 µm wavelength), commercial TiO₂ pigments for plastics average 0.2–0.3 µm in diameter.

Light scattering imparted by diffraction is affected by particle spacing and average pigment particle size. If particles are too large or too closely spaced, little diffraction takes place. If the pigment particles are too small, the light will not "see" the pigment particle.

**Table 1**

Indices of Refraction for Some White Pigments and Common Polymers

<table>
<thead>
<tr>
<th>White Pigment</th>
<th>R.I.</th>
<th>Plastic</th>
<th>R.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile TiO₂</td>
<td>2.73</td>
<td>Polystyrene</td>
<td>1.60</td>
</tr>
<tr>
<td>Anatase TiO₂</td>
<td>2.55</td>
<td>Polycarbonate</td>
<td>1.59</td>
</tr>
<tr>
<td>Antimony Oxide</td>
<td>2.09–2.29</td>
<td>SAN</td>
<td>1.56</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>2.02</td>
<td>Polyethylene</td>
<td>1.50–1.54</td>
</tr>
<tr>
<td>Basic Carbonate, White Lead</td>
<td>1.94–2.09</td>
<td>Acrylic</td>
<td>1.49</td>
</tr>
<tr>
<td>Lithopone</td>
<td>1.84</td>
<td>Polyvinyl Chloride</td>
<td>1.48</td>
</tr>
<tr>
<td>Clay</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium Silicate</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barytes (BaSO₄)</td>
<td>1.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium Carbonate (CaCO₃)</td>
<td>1.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3**

Diffraction of Light Around Pigment Particle
Particle Size and Scattering Power
Curves in Figure 4, derived from theoretical considerations in very dilute systems, show the relative scattering power of rutile TiO₂ for blue, green, and red light as a function of TiO₂ particle size. At about 0.2 μm, the sum of the light scattered at all wavelengths is maximized. When the particle size is increased to 0.25–0.30 μm, the scattering of blue light decreases rapidly, but the scattering of green and red light is relatively unchanged. At 0.15 μm, the diameter corresponding to the maximum scattering of blue light, light scattering in the red and green ranges of the spectrum drops markedly. Therefore, as TiO₂ pigment is made bluer, it can actually lose some of its light scattering capability.

Particle Size and its Effect on Product Color
In a nonabsorbing, white polymer that is pigmented to complete opacity, changing the TiO₂ particle size has no effect on color, because all light striking the surface is completely reflected. Figure 5, a cross-sectional view of such a white opaque film, demonstrates this point. The blue light, having the shortest wavelength and scattering path, and the red light, having the longest wavelength and path, are totally reflected; the visual effect is the same as if all light traveled the same path length.

For translucent white film, pigment particle size will affect both transmitted color and reflected color. Consider transmitted color: as particle size is reduced, a larger portion of the blue light is reflected and more yellow light is transmitted. On this basis, if blue transmitted light is desired, a larger rather than smaller particle size titanium dioxide pigment is preferred.

If an absorbing pigment such as carbon black or a colored pigment is added to the titanium dioxide-containing polymer Figure 6, red light with the longer path length has a greater chance of being absorbed. Decreasing TiO₂ particle size, in this case, reduces red light scattering and enhances blue. Thus, in an opaque polymer containing some light-absorbing matter such as colored pigment, decreasing TiO₂ particle size will increase blueness as viewed in reflectance. This phenomenon is inherent in light-scattering pigments and is described as “undertone.”
Optical Properties
Include Tinting Strength, Undertone, and Color
When selecting a commercial grade of TiO₂ for coloring or opacity purposes, the fundamental optical properties of opacity/tinting strength, undertone, and color must be considered. Opacity is the result of scattering of all wavelengths of incident light. Tinting strength describes the ability of a white pigment to efficiently scatter light and provide whiteness and brightness to a colored polymer system.

Tinting strength is easier to measure and most often used to describe the light scattering efficiency or opacity of a white pigment. To measure relative tinting strength, a sample of TiO₂ is dispersed into a black masterbatch at a prescribed ratio of carbon black to TiO₂. The resulting gray polymer is then formed into uniform, opaque sheets or molded chips. The TiO₂ sample with the greatest light-scattering efficiency will provide the lightest gray and the highest reflectance.

Undertone is the contribution of a TiO₂ to the color of a tint. It is a function of TiO₂ particle size and cannot be determined from the appearance of dry powders or white polymers. Undertone is usually expressed as the ratio of blue (or CIE Z tristimulus value) to red (or CIE X tristimulus value) reflectances as measured on gray tints using a three-filter colorimeter or a spectrophotometer (undertone = CIE Z/CIE X). In the gray tint, an undertone difference of 0.01 is visible only to a trained observer. The relative undertone can be measured as vinyl undertone using samples prepared the same way as for relative tinting strength.

In some applications, the appearance of transmitted light is important. The transmitted appearance of tints or whites that contain small particle size TiO₂ grades are more yellow than similar products containing a larger particle size TiO₂. Thus, in the manufacture of such objects as bottles, light covers, etc., neutral or yellow undertone TiO₂ grades are preferred for their bluer transmitted light. In color matching, it is important to understand the final application that the color will be used for, so that the TiO₂ grade with the correct undertone can be selected for an exact match. It is difficult to compensate for differences in undertone by the addition of pigment colors.

Color is the appearance of TiO₂ pigment alone and is entirely independent of undertone. Most commercial TiO₂ grades do not vary significantly in dry color; however, poor color can result from contamination. Color can occur in plastic systems from reactions of TiO₂ with the polymer or additives and heat stability failures.

Color and undertone are sometimes confused. It is entirely possible for a blue undertone TiO₂ to exhibit a yellow color due to one of the previously mentioned conditions that can result in poor color. It is not uncommon for different particle size TiO₂ grades to be equal in color. The most common method of measuring the color of TiO₂ is the CIE L* a* b*. The L* measures the brightness of the sample, while the a* measures the redness-greenness, and the b* measures the yellowness-blueness.
Dispersion In Plastics:  
**Important To Pigment Efficiency**

Dispersion

Titanium dioxide is used most efficiently and economically, that is, the value of the pigment is best realized, when it is well dispersed. Unfortunately, the primary particles of pigment tend to stick to each other in the course of manufacture and storage, resulting in aggregates and agglomerates many times the desired particle size. Manufacturers can use various techniques, such as surface coatings and micronization to make dispersion easier and to minimize the aggregates present. The object of dispersion is to reduce these remaining aggregates and agglomerates to an acceptable size at reasonable cost.

Agglomerates, consisting of collections of primary pigment particles, form during manufacture. The degree that these agglomerates are dispersed can affect important appearance and performance traits, such as those listed in Table 2. Each of these traits depends on the degree of reduction of agglomerates to an ideal of the primary particle size. Thus, agglomerates 30 µm or larger are primarily responsible for surface imperfections, specking, streaking, and such processing problems as pluggage of screen packs during extrusion. Particles as small as 5 µm can influence physical or electrical properties in critical applications. Still, smaller particles are generally needed to realize the optimum color, strength, opacity, or transparency, and weathering properties inherent in a pigment; it is in this area that the question of dispersion cost versus added value most frequently arises.

This varying response of dispersion traits to particles of different size means that some traits will develop more rapidly than others in the course of dispersion. Focusing on opacity and tinting strength, Figure 8 illustrates that these attributes will increase for a given pigment as the concentration of agglomerates decreases. It is obvious, then, that the means selected to measure dispersion must be meaningful in terms of the more important properties desired. The concentration of oversize agglomerates can be measured using a screen-pack test. The opacity and tinting strength would be a result of the dispersion quality.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Effects of Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Performance</td>
</tr>
<tr>
<td>Surface Texture</td>
<td>Cost</td>
</tr>
<tr>
<td>Specks</td>
<td>Processibility</td>
</tr>
<tr>
<td>Streaks</td>
<td>Physical Strength and Porosity</td>
</tr>
<tr>
<td>Opacity/Strength</td>
<td>Weatherability</td>
</tr>
</tbody>
</table>
Having established the dispersion quality needed and an appropriate basis for measuring it, we can consider the means of producing it. This requires some understanding of the mechanics by which dispersion takes place. Three elements are necessary for dispersion, regardless of the process, conditions used, or quality desired:

- **Initial blending** — formation of a suitable pigment/polymer mix
- **Size reduction** — fracture of pigment aggregates and agglomerates
- **Intimate wetting** — displacement of air from the pigment’s surface

It is not suggested that these necessarily occur separately, in sequence, or that any or all need be optimal if the final application does not require it. However, the dispersion process must allow for each to take place. These three elements will be discussed in further detail in terms of the three basic dispersion processes used in the plastics industry, i.e., dry blend, melt shear, and liquid shear dispersions.

Initial wetting, at a minimum, requires that the pigment and the polymer be sufficiently well mixed and have sufficient affinity for each other to avoid separation when further work is applied to the system. Better known and more quantitative measures of initial wetting exist, however. In fluid systems, for example, the time required to wet-out pigment in the vehicle, the amount of balling that occurs as pigment is added, the amount of tailings or separations observed in a three-roll grind, and the consistency changes that take place with mixing, all provide means by which the progress and quality of initial wetting can be followed. Similarly, in dry-blending, the tendency for pigment to pelletize or cake on equipment and the amount of loose pigment present following such a blend are measures of initial wetting. The importance of initial wetting is often underestimated because of the usually simple means by which it is obtained. Yet, it is not only essential but also often controls the quality of the final dispersion or at least the amount of time required obtaining it. TiO₂ producers can influence initial wet-in by the use of additives matched to the polymers in which the grade is to be used. Surfactants can aid in increasing the affinity between pigment and polymer, thereby improving the quality or reducing the time needed to obtain initial wetting. However, pigments vary substantially in their chemical compositions and surface characteristics, so no single surfactant should be expected to serve all situations equally well.

Size reduction may be achieved by impact, particle-to-particle attrition (a rupture mechanism), or by shear transmitted through an intermediate fluid layer (an erosion mechanism). In any case, sufficient mechanical energy must be introduced to overcome forces holding agglomerates together. Because this is often carried out in the presence of a polymer, physical characteristics of the polymer can be extremely important. For example, in the case of a dry blend, schematically illustrated in Figure 9, the size, shape, hardness, and softening temperature of the polymer can influence the extent and efficiency with which size reduction is accomplished. Size is of particular importance and will be discussed later. TiO₂ manufacturers use different methods from wet milling to micronization to surface treatments to break up and prevent aggregated particles and control particle size within a consistent narrow range.
In fluid dispersion processes, it must be first recognized that virtually all size reduction occurs either from shear transmitted through a liquid layer surrounding the aggregate or by impingement of the aggregate or agglomerate traveling at a high rate of speed against a hard surface. Figure 10 is intended to show that effective size reduction is not accomplished by “crushing” the agglomerates. In this example, the agglomerate is much larger than usually desired in a dispersion. When the agglomerate is exposed to the shearing forces of the flowing polymer, the agglomerate rotates in the polymer stream and the particle size is reduced through the erosion as shown in Figure 10. The factors which are important in the dispersion of pigment by erosion include the melt viscosity of the polymer and the shear rate.

Small particle-sized polymers, such as powder, are an important aid to dispersion in processes where dry mixing of pigment and resin are involved because of the significantly more uniform and intimate blends produced. This may be explained by the much greater polymer surface the pigment can come in contact with and adhere to during mixing. Loose pigment present after blending with the polymer is much more difficult to disperse than pigment attached to the resin surface.

**Table 3**

Dispersion Performance for Ti-Pure™ Titanium Dioxide Pigments

<table>
<thead>
<tr>
<th>Ti-Pure™</th>
<th>Melt Compounded</th>
<th>Dry Blended</th>
<th>Liquid Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-101</td>
<td>R</td>
<td>HR</td>
<td></td>
</tr>
<tr>
<td>R-103</td>
<td>R</td>
<td>HR</td>
<td>R</td>
</tr>
<tr>
<td>R-104</td>
<td>HR</td>
<td>HR</td>
<td></td>
</tr>
<tr>
<td>R-105</td>
<td>HR</td>
<td>HR</td>
<td>R</td>
</tr>
<tr>
<td>R-350</td>
<td>HR</td>
<td>HR</td>
<td></td>
</tr>
<tr>
<td>R-960</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
</tbody>
</table>

HR = Highly Recommended  
R = Recommended

Differences in dispersion will be observed because of differences in the surface treatments of pigment. This often results in one pigment being superior to another under one condition of dispersion and inferior under another. Table 3 provides guidelines for the selection of a grade to be used in a particular dispersion process. These guidelines only apply to the dispersion process, and other important end-use properties must also be considered before a final selection is made.
The foregoing discussion of dispersion principles can be summarized by offering some guidelines for achieving improved quality or more rapid dispersion by the three dispersion processes used in the plastics industry. These are listed in:

Table 4 Guide to Quality Dispersion by Dry Blending

<table>
<thead>
<tr>
<th>Polymer Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ Small particle size</td>
</tr>
<tr>
<td>■ Hard surface in preference to soft, when option exists. Chemically compatible with pigment under processing condition exists</td>
</tr>
<tr>
<td>■ Rheologically compatible with base polymer (especially in concentrate preparation) to minimize letdown difficulties due to difference in melt flow</td>
</tr>
<tr>
<td>Select pigment and additive loadings to provide proper flow under operating conditions</td>
</tr>
<tr>
<td>Short, intensive mix cycle (should be adequate for most pigments)</td>
</tr>
<tr>
<td>Encourage subsequent melt pressing of these dispersions at high shear</td>
</tr>
</tbody>
</table>

Table 5 Guide to Quality Dispersion by Melt Shear Processing

<table>
<thead>
<tr>
<th>Polymer Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ Good wetting of both pigment and grind surface</td>
</tr>
<tr>
<td>■ Small viscosity change with temperature.</td>
</tr>
<tr>
<td>■ Chemically compatible with pigment under processing conditions</td>
</tr>
<tr>
<td>■ Rheologically compatible with base polymer (especially in concentrate preparation) to minimize letdown difficulties due to difference in melt flow</td>
</tr>
<tr>
<td>Select pigment loading to develop high shear during operation</td>
</tr>
<tr>
<td>Pre-blend dry ingredients (see Table 4—Guide to Quality Dispersion by Dry Blending)</td>
</tr>
<tr>
<td>Flux resin by shear rather than by application of external heat where possible (e.g., Banbury mixer)</td>
</tr>
</tbody>
</table>

Table 6 Guide to Quality Dispersion in Liquid Systems

<table>
<thead>
<tr>
<th>Vehicle Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>■ Good wetting of both pigment and grind surfaces</td>
</tr>
<tr>
<td>■ Tack* to suit method, i.e., low tack in processes dependent on impact between particles, high tack in those dependent on shear through liquid layer</td>
</tr>
<tr>
<td>■ Chemically compatible with pigment under processing conditions</td>
</tr>
<tr>
<td>Select pigment and additive loadings to provide proper flow for equipment use</td>
</tr>
<tr>
<td>Select let-down procedure to avoid seeding, gelling, or poor mix-in (e.g., viscosity adjustment with thinner, high shear mixing, stepwise reduction)</td>
</tr>
</tbody>
</table>
**Bulk Flow Properties:**

**Bulk Handling Systems Can be Designed**

Dry titanium dioxide does not flow freely. It tends to bridge and rathole and cannot be considered to have a well-defined angle of repose. TiO$_2$ handling is also susceptible to environmental effects such as moisture absorption, as well as handling history. In the customer’s process, these effects are often viewed as erratic or random TiO$_2$ handling performance.

The flowability of powders and other bulk materials is an important, but poorly understood property. There are a number of definitions of both flowability as a measured parameter and also of what constitutes “good” or “bad” flowability. An industry accustomed to handling polymer pellets may consider all pigments to have poor flowability, while producers and consumers of fine powders may consider certain powders to have much worse flowability than others.

Flowability can be defined as the ability of a powder’s interparticle cohesive strength to resist gravitation forces trying to cause it to move. For example, free-flowing glass beads will not form an angle of repose if poured onto a level surface. They will flow out on the surface, virtually as a liquid. The gravitational forces trying to pull each bead downward are not significantly impaired by the various forces that might act between the beads. Conversely, it is usually possible to form a very steep angle of repose with many powders. In this case, the interparticle forces generally exceed the gravitation forces, making the formation of stable piles (and flow obstructions in bins) feasible. TiO$_2$ manufacturers can influence the flowability of a grade by the organic and inorganic coatings applied to the surface (see the Performance Properties section).

Material “piping,” otherwise referred to in the industry as “ratholes,” occurs when powder in a silo (or hopper) flows from the area directly above the discharge outlet or hopper section while material located near the walls of the silo remains stagnant, see Figure 11.

Material hang-up is due to significant resistance from the stresses imposed by the silo walls. These stagnant zones usually remain in place until external forces, such as vibration or other sources of mechanical intervention, are applied. The degree to which TiO$_2$ forms “ratholes” will depend on the specific grade and the silo-bin geometry.

If a poor flowing material with unfamiliar handling characteristics is stored in a bulk system without prior flowability testing, it is not always possible to discharge the material. However, there are simplified methods to determine the “flowability” of a material in order to predict handling characteristics. Figure 12 illustrates the relative ease of material flowability as a function of a measured flowability index (FI). The higher the FI, the more difficult the material will be to discharge from a standard silo or bulk storage unit.
The FI values for pigmentary TiO₂ generally range between 10 and 20. In addition to the flow characteristics of a particular material, the ability to discharge a material will depend in part on the specific storage system design. Experience has shown that the TiO₂ grades located in the region above the line in Figure 12 generally do not handle well, unless the system is equipped with well-designed external mechanical flow aids. In addition, handling difficulty increases greatly for TiO₂ at the high end of the FI range.

The FI of titanium dioxide is also sensitive to environmental effects such as absorbed moisture. Therefore, it is not uncommon for the handling difficulty to increase as ambient conditions fluctuate from dry to humid. The degree of sensitivity to environmental moisture will depend on the grade, because each grade has varying surface treatments. Figure 13 illustrates how the FI relates to handling behavior as a function of humidity.

**Figure 13**
Generalized Response Surface of Powder Handling

**Figure 14**
Effect of Humidity on Flowability Index (FI)

Figure 14 shows an example of this behavior for a typical general-purpose grade of titanium dioxide. After drying, the product has an FI of 12.6, but after exposure for 24 hr to 40% relative humidity, the FI increases to 13.1. Finally, after exposure for 24 hr to 95% relative humidity, the FI increased to 13.8. This example shows how a grade that normally flows from hoppers in dry conditions could convert into the “difficult to handle” zone upon exposure to high humidity.

Despite the problems illustrated, robust, reliable systems for handling dry bulk TiO₂ can be designed. It is recommended that your Ti-Pure representative be contacted for assistance relating to handling problems with TiO₂ and/or design questions relating to TiO₂ handling equipment. Often, powder handling equipment vendors may not have experience with the peculiarities of TiO₂ handling. It is therefore recommended that when considering a particular design for TiO₂ handling equipment that the vendor(s) be requested to supply the names of contacts who have used the system for at least one year. The equipment should have been operated under similar constraints as your process, in terms of size, conveying distance, etc., as well as operating with similar grades of TiO₂.
Manufacturing Process

Chemours uses the Chloride Process to Make Titanium Dioxide

Titanium dioxide pigments are made by two commercial processes: sulfate and chloride. Rutile pigment can be made by either process, while anatase can only be made by the sulfate process. Chemours operates only chloride process plants.

The flow charts in Figure 15 illustrate in simplified form the two processing routes to intermediate TiO₂ products. The lower part of Figure 15 illustrates finishing operations, which may be similar for either manufacturing method. The sulfate method was commercialized in 1931, producing anatase TiO₂ and later (1941) rutile TiO₂. In this process, ore containing titanium is dissolved in sulfuric acid, yielding a solution of titanium, iron, and other metal sulfates. Then the pigmentary-size intermediate TiO₂ is produced through a series of steps including chemical reduction, purification, precipitation, washing, and calcination. The crystal structure, anatase or rutile, is controlled by nucleation and calcination.

FeTiO₃ + 2H₂SO₄ → TiOSO₄ + FeSO₄ + 2H₂O TiOSO₄ + H₂O → TiO₂ + H₂SO₄

The chloride method was developed and commercialized by DuPont in 1948 to produce rutile TiO₂. This process is now owned by Chemours and includes two high temperature, anhydrous vapor-phase reactions. Titanium ore is reacted with chlorine gas under reducing conditions to obtain titanium tetrachloride and metal chloride impurities, which are subsequently separated. Highly purified TiCl₄ is then oxidized at a high temperature to produce intermediate TiO₂ of excellent brightness. The oxidation step in the chloride process permits close control of particle size distribution and crystal type, making it possible to produce TiO₂ with high hiding power and tinting strength.

2FeTiO₃ + 7Cl₂ + 3C → 2TiCl₄ + 2FeCl₃ + 3CO₂ TiCl₄ + O₂ → TiO₂ + 2Cl₂

In both sulfate and chloride processes, the intermediate products are clusters of pigmentary-size TiO₂ crystals that must be separated (ground) for optimum optical performance. Depending on end-use requirements, various processing methods are used to modify the TiO₂, including precipitation of hydrous oxides of silicon, aluminum, or zinc on the pigment particle surface. Individual hydrous or anhydrous oxide treatments or various combinations can be used to optimize performance for specific applications. Organic additives also can be applied by various methods to enhance specific performance attributes of the pigment.

Crucial to the manufacture of titanium dioxide pigments is the supply of titanium ore. Although titanium ranks among the top 10 elements in abundance, it is widely distributed in nature at low concentrations. Efficient mining and mineral processing operations are required to develop a viable ore supply to meet the economic requirements of TiO₂ manufacture.
Figure 15
TiO₂ Manufacturing Process

**Sulfate**

Titanium Ore/H₂SO₄

- Solution
- Crystallization
- Precipitation
- Filtration & Washing
- Calcination
- Intermediate TiO₂

- Ferrous Sulfate Crystals

**Chloride**

Titanium Ore/Chlorine/Carbon

- Chlorination
- Purification
- Oxidation
- Intermediate TiO₂

- Chlorides of metals other than Titanium
- Oxygen

**Finishing**

Intermediate TiO₂

- Surface Modification
- Filtration Washing & Drying
- Grinding
- Packing

- Slurry Makeup
- Finished Slurry Storage
- Loading & Shipping

- Additives
Quality Control

Chemours is committed to maintaining a leadership position in product quality and uniformity. Ti-Pure™ titanium dioxide pigments are routinely tested for properties that are appropriate for the intended application of the product. The results of the quality testing are collected and reported using SAP tools. The testing can include color, tinting strength, undertone, pH, resistance, screen-pack testing, acid solubility, nujol yellowing, and low shear dispersion. Brief descriptions of these tests are provided in this section.

Color
Three filter reflectance measurements are made on compressed dry TiO₂. These reflectance measurements are then used to calculate TiO₂ L*, a*, b* color.

Tinting Strength and Undertone
Gray medium-hard vinyl exhibits are prepared on a two-roll mill. Three filter reflectance readings on the exhibits from a colorimeter are then used to calculate relative tinting strength and undertone.

pH
The pH of a 5:1 water:TiO₂ slurry is measured as a standard quality control parameter. Product pH is known to affect performance properties in liquid systems such as surfactant demand and flocculation.

Resistance
Conductance measurements are used to determine the resistance of 5:1 water:TiO₂ slurries, reflecting the soluble salt content of the pigment.

Screen-pack Testing
50% TiO₂ concentrates in low-density polyethylene are prepared in a Banbury mixer. A given amount of this concentrate is then extruded through a series of screens; performance is rated based on the amount of TiO₂ retained on a 500-mesh screen following extrusion. For R-350, more stringent testing is done as a 70% concentrate.

Acid Solubility
For grades R-105 and R-960, acid solubility can be correlated to the degree of surface silica coverage and further extrapolated to the durability of the product in an end-use application such as vinyl siding or window profile. A sample of the pigment is mixed with sulfuric acid and heated for a specified time period. An indicator is used to determine the amount of TiO₂ that is dissolved by the acid.

Nujol Yellowing
Dry TiO₂ is dispersed in an oil containing hindered amine light stabilizer and phenolic antioxidant. The mixture is exposed to UV light and measured for rate of yellowing as delta b* color.

Low Shear Dispersion
Dry TiO₂ is dispersed in a paint formulation at relatively low shear. The degree of dispersion is measured using a draw-down gauge block. (This test is only used on grades like R-960 which are sold predominantly to paint applications.)
Product Stewardship

Chemours defines Product Stewardship as: “An integrated business process for identifying, managing, and reducing safety, health, and environmental risk throughout all stages of a product’s life in the best interest of our four stakeholders: customers, employees, shareholders, and society.”

Chemours places high value on Product Stewardship as a vehicle to differentiate our products and services. We firmly believe that proactive product management results in improved product performance and is responsible business management that positively affects our stakeholders.

The objectives of our Product Stewardship program are to use our understanding of our products to protect our customers, employees, the community, and the public; to anticipate and respond to societal expectations and requirements; and to minimize resource and energy consumption (the environmental “footprint” of our products).

In order to provide assistance to customers in achieving your Product Stewardship objective, we offer the following information:

FDA Status
Ti-Pure™ grades R-101, R-103, R-104, R-105, R-108, R-350, and R-960 are acceptable for FDA indirect food contact uses under 21 CFR 178.3297 (Colorants for Polymers). Ti-Pure™ grades R-103, R-104, R-108 and R-350 are acceptable up to 25 wt% maximum loading of TiO2 to polymer content. R-101, R-105 and R-960 have no loading limitations.

NSF Status
Ti-Pure™ titanium dioxide grades for polymers R-101, R-103, R-104, R-105 and R-108 have been certified as acceptable for use in potable water piping. NSF certification allows these grades to be interchanged in approved pipe compounds at loadings up to 5.0 phr (parts per hundred resin). For information on other grades, contact your Ti-Pure™ representative.

SDS
For safety information, please visit the product Safety Data Sheet (SDS) on our Chemours website or they can be obtained from your customer service or sales representative.
The information set forth herein is furnished free of charge and based on technical data that Chemours believes to be reliable. It is intended for use by persons having technical skill, at their own risk. Because conditions of use are outside our control, we make no warranties, express or implied, and assume no liability in connection with any use of this information. Nothing herein is to be taken as license to operate under or a recommendation to infringe any patents.

For more information, visit titanium.chemours.com
For sales and technical support contacts, visit titanium.chemours/globalsupport

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