Titanium dioxide (TiO$_2$) is a finely divided white powder that does not react with most chemicals. Its unique ability to efficiently scatter light compared to other commercially available pigments such as clays and calcium carbonate has made it the pigment of choice for coatings requiring opacity and high hiding power. Typical amounts added to paint or coating formulas range from 0.5 lb/gal to 2.5 lb/gal. There are many commercial TiO$_2$ grades available from different TiO$_2$ producers. These grades possess different properties which can have an impact on final paint performance and properties. This article explains why these grades are different and the impact they can have on final paint properties. It is important to understand that TiO$_2$ grades are different as a result of their design and the manufacturing process used to produce these pigments.

TITANIUM DIOXIDE MANUFACTURING PROCESS

There are two methods for commercially producing titanium dioxide pigments: the sulfate process and the chloride process (Figure 1). The sulfate process is the older of the two processes and dates back to the early 1900s.$^1$ The newer chloride process was pioneered by the DuPont Company in the early 1950s. The natural product for the sulfate process is anatase titanium dioxide, while that for the chloride process is rutile. However, by introducing rutile crystals as seeds in the sulfate process, the sulfate process is also capable of producing rutile titanium dioxide. A brief description of the two processes follows.

**Sulfate Process**

The titanium-bearing ore is reacted with sulfuric acid. After unreacted ore and insolubles are removed by clarification, the solution is concentrated by evaporation and cooled to crystallize the iron as hydrated ferrous sulfate (copperas), which is then separated from the solution and discarded. The remaining
solution is heated to hydrolyze the soluble titanium and precipitate it as amorphous hydrous titanium dioxide. If rutile titanium dioxide is the desired end product, the solution must be seeded with precisely prepared rutile crystallites before the hydrolysis step.

The hydrous titanium dioxide slurry is filtered and washed to displace the mother liquor and remove the undesirable metallic ions such as iron, chromium, etc. A large amount of waste dilute sulfuric acid is produced in this step.

The filtered-and-washed hydrous titanium dioxide is fed to a rotary kiln for calcination at temperatures around 800 to 1000°C to grow the proper size titanium dioxide crystals from very small, essentially amorphous hydrous oxide precipitate. The crystalline titanium dioxide pigment may be surface-treated (e.g., with silica and/or alumina) for desired product properties and receive further filtration and washing to remove the soluble salts generated by the surface treatment precipitation reactions. After drying and grinding, the titanium dioxide pigment is either packed out as a dry powder or re-slurried for shipment.

**Chloride Process**

In the chloride process, the titanium ore is reacted with gaseous chlorine at high temperature to produce anhydrous titanium tetrachloride and chlorides of other metallic constituents of the ore. These gaseous metallic chlorides are cooled, fractionally distilled, and chemically treated to remove impurities from the product stream of purified liquid-phase titanium tetrachloride.

The purified titanium tetrachloride is vaporized and reacted with preheated air or oxygen to form titanium dioxide crystals and chlorine. The product stream is cooled and the solid titanium dioxide particles are separated from the gaseous chlorine, which is recycled to the chlorination step.

The intermediate titanium dioxide is finished as either dry product or slurry product for shipment in a manner similar to the kiln discharge from the sulfate process.

**Impact on Pigment and Paint Properties**

When looking at the two different manufacturing processes (Figure 2), it is possible to look at in-process variables and pigment analysis and relate them to their impact on coatings properties. For color, pigments produced via the chloride process have a higher L*. This is a result of a more complete purification process that eliminates some impurities such as niobium, which gives a blue/gray color.
Since particles are grown from a seeding procedure in the sulfate process, there are many undersized or fine particles present which do not efficiently scatter light. This will lower the light-scattering ability of the pigment.

Lastly, adequate grinding can be achieved with either process. However, different manufacturers use different techniques to grind, which may have an impact on final paint dispersion quality.

**PIGMENT DESIGN**

**TiO$_2$** manufacturers have the capability of depositing metal oxides on the surface of the TiO$_2$ pigment in the finishing process to give specific functionality to the pigment. General oxides applied are hydrous oxides of aluminum, silicon, and zirconium. In addition, many pigments will have an organic treatment applied to the pigment.

The hydrous alumina is applied to the pigment in the needle-like boehmite form, which allows for the pigment to be more easily dispersed. Silica can be applied in two forms. The form of the hydrous silica as deposited is determined by careful control of pH, time, and temperature. One form is preferred for encapsulation to achieve improved durability. The other form is used to produce flat grade pigments. Flat grade pigments are designed to be used in formulations above Critical Pigment Volume Concentrations (CPVC). The coating is designed to improve spacing between TiO$_2$ particles, which improves scattering in these highly crowded systems. Some manufacturers will use a zirconia treatment. This is used to improve durability by keeping the alumina phase amorphous. Organic treatments are sometimes applied to pigments to reduce surface tension and improve flowability.
Generally, TiO\(_2\) grades can be placed into one of four categories as illustrated in Figure 3. X-ray fluorescence analysis is usually a good way to determine the intended application for the TiO\(_2\) grade.

**PIGMENT CATEGORIZATION—OPTICAL PROPERTIES**

The main attribute of titanium dioxide is its ability to provide opacity and brightness at the same time. In other words, the opacity is achieved by light scattering and not by light absorption, which would reduce brightness. However, since there are some impurities (color sites) in pigments, a pigment will have an absorption coefficient (K) as well as a scattering coefficient (S).

The K value for pigments is a function of the pigment color as measured by L\(*\) (see Figure 4). As described earlier in this article, pigment color is a function of the process from which it is made. Figure 5 shows the color performance of a large sample set of commercially available pigments. As a general rule, chloride pigments possess a higher whiteness level as measured by L\(*\) and are less yellow as measured by b\(*\). So, knowing the color of the pigment, the absorption coefficient can be calculated.

The scattering coefficient for TiO\(_2\) pigments is a function of the crystal refractive index, the purity of the pigment, and the particle morphology of the underlying TiO\(_2\). For almost all coatings applications, the rutile form of TiO\(_2\) is used. Therefore, the crystal refractive index is the same. The purity of the TiO\(_2\) is the actual TiO\(_2\) content of the pigment which varies because of surface oxide dilution. The underlying particle morphology is determined by the particle size distribution of the pigment.

**HIDING POWER AND TINT STRENGTH**

An optical density test has been developed. By measuring the transmitted light of TiO\(_2\) in a water solution at very low concentration (20 ppm), it is possible to determine the hiding power potential of a TiO\(_2\) grade.

\[
\text{Optical Density} = \text{Hiding Power} = S + K
\]

\[S = \text{Scattering Coefficient} \]

\[K = \text{Absorption Coefficient} \]

Since K has been determined by pigment color, we can calculate S with the following equation:

\[S = \text{Hiding Power} - K\]

Knowing S and K, we can now calculate another important paint property, tint strength in a colored coating:

\[\text{Tint Strength} = 100 \times \left( \frac{K/S_{\text{control}}}{K/S_{\text{sample}}} \right)\]

K/S for the control and sample can be expressed by the following equation:

\[
\frac{K}{S} = \frac{C_{\text{TiO}_2} K_{\text{TiO}_2} + C_{\text{imp}} K_{\text{imp}}}{C_{\text{TiO}_2} S_{\text{TiO}_2} + C_{\text{imp}} S_{\text{imp}}}
\]
PARTICLE SIZE DISTRIBUTION AND GLOSS

Figure 7 illustrates the impact TiO₂ particle distribution has on many paint properties. The average particle size and the distribution have an impact on paint gloss potential. A smaller average particle size will allow higher gloss, but scattering will suffer if the average is smaller than the optimum (.25 microns). A wider distribution, resulting from poor pigment morphology, poor grinding, or inadequate dispersion will decrease the gloss potential in the final paint. Figure 8 shows the relationship between gloss and particle size.

DEGREE OF DISPERSION

Pigment producers have different grinding capabilities. A simple test is to put TiO₂ in an alkyd resin under low shear conditions then run a Hegman analysis. There is now digital photographic software available that allows for more accurate analysis of the Hegman reading. Figure 9 illustrates a digital output of a coating on a Hegman scale.

Keeping tint base and concentration of the tint constant, we can now calculate the relative tint strength of different TiO₂ grades. In summary, the higher K for the sulfate grades adds to hiding power but reduces reflectance and tint strength. Figure 6 shows how this can be applied to evaluate the hiding power and tint strength potentials of various grades of TiO₂. In this example, grades sold into the multi-purpose TiO₂ market were evaluated.
When analyzing commercial available pigments (Figure 10), it is apparent that there are different capabilities among TiO₂ manufacturers regarding their ability to grind. Experience has shown that a high speed disperser can be used to make quality coatings if the scattered particle count is below 30. Above 30 scattered particles, a media mill will be required and/or there may be sheen limitations for the pigment.

**SUMMARY**

Final coatings properties are a function of fundamental pigment properties. Titanium dioxide grades are different because of product design and how they are manufactured. A basic understanding of fundamental pigment properties such as % metal oxides, optical density, pigment color, particle size distribution, and scattered particles will help coating formulators in selecting the right grade to achieve the desired final coatings properties.

**References**


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