



Ti-Pure™
Titanium Dioxide

Titanium Dioxide For Coatings

Product Overview

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Titanium Dioxide for Coatings



This booklet is your guide to the use of Ti-Pure™ titanium dioxide (TiO_2) in coatings. It describes the properties and functions of TiO_2 pigments in a manner useful as an introductory guide for those new to the industry, and useful as a reference guide to those with experience.

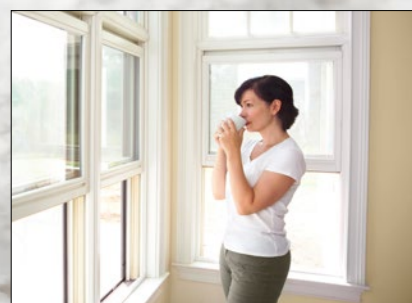
The first three sections describe titanium dioxide pigments, their function as white pigments in coatings systems and properties of TiO_2 pigments which affect finished product performance. The fourth section serves as your guide to selecting the right Ti-Pure™ titanium dioxide grade for your specific application, and the last section describes the titanium dioxide manufacturing process, quality assurance, and customer service.

No booklet can replace direct, personal contact with Ti-Pure™ sales representatives and technical service personnel. For more information, please contact your regional Chemours TiO_2 office. Telephone numbers and web address are listed on the back cover.

Chemours ranks first among titanium dioxide manufacturers in production capacity, product quality, and customer service. As a worldwide supplier of Ti-Pure™ titanium dioxide pigments, Chemours is committed to maintaining a leadership position in these areas.

Ti-Pure™ titanium dioxide is made only by Chemours.

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I. TITANIUM DIOXIDE PIGMENTS

Titanium dioxide (TiO_2) is the most important white pigment used in the coatings industry. It is widely used because it efficiently scatters visible light, thereby imparting whiteness, brightness and opacity when incorporated into a coating. Titanium dioxide is commercially available in two crystal structures—anatase and rutile. Rutile TiO_2 pigments are preferred because they scatter light more efficiently, are more stable and are more durable than anatase pigments.

Titanium dioxide pigments are insoluble in coating vehicles in which they are dispersed; accordingly, performance properties, e.g., chemical,

photochemical, and physical characteristics, are determined principally by the particle size of the pigment and the chemical composition of its surface. Most commercial grades of titanium dioxide have inorganic and in some cases organic surface treatments. Inorganic surface modifiers most often are precipitated coatings of alumina and silica, which are meticulously controlled for type, amount, and method of deposition.

These inorganic surface treatments provide improvements in one or more important performance properties such as dispersibility in water and in a range of organic liquids, hiding

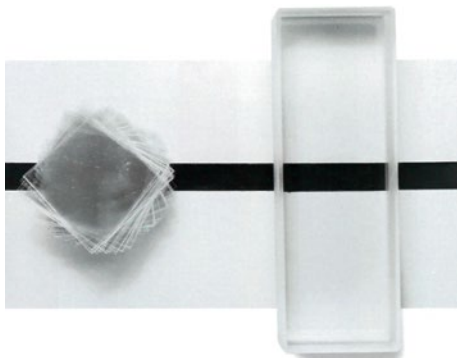
power efficiency, chalk resistance, and resistance to discoloration by heat and/or photoreduction. Organic surface treatments can enhance the dispersibility of the pigment in selected coatings systems. Numerous grades are produced with varying combinations of surface treatment to maximize value-in-use in a variety of coatings formulations.

It is inappropriate to equate superior performance of TiO_2 pigment in paint with high TiO_2 analysis. For example, Ti-Pure™ titanium dioxide grades specified at 80–88% minimum TiO_2 content are markedly superior to higher-content TiO_2 grades in hiding power efficiency in some highly pigmented flat paints.

II. OPTICAL THEORY

Figure 1

Reflective Scattering



Titanium dioxide (TiO_2) and other white pigments opacify paint films primarily by diffusely reflecting light. This reflection occurs because the white pigment scatters or bends light strongly. If there is enough white pigment in a paint film, almost all visible light striking it (except for a very small amount absorbed by vehicle or pigment) will be reflected, and the film will appear opaque, white, and bright.

The primary control of opacity and brightness in white paint films depends on scattering of light. Scattering of light means bending of light, and in coatings, light can be bent by surface reflection, by refraction and by diffraction.

Reflection

Figure 1 shows light scattering by reflection. For the single glass bar over the black line on the right, the line shows clearly because light has been reflected only twice (front and back of the bar) and only a small amount (~4%) is reflected at each surface. At the left, a stack of thin glass plates at equal thickness to the solid bar is placed over the same black line. The line is invisible because light has been

reflected at the air-glass interface of each plate. If the stack were immersed in oil until all air was displaced, or compressed sufficiently that all air were removed, the stack would become as transparent as the glass bar. A change of refractive index promotes reflection. In this illustration, it is the difference in refractive index of the glass (1.5) and the air (1.0) that produces scattered reflections from successive surfaces of the thin plates. In a like manner, reflection of light will occur from the surface of TiO_2 pigments with high refractive index (2.7) in contact with various coatings vehicles at low refractive index (1.5).

Refraction

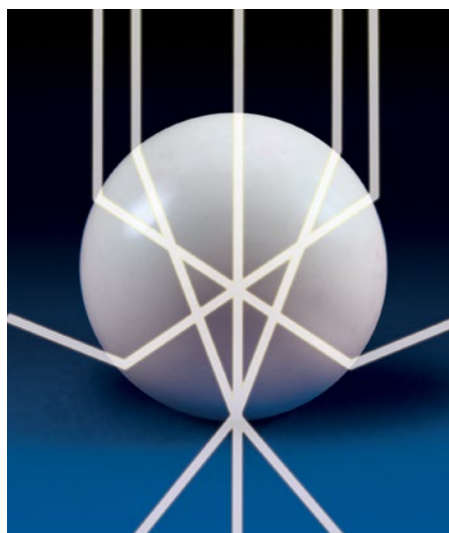
When light strikes a single high (in relation to the surrounding vehicle) refractive index transparent particle, the portion that is not reflected enters the particle and undergoes a deviation

from its original path. When the light enters a medium of higher refractive index, it is bent toward a line drawn perpendicular to the surface at the entrance point. When the light emerges, it is bent away from this perpendicular. The greater the difference in refractive index between the particle and the medium, the more the light is bent.

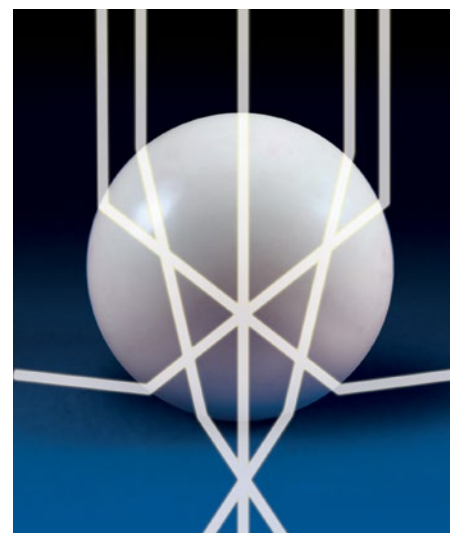
In Figure 2, the sphere on the left has a higher refractive index than the sphere on the right, thus bending the light more sharply; the left sphere scatters more light than the right.

Cross sections of two white paint films are shown in Figure 3. In the top illustration (high refractive index pigment), light entering the film travels a shorter path length than in the bottom (low refractive index pigment). Both films appear opaque and white, since practically all incident light is returned to the surface. If the films were reduced

Figure 2
Refraction of Light by Particles



Higher Refractive Index

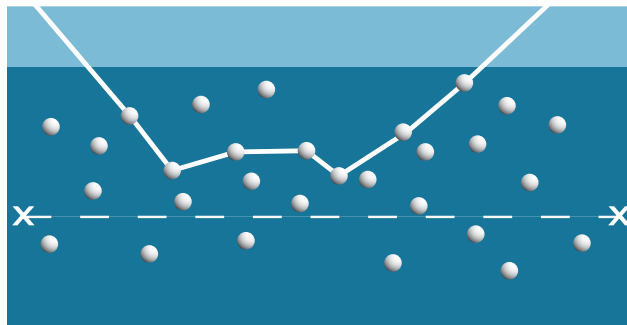


Lower Refractive Index

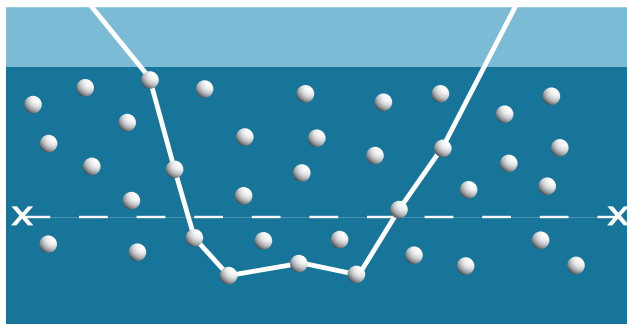
II. OPTICAL THEORY

Figure 3

Path of Light in White Paint Films



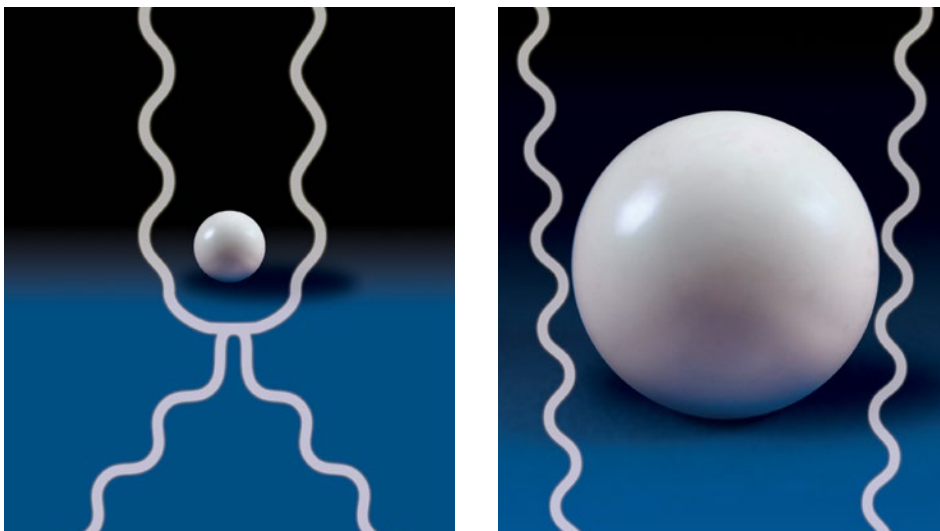
Higher Refractive Index Pigment



Lower Refractive Index Pigment

Figure 4

Diffraction Around Particles



in thickness to "X" and placed over a black background, the top illustration would remain opaque and white, while the bottom containing the lower index pigment would allow some light to pass into the black background and be absorbed. This film would appear gray in comparison.

Diffraction

The phenomenon of diffraction can be approached by consideration of one characteristic of wave motion. When a wave passes an obstruction, it tends to bend from its original path. As an example, waves of water passing a vertical piling will bend in behind the piling. The same is true of light waves as they pass near an object, they tend to bend behind the object. With large objects the amount of bending is generally insignificant to the eye, but when the object's dimensions approach the wavelength of incident light, bending (diffraction) becomes appreciable.

When the size of the TiO_2 particles approaches half the wavelength of incident light, the particles can bend four to five times as much light as actually falls on the particle because a large amount of the light is diffracted when it passes close to the particles. In other words, the scattering cross section can be four to five times the geometric cross section of the particles.

Figure 4 is a qualitative consideration of the difference between diffraction efficiency and particle size. The increase in diffraction at very small particle size (ideally one-half the wavelength of light desired to be scattered) is due to electromagnetic resonance between the particle and light. In other words, the particle tunes in to the light wave in the same way a radio antenna responds to radio waves.

II. OPTICAL THEORY

The ability of well-spaced particles of well-controlled size to diffract light is a major consideration in the design of fully functional coatings systems.

Why TiO₂?

TiO₂ is unique in that it combines high refractive index with a high degree of transparency in the visible region of the spectrum (Figure 5). This combination affords the coatings formulator a route to highly opaque and bright whites or tints at minimum film thicknesses.

To understand why TiO₂ and especially rutile TiO₂ offer such great advantages in hiding, it is only necessary to compare the refractive indices of rutile and anatase with those of other commercial white pigments and paint vehicles (Table 1). The larger the difference between the refractive index of the pigment and that of the medium in which it is dispersed, the greater the refractive light scattering.

Table 1

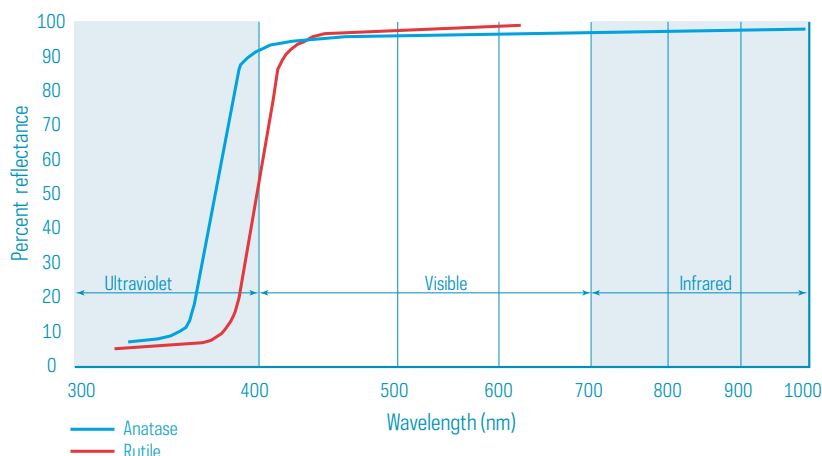
Refractive Indices (R.I.) for Pigments and Vehicles Used in the Manufacture of Paint

White Pigments	R.I.	Vehicles or Media	R.I.
Diatomaceous earth	1.45	Vacuum	1.0000
Silica	1.45–1.49	Air	1.0003
Calcium carbonate	1.63	Water	1.3330
Barytes	1.64	Polyvinyl acetate resin	1.47
Clay	1.65	Soybean oil	1.48
Magnesium silicate	1.65	Refined linseed oil	1.48
Lithopone	1.84	Vinyl resin	1.48
Zinc oxide	2.02	Acrylic resin	1.49
Antimony oxide	2.09–2.29	Tung oil	1.52
Zinc sulfide	2.37	Oxidizing soya alkyd	1.52–1.53
Titanium dioxide (anatase)	2.55	Styrene butadiene resin	1.53
Titanium dioxide (rutile)	2.73	Alkyd/melamine (75/25)	1.55

$$\text{Refractive Index} = \frac{\text{Speed-of-light-in-vacuum}}{\text{Speed-of-light-in-substance}}$$

Figure 5

Reflectance of TiO₂ Pigment in Various Regions of the Spectrum



II. OPTICAL THEORY

Figure 6

Effect of Refractive Index on Opacity



Figure 7

Relative Light Scattering Power versus Rutile Particle Size

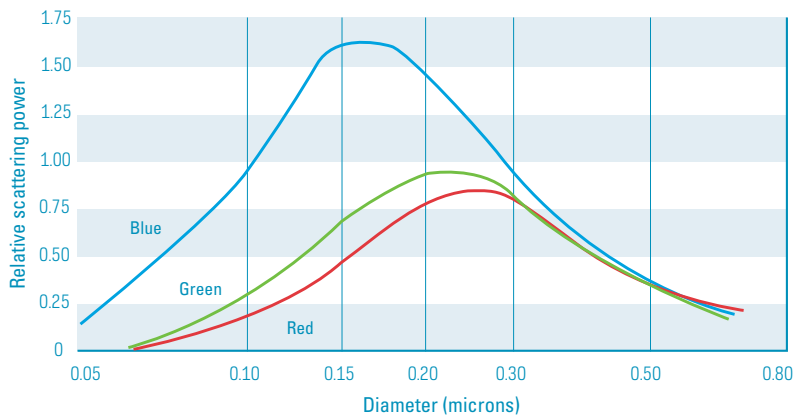


Figure 6 shows a practical demonstration of the effect of refractive index on opacity. The films were formulated at constant volume percent pigment in an acrylic vehicle. The film made with rutile TiO₂ does the most complete job of hiding the substrate.

TiO₂ Particle Size

As has been previously covered, for most efficient light scattering, the TiO₂ pigment diameter should be slightly less than one-half the wavelength of light to be scattered. Since the human eye is most sensitive to yellow-green light (wavelength about 0.55 microns), the theoretical optimum particle size for TiO₂ pigments for coatings is between 0.2 and 0.3 microns in diameter. Studies by microscopy have confirmed this range for the primary particle size. However, different measurement technologies can give different results.

Scattering Power

Curves in Figure 7 derived from theoretical considerations in highly dilute systems show the relative scattering power of rutile TiO₂ for blue, green and red light as a function of particle size. At about 0.2 microns, the sum of light scattered at all wavelengths is maximized. When the particle size is increased to between 0.25 and 0.30 microns, the scattering of blue light decreases rapidly, but the scattering of green and red is relatively unchanged; however, at 0.15 microns, the diameter corresponding to maximum scattering of blue light, light scattering in the red and green regions drops markedly.

II. OPTICAL THEORY

Undertone

In an ideal white film that is pigmented to complete hiding, changing pigment particle size has no effect on color since all the light striking the film is completely scattered. This is illustrated in Figure 8 which shows that both blue light with the shortest path length and red light with the longest are both totally reflected—the visual effect is the same as if all light had the same path length. Figure 9 illustrates the case in which an absorbing pigment such as carbon black is added to the white paint formula. On one hand, smaller particles scatter blue light more efficiently than the red light (see Fig. 7). That means shorter path/less absorption for the blue light. On the other hand, red light with the longer path length now has a greater chance to be absorbed. As a consequence, the reflected hue appears bluer. Thus, in a paint film containing some light-absorbing matter, decreasing TiO_2 particle size will increase blueness. This phenomenon is called undertone.

Pigment Volume Concentration (PVC)

Coatings properties such as gloss, permeability, porosity, hiding power, tinting strength and undertone are directly related to PVC. A dry paint film is a three-dimensional structure and as such the volume relationships among its components will bear importantly on paint performance.

$$\% \text{ PVC} = \frac{\text{Pigment volume (TiO}_2 + \text{ extenders)}}{\text{Pigment volume} + \text{volume of binders}} \times 100$$

PVC is the ratio, by volume, of all pigments in the paint to total nonvolatiles.

At a particular PVC called the critical pigment volume concentration (CPVC), many physical and optical properties of paint change abruptly. Generally, CPVC is considered to be the PVC where there is just sufficient binder to coat pigment surfaces and provide a continuous phase throughout the film.

Figure 8

Scattering of Light by White Paint

Incident Light: Equal parts of short and long wavelength (blue and red)

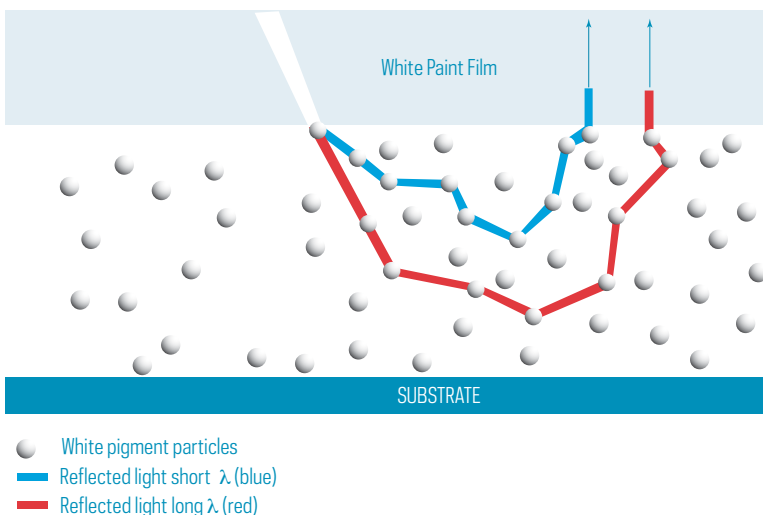
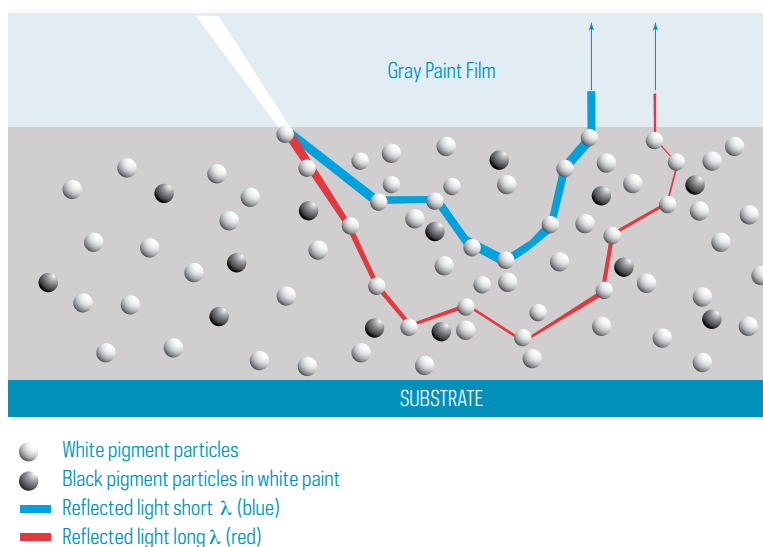


Figure 9

Scattering and Absorption of Light by Gray Paint

Incident Light: Equal parts of short and long wavelength (blue and red)



II. OPTICAL THEORY

Figure 10

Constant TiO_2 Spreading Rate (per unit area of dry film)

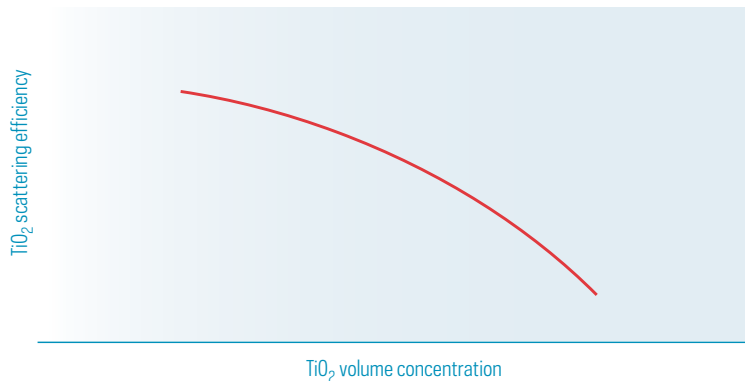
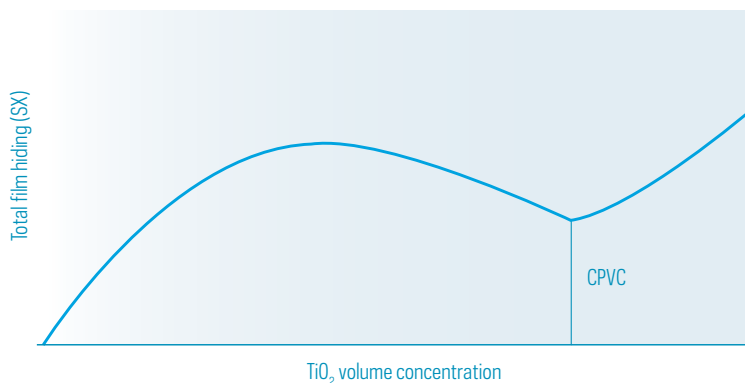


Figure 11

Constant Dry Film Thickness



Dry Flat Hiding

Interestingly, as air is incorporated into a paint film as a result of formulating highly pigmented coatings above the CPVC, the average refractive index of the vehicle matrix decreases, increasing the refractive index difference between the pigment and surrounding medium. The result is increased light scattering. Formulators often use dry flat hiding to improve hiding of low-gloss flat interior architectural finishes.

Scattering Efficiency and Coating Opacity

As the TiO_2 PVC or TiO_2 volume concentration (volume ratio of TiO_2 in the paint to total nonvolatiles) increases above approximately 10%, diffractive light scattering decreases because of TiO_2 particle crowding. The result of this effect can be shown by formulating a series of coatings with increasing TiO_2 volume content, but at constant TiO_2 per unit area of the dry film (decreasing film thickness). This is illustrated in Figure 10. On the other hand, an increase in TiO_2 volume concentration at equal film thickness will initially show an increase in total opacity of the coating (despite the loss in efficiency) up to about 30 PVC, and then hiding or opacity decreases with further additions of TiO_2 because the scattering efficiency is falling more rapidly than compensated for by higher TiO_2 concentration. This continues until the CPVC is reached, at which point the onset of dry flat hiding causes opacity to increase again (Figure 11).

II. OPTICAL THEORY

TiO₂ Surface Treatment

One way to prevent crowding of TiO₂ particles in highly pigmented systems is to coat the pigment surface in a controlled manner. The surface coating then acts as a physical spacer, maintaining separation between adjacent TiO₂ particles and minimizing losses in diffractive light-scattering efficiency as pigment concentration is increased. A unit weight of this specially coated pigment contains less TiO₂ than its uncoated counterparts, but the light-scattering ability of the heavily coated grade is higher in most high-PVC paints.

Color, Particle Size, and PVC

Color and undertone are sometimes confused. It is possible for a paint containing blue undertone TiO₂ to have a yellow color because of one of the undesirable effects listed in Table 2. Blue and yellow undertone pigments will have equal color or brightness when measured in pure white coating formulas at complete opacity.

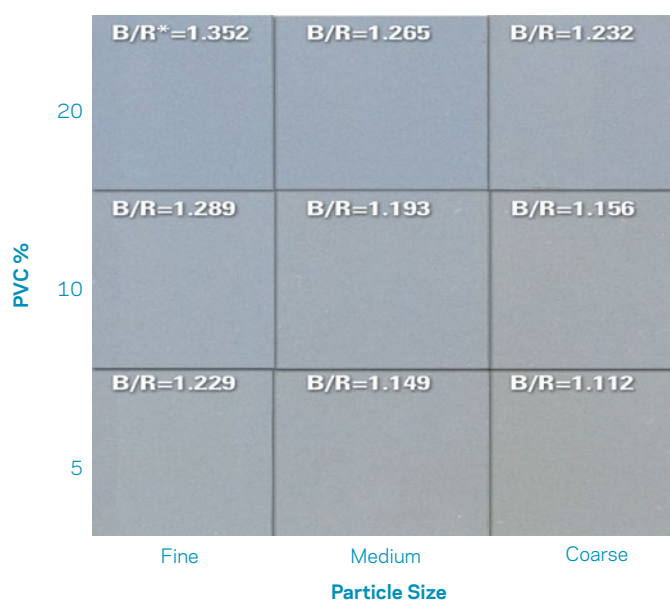
Probably more color-matching problems result from the use of the wrong particle-size TiO₂ and/or failure to recognize undertone changes that occur with TiO₂ concentration than from improper combinations of colored pigments. The combined effects of particle size and TiO₂ PVC on the color of a tinted paint are substantial and are shown in Figure 12. The decrease in scattering efficiency as TiO₂ PVC increases occurs to the greatest extent in the red part of the spectrum; hence, reflected light shifts to the blue region as PVC increases.

Table 2

Some Causes of Undesirable Color Effect
1. Contamination—including abraded processing equipment, usually resulting from problems during the dispersion process.
2. Colored products of reactions of TiO ₂ with other paint ingredients such as phenolics, strong reducing agents, etc.
3. Blue, purple or gray discoloration in oxygen-impermeable films exposed to ultraviolet radiation.
4. Excessive heat exposure—vehicle discoloration.
5. Inadequate hiding—show-through of substrate.

Figure 12

Titanium Dioxide Effect of Particle Size and PVC on Tinted Paint Undertone



*Blue/red reflectance values

III. OPTICAL PROPERTIES

Extenders

In addition to TiO_2 and vehicle, many paints also contain extender pigments. These normally low-cost materials perform a variety of functions. White extender pigments are mineral compounds of relatively low refractive index. They differ in composition, size and shape. White extender pigments develop very little hiding in gloss and semigloss paints, but they contribute dry-flat hiding (air-pigment interface) to paints at low cost and are used to control gloss, texture, suspension, and viscosity. The main types of extenders are carbonates, silicates, sulfates, and oxides. Their particle sizes range from 0.01 to 44 microns. Often more than one extender is used to obtain optimum properties. A high-gloss white paint usually contains only TiO_2 ; a semigloss paint contains TiO_2 and some extender pigments; a flat paint contains TiO_2 but has a high extender content.

Hiding Power and Tinting Strength

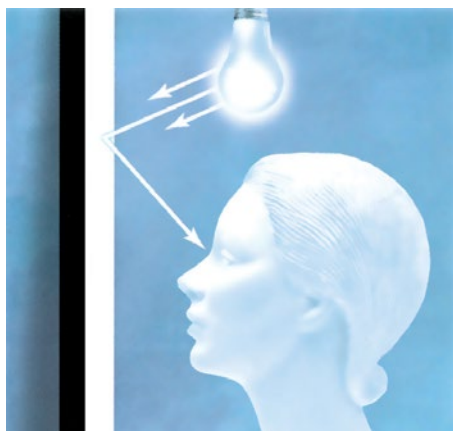
Hiding power and tinting strength are two optical properties used to describe the light-scattering efficiency of a white pigment, and must be considered when selecting a commercial grade of TiO_2 . The hiding power of a paint is a measure of its ability to obscure a background of contrasting color, and results from interactions between incident light and the pigments present in the paint film. White pigments provide opacity by scattering incident visible light at all wavelengths, and color pigments provide opacity by absorbing incident visible light at characteristic wavelengths. Figure 13 illustrates two coatings (A and B) at complete hiding and one coating (C) at incomplete hiding, all covering a black substrate. Coating A is pure white and reflects or scatters all the light hitting it before any of the light reaches the substrate. Coating B is pure black and absorbs all the light

hitting it. Coating C is a white coating but is at incomplete hiding. Some of the light hitting it penetrates through to the black substrate and is absorbed while the rest is scattered. This coating therefore appears gray.

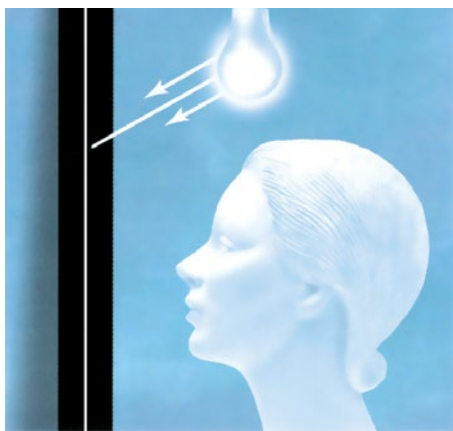
While hiding power is a measure of the ability of TiO_2 to opacify a white paint film, tinting strength describes its ability to add whiteness and brightness to the color of a tinted paint. The tinting strength test describes TiO_2 light-scattering contribution relative to the light-absorbing ability of a colored pigment when a white paint is tinted to about 50% reflectance with the colored pigment. To be sure that flocculation does not give misleading tinting strength results, the tinting strength measurement should be accompanied by some measure of flocculation such as a rub-up test on the partially dried tinted paint.

Figure 13

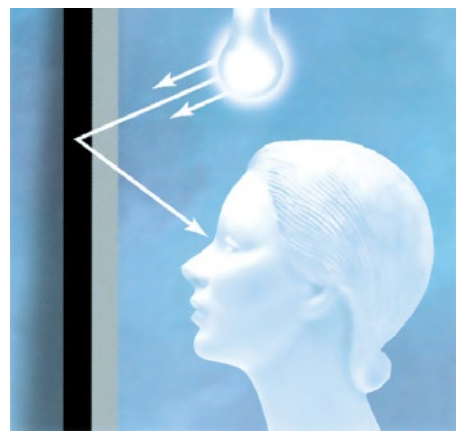
Opacification of a Film



A: Complete Hiding—Light Scattering



B: Complete Hiding—Light Absorption



C: Incomplete Hiding

III. OPTICAL PROPERTIES

Color

Dry compacted TiO₂ samples are characterized by their brightness and whiteness, and exhibit reflectance properties approaching that of the perfect reflecting diffuser. "Color" is carefully controlled during the TiO₂ manufacturing process through the removal of trace amounts of metal oxide contaminants. These light-absorbing contaminants will detract from the brightness and whiteness of the pigment, and can affect the appearance of white and near-white paints containing that pigment. The TiO₂ present in a white paint contributes to the color of the paint film by scattering light and providing brightness, whiteness, and opacity. However, there are many circumstances which can cause undesirable color effects in a white paint film; some have been shown in Table 2. As described earlier, the appearance of a nonabsorbing white paint film at complete hiding is unaffected by TiO₂ particle size or undertone.

The color of dry TiO₂ and white (and near-white) paint films is often expressed in terms of their CIE L*a*b* color coordinates (10° Standard Observer, Illuminant D65), wherein L* is a measure of brightness, a* is a measure of redness-greenness and b* a measure of yellowness-blueness. CIE color difference values such as L* and b* are also used to describe the color of a sample relative to an agreed-upon reference sample. Other commonly used expressions to describe the color

of dry TiO₂ and white paints include brightness (measured either as Hunter green filter reflectance G, or as CIE Y tristimulus value) and yellowness index as shown below:

Yellowness Index (Y.I.) by ASTM D1925

$$Y.I. = \frac{\frac{A}{G} - \frac{B}{G}}{G} \times 100$$

OR

$$Y.I. = \frac{(1.28X - 1.06Z)}{Y} \times 100$$

A, B and G = Hunter or Gardner Reflectometer Reflectances (tristimulus colorimeter readings, normalized to 100)
X, Y and Z = CIE Tristimulus Values, 2° Standard Observer, Illuminant C

Gloss

Of all the optical properties of a coating, the perception of gloss is the most complex. Analysis of visual gloss observations reveals that several criteria are involved in the psychology of gloss:

- Specular reflectance
- Distinctness of image (eyes focused on virtual image behind surface)
- The contrast between light and dark images
- Haze

Of these, specular reflectance has proved the most popular for widespread analytical evaluation of the surface phenomena we call gloss. This is typically measured as the amount of light reflected off a surface at an angle equal to a beam of carefully focused incident light. Most gloss evaluations are performed at angles of 20, 60

or 85 degrees as measured from perpendicular. We speak of 20-degree gloss for the highest-gloss surfaces, 60-degree for low-gloss and semigloss paints, and typically reserve 85-degree gloss for eggshell and flat paints.

The gloss of a coating is primarily determined by PVC, pigment type and vehicle type. Within a specific formula, TiO₂ selection is important because the gloss will be negatively affected by exceedingly large fraction of hard, unground agglomerates in the paint. Therefore, the fraction of particles larger than a certain diameter (dependent upon the system) is an excellent predictor of gloss. Proper TiO₂ grade selection, correct formulation and procedures to maximize dispersion are needed. Also, finishes are subjected to a variety of conditions during manufacture, storage, application, curing and use that can affect final gloss. Table 3 lists some of these factors.

III. OPTICAL PROPERTIES

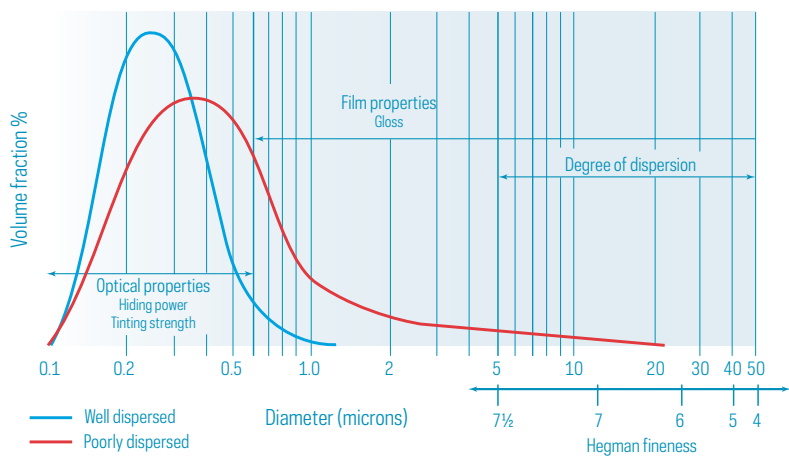
Table 3

Some Factors Affecting Gloss
Manufacture Fineness of grind Type of mill Raw materials Ratio of pigment to binder
Storage Gradual wetting of pigment Poor reincorporation of settled coarse particles Seeding, soap or crystal formation Gradual increase of viscosity
Application Smoothness of substrate Loss of binder into substrate Dissolving of binder from priming coat Varying degrees of shear during application Various degrees of leveling or flow resulting from the particular method of application (e.g., orange peel on spraying) Contamination with dust Film thickness Rate of solvent loss (e.g., flash time before baking) Baking temperature and time Humidity during drying
Use Variation with age of film and conditions of exposure

Dispersion

The particle size of TiO₂ is small compared to the thickness of the film in which it is used. As discussed in “Optical Theory” (p. 7), TiO₂ has a theoretical optimum particle size between 0.2 and 0.3 microns, but as received is considerably larger because of the formation of agglomerates in handling during the manufacturing process. The energy of simply stirring pigment into water or binder is not great enough to overcome the particle attractive forces preventing the breakup of the agglomerates. By not minimizing the number of these agglomerates, the end-use properties will all be adversely affected (e.g., gloss, hiding power, tint strength, poor suspension, color streaking in tints and grit in the film). Although the pigment is designed to yield optimum hiding power, gloss and color, these basic properties may not be realized if the initial dispersion of TiO₂ is inadequate. Figure 14 shows the particle size distribution of a poorly dispersed pigment versus a well-dispersed pigment. The optimum dispersion for the pigment is defined where further grinding will not change this distribution.

Figure 14
TiO₂ Dispersion States vs. Particle Size Distribution and Pigment Properties



- The actual process of breaking agglomerates (i.e., dispersion) can be visualized as occurring in three steps in the grinding process:
1. Wetting, where air and other substances are displaced from the pigment surface by solvent, dispersant/surfactant and binder.
 2. Grinding, in which the agglomerates of pigment particles are broken and separated into an optimum particle distribution.
 3. Stabilization, by which the optimally separated particles are maintained by either charge or steric stabilization.

III. OPTICAL PROPERTIES

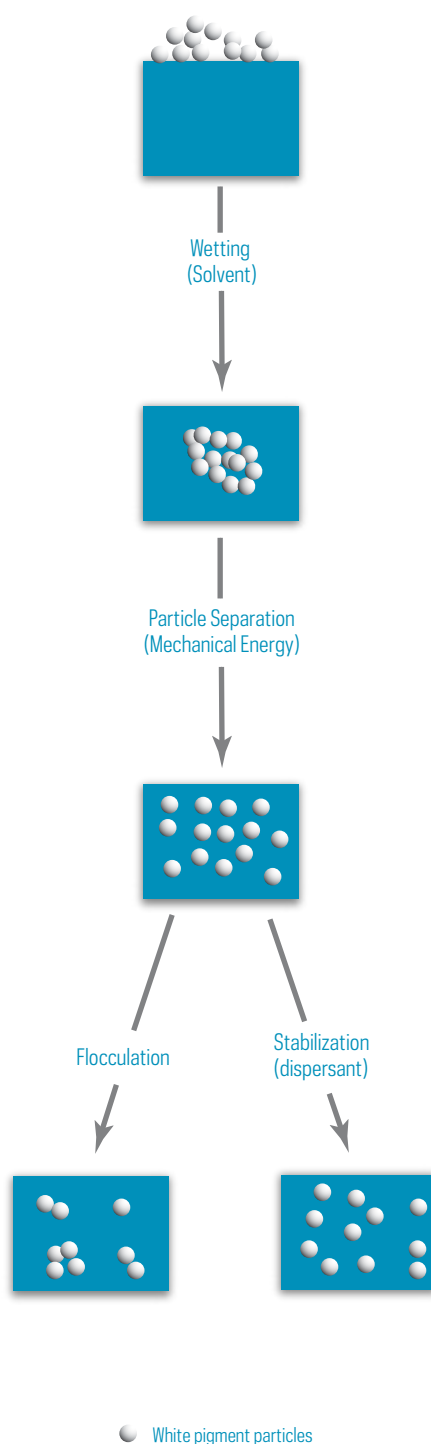
This classification is useful because our experience shows that one pigment may differ from another in one or more of these steps of the dispersion process. However, the three phases are not always taken into consideration by pigment users; consequently, a pigment is frequently described simply as “poor in dispersion properties” regardless of the specific phase in which it is actually deficient. Figure 15 visually illustrates this concept.

TiO₂ dispersion in oleoresinous binders (i.e., solvent-based paints) usually depends on shear rate, mill base viscosity, time and degree of wetting provided by the vehicle. Although the resin is often the sole dispersing agent, there are dispersants formulated for specific resins and solvent systems.

In water systems, dispersants are required for wetting and stabilization. It is important to recognize that both amount and type of dispersant affect dispersion quality. Excess dispersant is self-defeating, particularly with ionic types, and should be avoided. The optimum amount varies with the particular dispersant used, the TiO₂ grade and water hardness. A very simple test for determining dispersant demand involves measuring the Brookfield viscosity of a 70 weight-percent TiO₂ aqueous slurry prepared using a high-speed disperser and several different dispersant concentrations. The optimum dispersant concentration yields minimum viscosity. Using dispersant at this level, pigment concentration can be varied to achieve desired mill base rheology. Dispersant selection is even more critical in paints utilizing anionic and nonionic rheology modifiers.

Figure 15

Dispersion Process



Flocculation

Flocculation is the formation of loose clumps of TiO₂ particles (i.e., flocculates) in a fluid system. Flocculation is often the result of an inadequate initial grind (dispersion), improper type or concentration of dispersant, pH mismatch, and temperature. Characteristically, these clumps are easily broken under moderate shear, but will quickly reform if the particles are free to move in the matrix. Flocculation can cause several major problems, including:

- Loss of opacity and tinting strength—flocculates do not scatter as efficiently as primary TiO₂ particles.
- Excessive viscosity and poor flowability—often, stirring will thin the suspension, but flocculation will recur on standing.
- Low gloss.

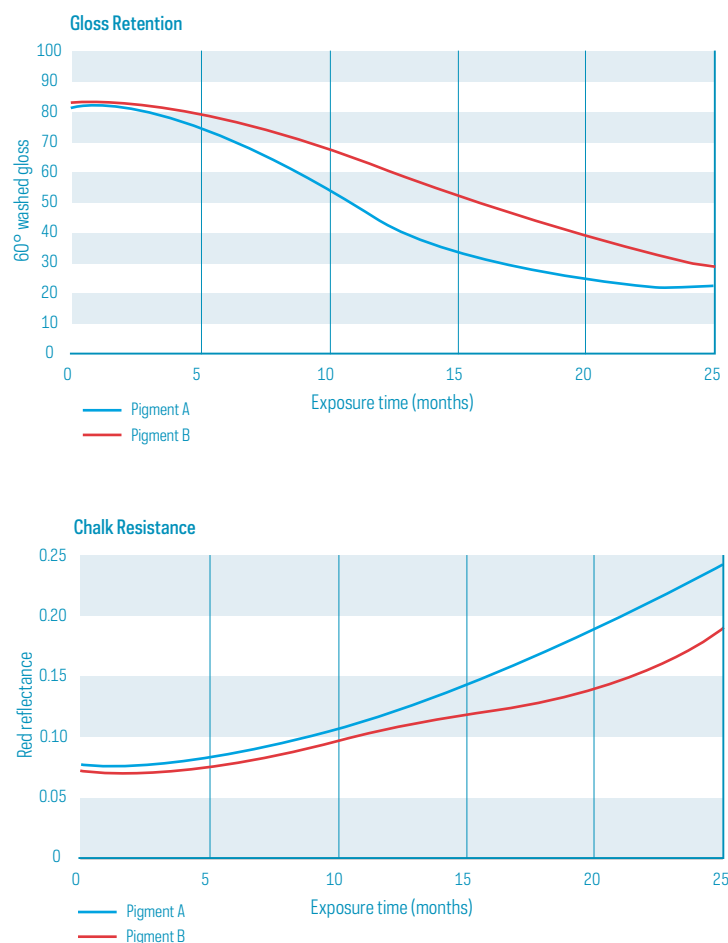
Weatherability

Weatherability is a term applied to the various changes in appearance and functional value of exposed pigmented coatings. It includes all parameters of exterior serviceability, such as retention of color, retention of gloss, chalking, adhesion (blistering, flaking, peeling) and film integrity (i.e., checking, cracking, erosion, corrosion protection). These performance properties are controlled principally by formulation (e.g., choice of vehicle, extender, pigment volume concentration, etc., which are relatively independent of the grade of TiO₂ used). However, chalk resistance, retention of color (tinted paints) and gloss, and resistance to discoloration by mildew and dirt collection can be influenced by TiO₂ grade selection.

III. OPTICAL PROPERTIES

Figure 16

Gloss Retention and Chalk Resistance Florida Exposure Series
(Blue-tinted Architectural Alkyd at 15PVC)



The weatherability of pigmented coatings is best evaluated through exterior exposure studies over a range of representative climate conditions. Frequently, test panels are placed on exposure at locations like Florida, Arizona, and Australia to measure performance under extreme conditions. Appearance and film properties can be monitored over the expected service life of the coating. Use of accelerated testing equipment to simulate exterior exposure is frequently used within the coatings industry to obtain a preliminary

assessment of exterior performance; however, reliability of this testing is such that results need to be confirmed through exterior exposure experiments.

Chalk Resistance and Gloss Retention

The initial effects of weathering are usually detected at the surface of the paint film and are caused by degradation of the organic binder on exposure to sunlight, moisture, temperature change and environmental pollutants. The organic binders used in coatings applications are

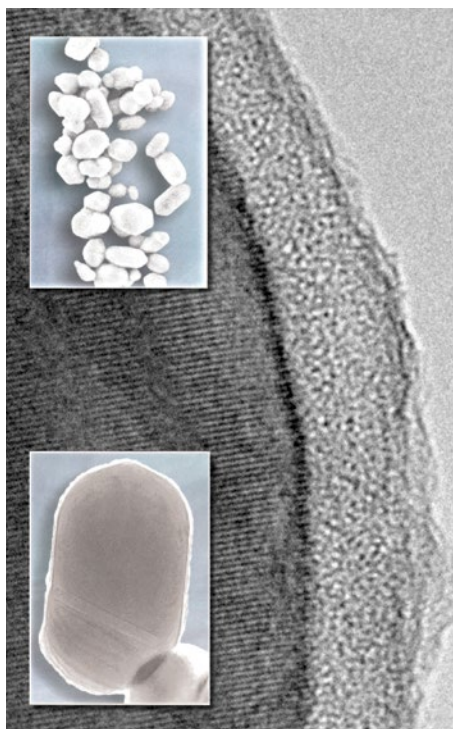
high-molecular-weight polymers. These polymers are susceptible to photochemical attack, and degrade over time to form low-molecular-weight oxygenated species that solubilize and wash from the surface of the film. This process increases surface roughness and reduces gloss. Chalking occurs as increased amounts of organic binder are removed from the surface of the film, causing TiO_2 and extender pigments to protrude through the film surface producing a white, chalky appearance. Chalking in tinted paints is a particular concern, since its onset causes color change—increased lightness and reduced chromaticity. In this regard, the most chalk-resistant pigments are essential for best color and gloss retention in tinted paints. For example, Figure 16 illustrates the improvements in gloss retention and chalk resistance in a blue-tinted architectural alkyd that can be obtained through selection of a durable TiO_2 grade. As shown in the upper graph, the paint containing Pigment B exhibits higher 60° washed gloss over the exposure period than the paint containing Pigment A. Similarly, the lower graph shows the paint containing Pigment B to be more resistant to chalking than the paint containing Pigment A. In this case, the degree of chalking is determined by measuring the red reflectance, wherein increased reflectance is due to the increased levels of white pigment protruding through the surface of the film.

Rutile TiO_2 is inherently more chalk-resistant than anatase because it absorbs significantly more UV-A ultraviolet radiation in the region of 350–400 nanometers (Figure 5, page 7), converting it into energy in

III. OPTICAL PROPERTIES

Figure 17

Impervious Shell of SiO₂ on Pigment Surface



the form of heat and protecting the organic portions of the paint film from UV degradation. The surface of the TiO₂ pigment particle is, however, photochemically active and can, in the presence of H₂O and O₂, promote degradation of the organic binder at the pigment surface. This form of degradation can be controlled through the application of inorganic oxide surface treatments, which act as barriers between the TiO₂ surface and the organic binder. Ti-Pure™ Select TS-6200 and R-960 are outstanding commercial examples, wherein each pigment particle is encased in an impervious shell of SiO₂. This tight SiO₂ coating provides a high degree of protection against photochemical activity. The SiO₂ surface treatment is shown in Figure 17. For applications requiring maximum chalk resistance and tint retention, Ti-Pure™ R-960 and TS-6200 are the preferred grade. The relative chalk resistance of several Ti-Pure™ titanium dioxide grades is illustrated in Figure 18. For applications

demanding high initial haze-free gloss and a high degree of gloss retention over the service life of the coating, selection of a TiO₂ grade with high gloss and durability, like TS-6200, is critical to a successful formulation. These types of pigments are required to complement the performance of photochemically stabilized vehicle systems used in a range of high-performance architectural and industrial coatings systems.

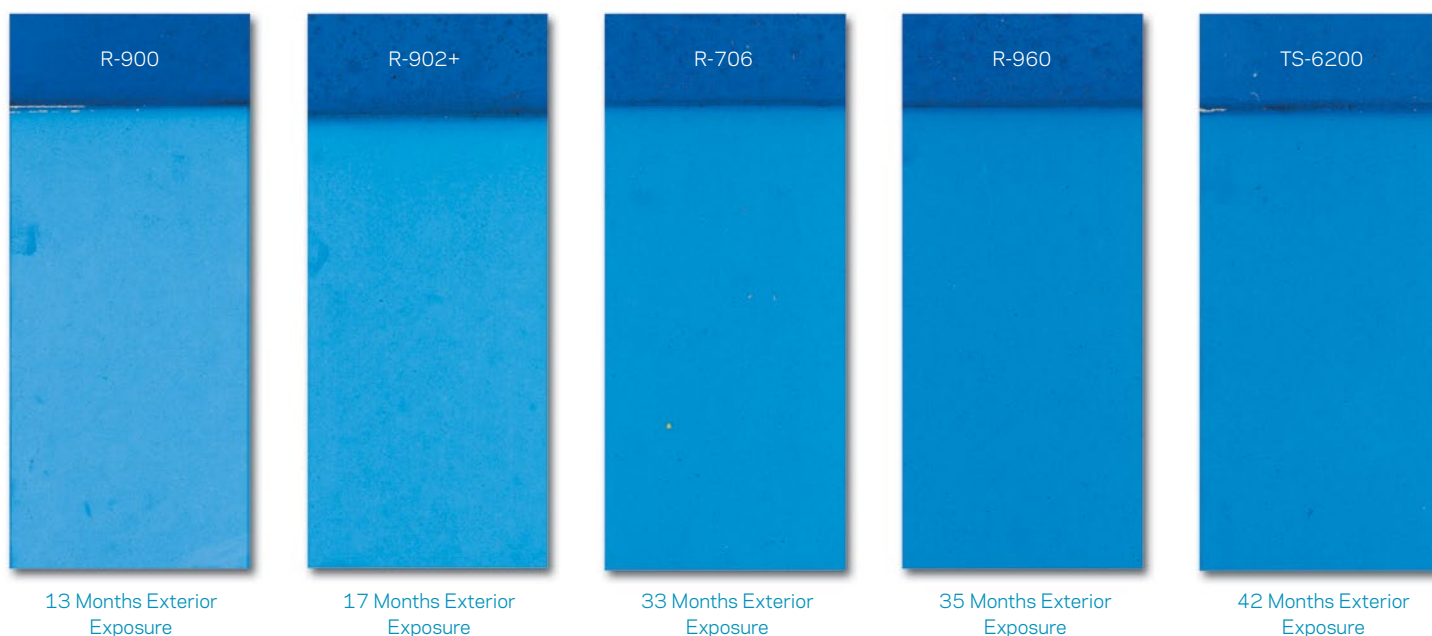
Occasionally, pigment chalking is desired. If “cleanup” of dirt (e.g., white house paints) is desired, the formulator may do the following:

- Increase pigment volume concentration.
- Use a less chalk-resistant grade of rutile or extender.
- Use some anatase in combination with the rutile pigment.

However, use of these methods will decrease tint and gloss retention.

Figure 18

Chalk Resistance of Ti-Pure™ Pigments



III. OPTICAL PROPERTIES

Standard Classifications

Table 4 identifies paint grade Ti-Pure™ titanium dioxide pigments conforming to each of the four types specified in ASTM D476 classifications.

Table 4

ASTM Specification for Paint Grade Ti-Pure™ Titanium Dioxide Pigments

	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII	ASTM Standards
	Anatase*—free chalking	Rutile—low-medium chalk resistance	Rutile—medium chalk resistance	Rutile—high chalk resistance	Rutile—high chalk resistance	Rutile—medium-high chalk resistance	Rutile—medium-high chalk resistance	D 3720
Typical end-use application(s)	White exterior house paint and interior uses	Low-medium percent PVC	High percent PVC	Exterior coatings requiring excellent durability	Exterior coatings requiring excellent durability with high gloss	Interior-exterior coatings medium-high percent PVC	Interior-exterior coatings low-high percent PVC	
Titanium dioxide (TiO ₂) content, min, percent	94	92	80	80	90	90	92	D 1394
Specific resistance, min, Ω	5000	5000	3000	3000	3000	5000	5000	D 2448
Moisture content as packed, min, percent	0.7	0.7	1.5	1.5	1	0.7	0.7	D 280
Specific gravity	3.8–4.0	4.0–4.3	3.6–4.3	3.6–4.3	3.6–4.3	3.6–4.3	4.0–4.3	D 153
45-µm screen residue, max, percent	0.1	0.1	0.1	0.1	0.1	0.1	0.1	D 185

Type I	Anatase
Type II	Rutile — low-medium chalk resistance — R-706, R-900, R-902+
Type III	Rutile — medium chalk resistance — R-706, R-902+, TS-6300**
Type IV	Rutile — highly chalk resistant — R-706, R-960, TS-6200
Type V	Rutile — exterior applications with high gloss — R-706, TS-6200
Type VI	Rutile — interior exterior, medium-high PVC — R-706, R-902+
Type VII	Rutile—interior exterior, low-high PVC—R-706, R-902+

* Identification of anatase or rutile or mixtures thereof is made by X-ray analysis (Test Method D 3720).

** Preferred Ti-Pure® grade for high PVC flat finishes.

IV. END USES — TiO₂ GRADE RECOMMENDATIONS



Interior Architectural Paints

Gloss and Semigloss Paints

Ti-Pure™ R-900 is recommended for general use in alkyd and latex paints for interior gloss and semi-gloss applications. This pigment disperses easily, develops high gloss and shows maximum hiding power over a wide range of gloss grade applications.

Two multipurpose gloss grades, Ti-Pure™ R-706 and Ti-Pure™ R-902+, are recommended for use when a single pigment is required to perform well in both interior and exterior gloss and semi-gloss systems. R-706 is the ideal selection for applications requiring high gloss, maximum gloss retention and chalk resistance. Both R-706 and R-902+ will deliver bright,

clean colors in tinted systems with R-706 providing a blue undertone and R-902+ providing a more neutral undertone.

For paint manufacturers capable of handling TiO₂ in aqueous slurry form,

Ti-Pure™ R-706 and R-902+ are available as slurry grades, Ti-Pure™ R-746 and R-942 respectively.

Flat Paints

These coatings are formulated at relatively high levels of extenders and TiO₂ pigments, and are frequently above the critical PVC for interior applications. Ti-Pure™ Select TS-6300 is recommended for these applications. Because it is a highly surface-treated TiO₂ grade, TS-6300 will provide superior performance in this class of highly crowded paint systems.



IV. END USES — TiO₂ GRADE RECOMMENDATIONS



Exterior Architectural Paints

In addition to normal criteria, selection of the proper Ti-Pure™ titanium dioxide grade for these coatings will depend upon the desired balance between gloss and tint retention, self-cleaning ability, and prevailing atmospheric conditions. For high gloss and maximum exterior durability in architectural coatings systems, Ti-Pure™ R-706 is recommended. Ti-Pure™ R-902+ is also highly chalk resistant; it performs well over a wide range of solvent-based and aqueous systems where tint retention is important. Both R-706 and R-902+ will deliver bright, clean colors in tinted systems with R-706 providing a blue undertone and R-902+ providing a more neutral undertone. Ti-Pure™ R-900 has medium chalk resistance and is preferred when dirt collection is a problem. These pigments can be used in both alkyd and emulsion paints.

Tinted house paints and both white and tinted trim paints require a high degree of chalk resistance and gloss

retention. Ti-Pure™ R-706 is the ideal choice for emulsion trim paints because it provides maximum initial gloss and outstanding exterior durability. These last two properties result from lower PVC and generally better binder durability associated with exterior emulsion trim paints. Ti-Pure™ R-902+ also satisfies these requirements over a wide range of solvent-based and aqueous systems.

Ti-Pure™ Select TS-6300 performs well in selected exterior white latex house paints, following reformulation to accommodate the higher surface area of the pigment, and to maintain film integrity. When exterior durability is desired in a flat paint, R-902+ is also highly recommended.

Industrial Finishes

Industrial finishes include a variety of market subsegments such as automotive finishes, powder coatings, coil and can coatings, and maintenance paints. Each has substantially different quality and performance requirements. TiO₂



is used primarily to provide hiding or opacity, but grade selection can also have a significant effect on coating gloss, exterior durability and, for acid-catalyzed coatings, film cure. The TiO₂ grade most appropriate for a particular application depends on the end-use coating properties it affects.

Automotive OEM and Refinish Coatings

Automotive coatings are among the most demanding applications for TiO₂ pigments. Proper selection of pigment grades is critical to optimize:

- Manufacturing and application processes.
- Mechanical and chemical integrity.
- Aesthetics, which are required for today's automotive coating systems.

Several Ti-Pure™ grades are available for automotive coating applications, offering both Original Equipment Manufacturers (OEMs) and refinish formulators a selection of the desired combination of properties.

IV. END USES — TiO₂ GRADE RECOMMENDATIONS

**Electrodeposition Primers:**

Ti-Pure™ R-900 is ideally suited for electrodeposition primer applications. R-900 provides easy dispersion, excellent hiding, high resistivity, and low soluble ion content that provides excellent application properties and high corrosion resistance.

Topcoats: TS-6200 combines high gloss and distinctness of image with excellent resistance to weathering for high-quality OEM and refinish topcoats. TS-6200 and R-960 are the most durable Ti-Pure™ pigments available, making them also ideal for OEM and refinish applications.

Processing: Optimization of optical and mechanical properties of an automotive coating depends on properly dispersed pigment. Choosing a pigment that is ideally suited for each coating system is critical to maximizing coating

performance. The fast wet-in and easy dispersion properties of TS-6200 can provide increased throughput in manufacturing operations.

Powder Coatings

The continuing emergence of powder coatings as a significant and high-growth market segment has led to the development of thousands of specific formulations from only a handful of primary resin/crosslinking systems. Technological advances have been based primarily on developments and improved understandings in resin chemistry. Recently, the influence of TiO₂ in powder coating systems has been explored, allowing formulators to select pigments with varying chemical and physical properties. Several Ti-Pure™ grades are available to optimize processing and end-use performance of specific powder formulations.

Flow and Optics: Ti-Pure™ R-706 provides easy dispersion, high-cure flowability (which yields decorative coatings of high gloss and reflectance) and increased opacity. These properties combined with high durability performance make R-706 suitable for both interior and exterior use.

Durability: TS-6200 is the most durable Ti-Pure™ pigment available and is suggested for use in systems such as triglycidyl isocyanurate (TGIC) and Primid cured polyesters where outdoor weatherability is of primary concern.

Overbake Yellowing Resistance: Both Ti-Pure™ R-960 and R-900 provide excellent resistance to overbake yellowing during cure.

IV. END USES — TiO₂ GRADE RECOMMENDATIONS



Other Industrials

All Ti-Pure™ grades are commonly used in industrial coatings. The performance differences in these grades are determined by their surface treatment, particle size and particle-size distribution. Silica provides exterior durability (chalk resistance and gloss retention). Alumina provides ease of dispersion and flocculation resistance. Smaller particle size, narrower particle size distribution and smaller particle coarse tail contribute to the superior gloss of R-706. Although high hiding is important in all coatings, grade choice often depends on the level of gloss and exterior durability required.

Ti-Pure™ Select TS-6200 is the most widely applicable grade, possessing a combination of exceptionally high

gloss and excellent exterior durability unique in the industry. It can be used in both interior and exterior coatings where this combination of gloss and durability combined with excellent dispersibility is of value. Applications include coil coatings for residential aluminum siding and architectural building panels, aerospace coatings and other high-durability applications. Because of the silica surface treatment, TS-6200 provides better film cure in acid-catalyzed coatings than non-silica-treated grades.

Ti-Pure™ R-902+ is used in high-quality finishes that require very good chalk resistance and gloss retention, but not the exceptional performance provided by R-706 and TS-6200. This grade is often used in industrial maintenance,

implement and transportation finishes, and some container coatings.

Ti-Pure™ R-900 is used primarily for interior coating applications. Ti-Pure™ R-900 is widely used for can coatings where its neutral undertone and high gloss are valued. Other applications include appliance coatings, metal furniture finishes and high-reflectance white coil coatings.

V. THE TI-PURE™ OFFERING

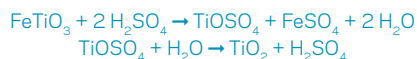
Product Manufacture

Titanium dioxide pigments are made by two commercial processes—sulfate and chloride. Both anatase and rutile can be produced by either process.

The chloride process has become the dominant process because it produces a superior pigment with significantly fewer waste products. Chemours operates only chloride process plants.

The flow charts in Figure 19 illustrate, in simplified form, the two processing routes to intermediate TiO₂ products. The lower part of Figure 19 illustrates finishing operations, which are the same for either manufacturing method.

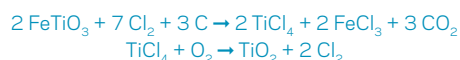
The sulfate method was commercialized in 1931, producing anatase TiO₂ and later (1941) rutile TiO₂. In this process, ore containing titanium is dissolved in sulfuric acid, yielding a solution of titanium, iron and other metal sulfates. Then, through a series of steps including chemical reduction, purification, precipitation, washing and calcination, pigmentary-size intermediate TiO₂ is produced. The crystal structure, anatase or rutile, is controlled by nucleation and calcination.



The chloride method was commercialized by DuPont in the 1950s to produce rutile TiO₂ and is now owned by the Chemours Company. This process includes high-temperature, anhydrous vapor phase reactions. Titanium ore is reacted with chlorine gas under reducing conditions to obtain titanium tetrachloride (TiCl₄) and metallic chloride impurities, which are subsequently removed.

Highly purified TiCl₄ is then oxidized at 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.



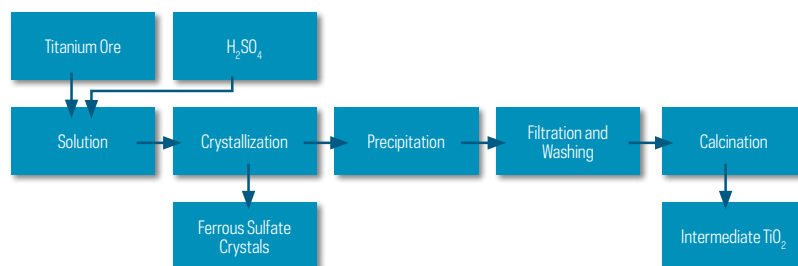
The worldwide capacity to produce pigment by the chloride process is now greater than the sulfate capacity and continues to grow. In both sulfate and chloride processes, intermediate products are clusters of TiO₂ crystals of pigmentary size which must be separated (ground) for optimum optical performance.



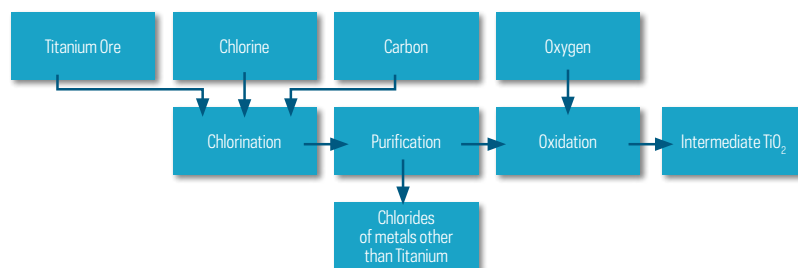
Figure 19

TiO₂ Manufacturing Processes

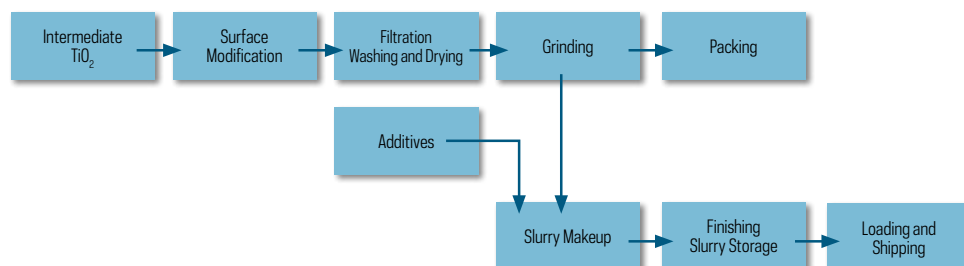
SULFATE



CHLORIDE



FINISHING



V. THE TI-PURE™ OFFERING

Depending on end-use requirements, various wet processing methods are used to modify the TiO_2 , including precipitation of hydrous oxides such as silica and alumina on the pigment particle surface. Individual hydrous oxide treatments or various combinations can be used to optimize performance for specific applications.

Crucial to the manufacture of titanium dioxide pigments is the supply of titanium ore. Although titanium ranks among the top ten elements in abundance, it is widely distributed in nature at low concentration. Efficient mining and mineral processing operations are required to develop a viable ore supply meeting the economic requirements for TiO_2 manufacture. Chemours has extensive operations worldwide to ensure a continuing supply of economic titanium-bearing concentrate to our several manufacturing sites.

Chemours titanium dioxide manufacturing facilities are located around the world to best meet your supply needs (Figure 20).

Quality Assurance in Product Design

In order to ensure that new products are designed to meet the changing needs of our customers, Chemours employs a product development methodology called Product And Cycle-Time Excellence (PACE). This multiphased process prescribes the key to a successful product development effort from concept through commercial reality. By recognizing customer needs and focusing resources to meet those needs, quality is designed into Ti-Pure™ pigments.

Table 5

Important laboratory tests are:

- Particle size distribution using a laser-light-scattering technique.
- X-ray fluorescence analysis for precise process control of surface treatments.
- Dispersion as measured by Hegman fineness of an alkyd mill base or by screening technique for aqueous dispersion.
- Dry color of a compressed TiO_2 pigment in CIE $L^*a^*b^*$ color space.
- pH and resistance of 20% aqueous dispersions.
- Carbon black undertone, blue/red reflectance ratio of a mulled mixture of 20 parts TiO_2 to 1 part carbon black in silicone oil.
- Oil absorption, a spatula rubout linseed oil test similar to ASTM D281-31.

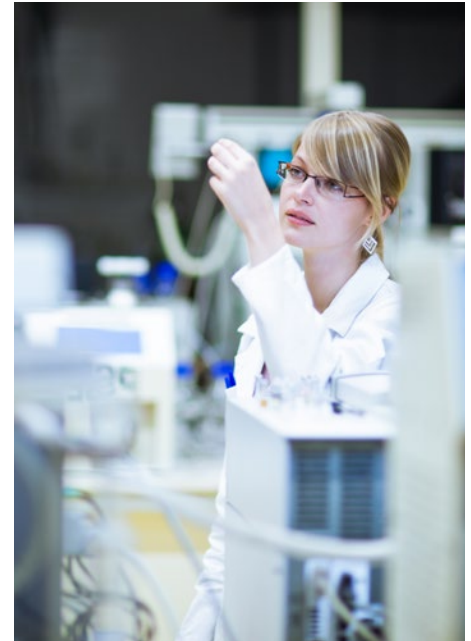


Table 6

Checklist: Bag TiO_2 versus Slurry — Potential Savings

Bag handling cost

- ☐ Unload and transfer to storage
- ☐ Deliver to process area
- ☐ Charge process
- ☐ Remove bags and pallets

TiO_2 losses

- ☐ Warehouse—broken bags
- ☐ Process spillage and dust
- ☐ Left in bag— $\frac{1}{4}$ to $\frac{1}{2}$ lb/bag

Waste disposal cost

- ☐ Bags
- ☐ Pallets

Storage cost

- ☐ Bag TiO_2
- ☐ Slurry TiO_2

Quality control

- ☐ TiO_2 errors eliminated
- ☐ Uniform batch-to-batch dispersion
- ☐ Uniform quality

Inventory control

- ☐ Eliminate counting errors
- ☐ Running total—lbs in versus lbs out
- ☐ Batch totals—cumulative

Process utilization

- ☐ Faster TiO_2 charge time
- ☐ Optimize batch size—eliminate 50 lb increments
- ☐ Increase throughput—no dispersion required

Safety and housekeeping

- ☐ Cleaner work area—no dust and spillage
- ☐ Eliminate exposure to forklift/hand truck hazards

V. THE TI-PURE™ OFFERING

Quality Assurance in Product Manufacture

Chemours has long recognized that manufacturing process control has a direct bearing on the product's fitness for use. For these reasons, we employ the most sophisticated process control technology available.

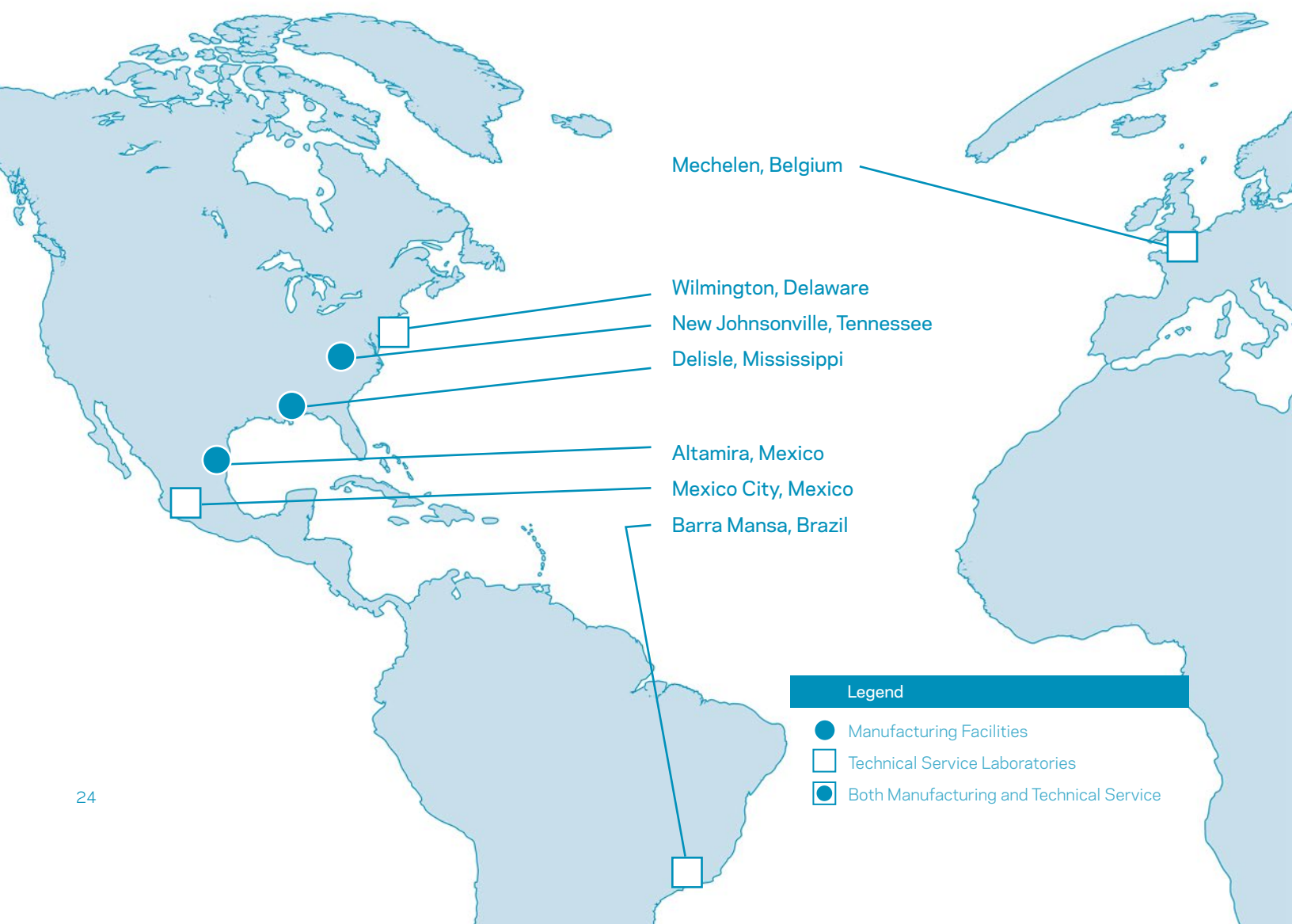
Chemours is a pioneer in the use of cumulative sum statistical process control (CUSUM). CUSUM

SPC provides fast response for more consistent on-aim operation. Chemours also uses process capability analysis (Cpk and Ppk) and Six Sigma Methodology to drive continuous improvement.

In our laboratories, we measure the Ti-Pure™ TiO₂ performance opposite our understanding of customer needs, determine if product is fit for use and control our manufacturing process

In all laboratory test operations, we employ a rigorous intra-laboratory cross-check program and statistical process control for monitoring methods to ensure the consistency of Ti-Pure™ TiO₂ performance data. Finally, all of our manufacturing sites, customer service operations and supply chain operations maintain quality systems registered to ISO 9001. In this way, the customer is assured of unmatched reliability and consistency regarding titanium dioxide supply.

Figure 20 Ti-Pure™ Facilities



V. THE TI-PURE™ OFFERING

Product Packaging and Delivery

Ti-Pure™ titanium dioxide dry pigments are available in 25-kg paper bags and 1-tonne flexible intermediate bulk containers. Ti-Pure™ bulk bags, often called semi-bulk containers, are available in one-tonne sizes. In some locations, dry bulk truckload quantities are available.

In certain regions of the world, aqueous slurries of several grades of TiO_2 are available via railcar and tank truck. Slurry handling facilities are relatively simple and are frequently justified by

system savings achieved. Additional information about TiO_2 slurries and slurry facilities can be obtained by contacting your local Ti-Pure™ sales representative.

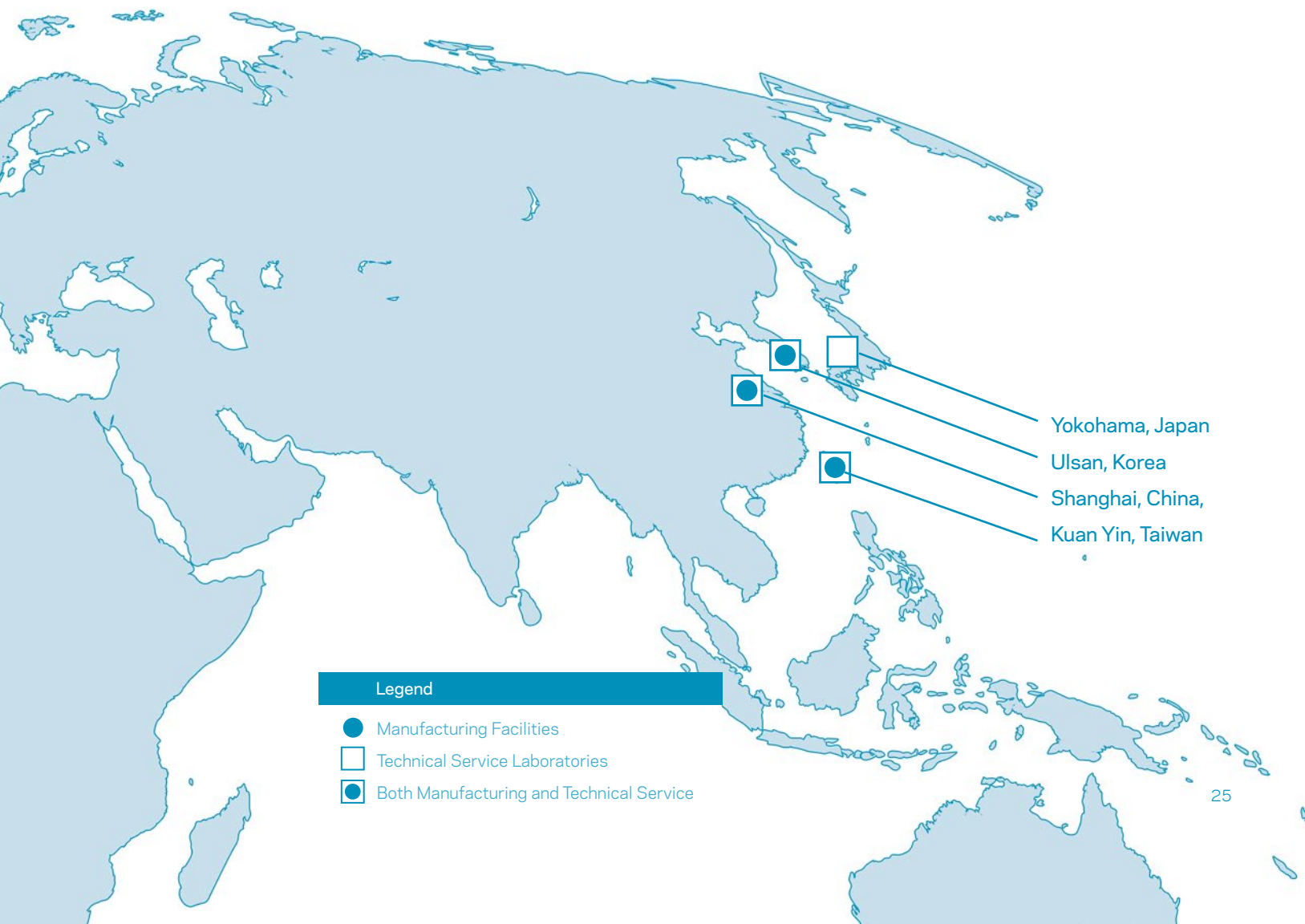
Technical Service

In addition to the products and packages we offer, our commitment to customers includes having accessible and knowledgeable sales and technical service representatives to help determine which elements of our offerings best meet your needs. To

support your individual formulation needs, our technical service laboratories are fully equipped to assist you (Figure 20).

Samples/Order Placement

Samples of dry and slurry Ti-Pure™ titanium dioxide grades are readily available from www.titnaum.chemours.com and are recommended for your use in product development and testing. To place an order, please contact your local 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.

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C-10416-1 (3/16)