CHAPTER 12.37

Titanium Dioxide Pigment

Thomas P. Battle

The dominant color used in coatings around the world is white. Titanium dioxide white pigment alone was 69% of all inorganic pigment tonnage in 2000 (Buxbaum and Pfaff 2005). This is not only because of the many objects that actually need to be painted white, but part of the value of a quality white pigment is being an opacifier—coating whatever is below such that it can no longer be seen. In fact, the major cost differential in paints that are advertised as needing only one coat is because of the amount and quality of the white pigment used to increase the opacity. Specific advantages of titanium dioxide (TiO_2) pigment are (Elsner 2010)

- High refractive index of 2.55 or 2.70, for high opacity (covering power);
- Good reflectivity, resulting in luminosity and whiteness;
- Inertness and chemical stability (insoluble in acids, bases, organic solvents, and air pollutants);
- High resistance to ultraviolet (UV) light degradation (color retention);
- Nontoxicity; and
- High thermal stability.

It is the "strongest, most brilliant white available to artists in the entire history of art. Its chemical stability is likewise outstanding" (Douma 2008).

White pigments have been used for centuries, but use of TiO_2 in this context is comparatively recent. The white characteristics of TiO_2 were discovered as early as 1821, but it was another 100 years before an economically viable technology was developed to convert a low-grade ilmenite ore to a quality pigment that could compete with white lead, zinc white, and lithopone, a compound of zinc sulfide and barium sulfate (Douma 2008). Lithopone had been developed for use in pigmentary applications in the 1870s and had grown to a total production of more than 180,000 t/yr (metric tons per year) in the United States in 1928 (Hounshell and Smith 1988). By that time, however, at least two companies had developed the technology to make quality TiO_2 pigment. A U.S. company subsequently bought the rights to the sulfate process developed in Norway (Korneliussen et al. 2000) and commercialized it in 1920 under the ownership of the National Lead Corporation (Hounshell and Smith 1988; BNP Media 2004).

The development of cost-effective TiO_2 pigments was monitored by the major U.S. producer of lithopone, DuPont, but no concern was expressed until familiarity with the sulfate process allowed National Lead to significantly lower the cost of TiO_2 in 1929. When DuPont realized that the lithopone market might be overtaken by TiO_2 (lithopone sales dropped 20% in 1930), it began a frantic program to develop its own version of the technology (Hounshell and Smith 1988). DuPont soon realized that this was unlikely in the time frame of concern, and it eventually purchased Commercial Pigments Corporation, which owned some patents in the field, and signed a patent- and process-sharing agreement with National Lead. As the market grew, the first DuPont sulfate plant, Edge Moor, was built in Delaware (United States).

The market for pigment continued to grow, and DuPont continued to look for ways to differentiate its technology from the competition. First, DuPont discovered the added 20% hiding power of rutile TiO_2 pigment (compared to the standard anatase) and a cost-effective way to make rutile pigment from the sulfate process, which makes anatase by default. Then DuPont started developing an entirely new production technology, using chlorine gas instead of sulfuric acid liquid as the main reactant. The chloride process was commercialized in the early 1950s, again at Edge Moor. This technology has subsequently spread over the world.

Figure 1 shows the evolution in production of TiO_2 worldwide, by technology, over the past 45 years. Sulfate technology dominated until about 1990, when chloride took the lead, which it held until about 2010, when the large number of new plants in China (virtually all sulfate) led to sulfate pigment taking the lead again (Iluka 2014).

Using the new chloride technology, DuPont was able to regain its share of the U.S. market, but it took close to 50 years to get back to the level of dominance (37%) it had held in the lithopone market. (In 2015, DuPont spun off its performance chemicals division and the new company was rebranded as Chemours [Sanati 2016]; for simplicity, the DuPont name will

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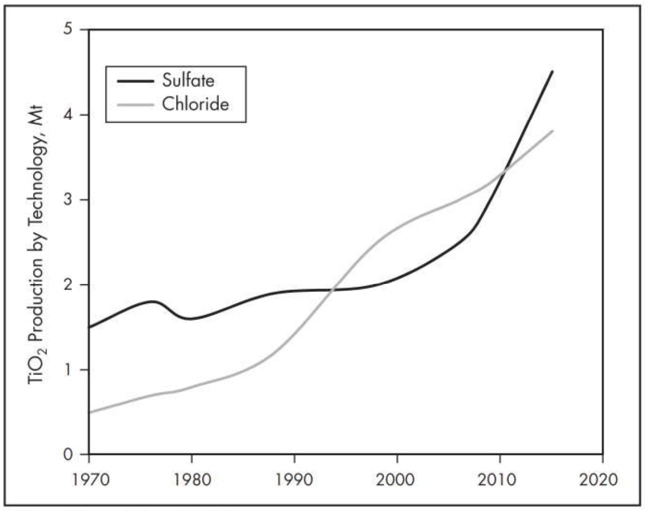


Adapted from Adams 2015

Figure 1 Titanium dioxide production by technology

continue to be used for the rest of this chapter.) DuPont is still the largest individual producer of TiO_2, although the cumulative production in China now exceeds DuPont's production, as shown in Table 1 (Iluka 2014) and Figure 2 (USGS 1996–2017). The dominance of production in the United States over this period is overshadowed by the immense growth in China. Only minor changes in production occurred in the other four major TiO_2-producing countries: Germany, Japan, United Kingdom, and Australia.

Whereas the sulfate process operates by liquid–solid interactions of titanium ores with various sulfuric acid or aqueous solutions, the chloride process operates by gas–solid interactions of the titanium ores with chlorine. The two processes differ in the method of separation of titanium from impurities. In the chloride process, gaseous metallic species are separated because of their differing melting and boiling points; in sulfate liquid-phase processing, separation occurs through the differing solubilities of metal sulfate species with temperature and pH.

In the following sections, after a brief consideration of feedstocks, the sulfate and chloride routes to make TiO_2 are discussed. This is followed by a brief consideration of TiO_2 pigment properties, applications, and future prospects.

FEEDSTOCKS

Titanium ores and mineralogy are discussed in detail in Chapter 12.38, "Titanium Ores." Because the most common titanium-rich ore is ilmenite (nominally 50% TiO_2), rather than rutile (90%–97% TiO_2), an entire industry has developed to upgrade ilmenite to a higher-grade product, either titanium slag or synthetic rutile. Because the sulfate and chloride processes have different requirements for their feeds, a differentiation has been made between *sulfatable* and *chlorinatable* ilmenites and similarly with titanium slag. The feeds available to a pigment producer are thus wide and varied. In 2006, of the three feedstock classes (rutiles, slags, and ilmenite), the largest fraction was the titanium slags (990,000 t chloride slag; 780,000 t sulfate; 170,000 t upgraded slag), followed almost equally by the ilmenites and natural and synthetic rutile.

Although, theoretically, a given pigment plant can use many of the options shown in Table 6 of Chapter 12.38, "Titanium Ores," in widely varying fractions, this is not really true in practice (McCoy et al. 2011):

Table 1 Major producers of TiO_2 pigment, 2011

Company	Percentage of 5.6 Mt
DuPont	19
Cristal	13
Huntsman	9
Kronos	9
Tronox	6
Sachtleben (has since been purchased by Huntsman)	4
Ishihara	3
Other	37

Adapted from Iluka 2014

> Significantly changing a feedstock, or blend of feedstocks, is not a short-term option for most pigment producers. Once a pigment plant has been optimised for a known feedstock blend, slight variations can have a dramatic effect on the plant performance and final pigment quality.

More importantly, most of the DuPont TiO_2 plants were built to accommodate use of at least some fraction of ilmenite ores, rather than the high-grade ores of its competitors. Because much of the upstream equipment in a pigment plant must be sized to handle the impurities in the ore, not just the titanium fraction, the DuPont plants are much larger in those areas than competitors' plants; and even if the competitors wanted to switch to lower-grade feedstocks, their overall production rate would suffer (Minkler and Baroch 1981; Charlier et al. 2010).

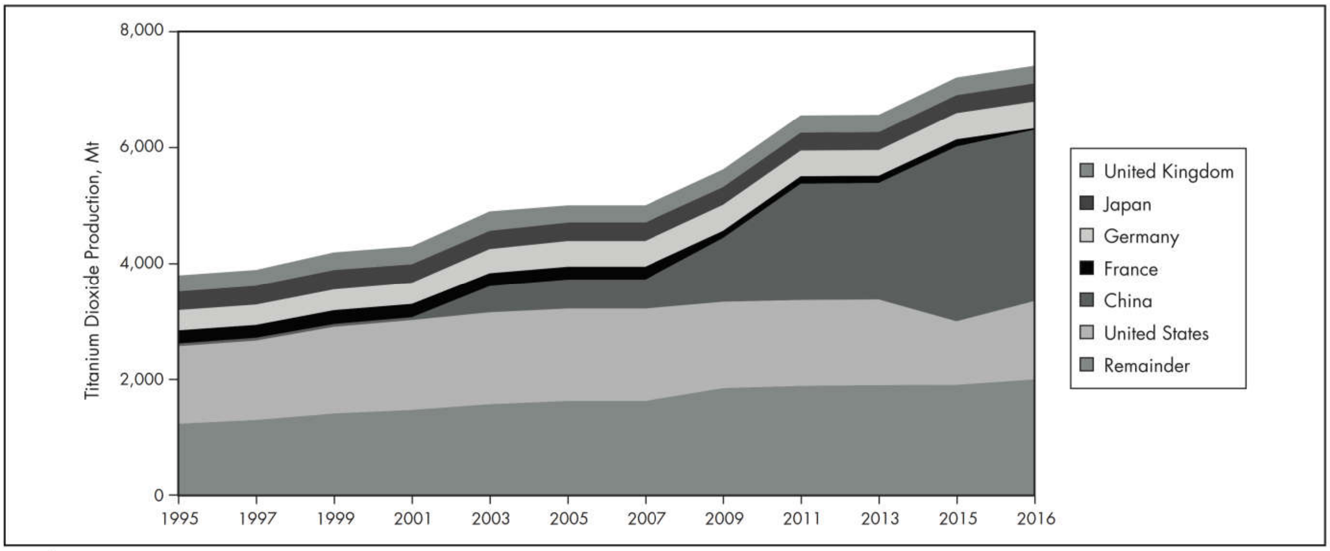
That said, as in other industries, having flexibility in feedstock capabilities is a desirable attribute. The company or plant with this flexibility can change ore blends or particular ores over a wide range, which can allow them to take advantage of short-term opportunities, increase or decrease production rates while still utilizing plant facilities efficiently, and so on (McCoy et al. 2011; Iluka 2014). Many TiO_2 producers have some level of vertical integration, including Cristal, Tronox, DuPont, Pangang, and some other Chinese producers.

SULFATE PROCESS

In the sulfate process, the titanium ore is reacted with concentrated sulfuric acid to form a solution rich in metal sulfates. The main reaction (as defined for a pure ilmenite feed) is given by Equation 1 (Elsner 2010; Buxbaum and Pfaff 2005); a process flow sheet can be seen in Figure 3 (McNulty 2008). This reaction generally takes place in batch mode in a digester that is fed ore sized finer than 40 μm and sulfuric acid of a strength between 80% and 95%. During the course of the reaction, the liquor heats up to 200°C or more during the 1- to 12-hour reaction time (Buxbaum and Pfaff 2005).

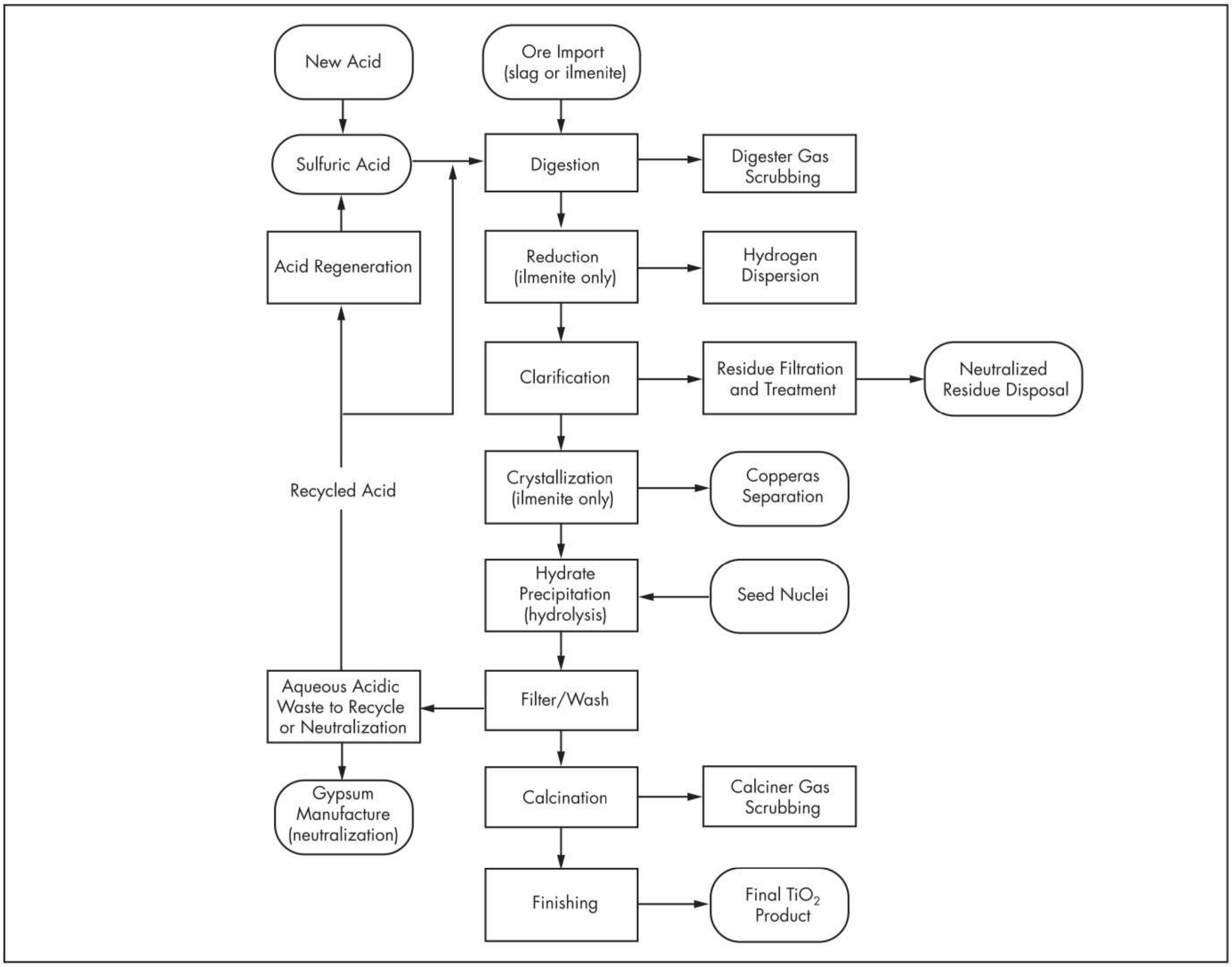
$$FeTiO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O \qquad \textbf{(EQ 1)}$$

The cake produced in the digester is often redigested in water or recycled weak acid; if any ferric ion is present, it is converted to ferrous, using scrap iron, as ferric sulfate species are very difficult to remove from the titanium product (Buxbaum and Pfaff 2005). With digestion complete, unreacted solids are



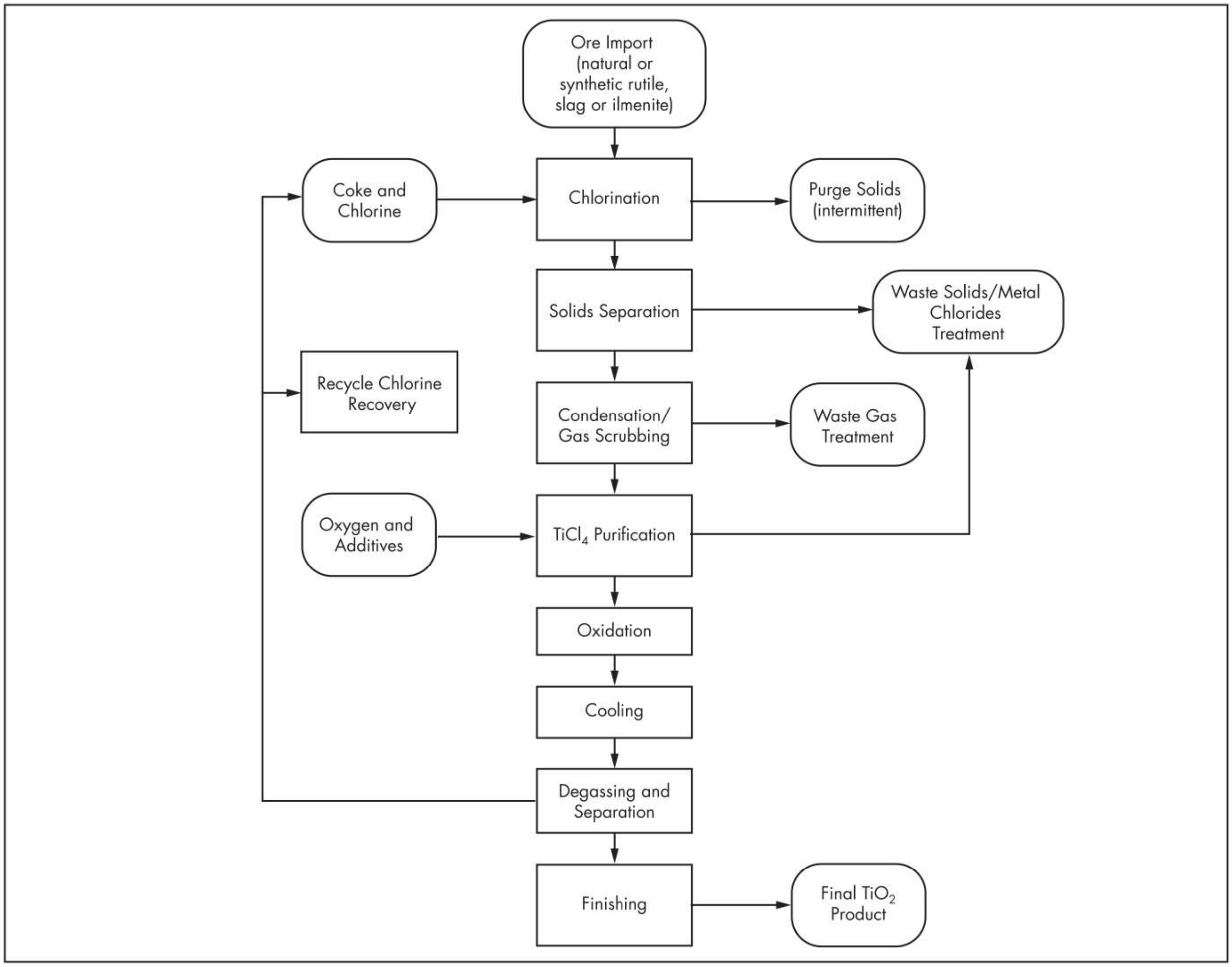
Data from USGS 1996–2017

Figure 2 Major producers of titanium dioxide pigment, by country



Source: McNulty 2008

Figure 3 Titanium dioxide (TiO_2) sulfate process



Source: McNulty 2008

Figure 4 Titanium dioxide chloride process

removed using a clarifier and a filter press. After this, the temperature in the bath is lowered to crystallize much of the iron as copperas, $FeSO_4{\cdot}7H_2O$. Steam is then added to bring the titanium out of solution as an oxyhydroxide (Equation 2). This titanium intermediate is often doped with additives (depending on the exact pigment grade to be produced) and then calcined in a rotary kiln at 800°–1,100°C for 7–20 hours. The final product is ground and coated as necessary.

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \qquad \textbf{(EQ 2)}$$

Depending on the titanium source used, sulfuric acid consumption in the sulfate process is 2.4–3.5 t of concentrated acid per metric ton of TiO_2 produced (Buxbaum and Pfaff 2005). In the early days of the technology, this was virtually all lost, as copperas was landfilled and the weak acid product (with impurity salts) was dumped into rivers or the ocean (Elsner 2010; Buxbaum and Pfaff 2005; Battle et al. 1993). Since then, regulations have been tightened, and producers have altered their processes to convert former waste products to coproducts or stable wastes that can be landfilled or disposed of as liquids. In some cases, copperas and ferrous sulfate monohydrate products are produced, with much of the recovered sulfuric acid strong enough to be used as recycle in the process. The remaining weak acid is neutralized with lime or limestone to make a mixture of calcium sulfate, iron, and calcium oxides known as *red gypsum* (Gázquez et al. 2014). Titanium recovery from feed to product is typically 80% (Henry et al. 1987).

CHLORIDE PROCESS

A typical flow sheet for the chloride process can be seen in Figure 4. The core reactor is a fluidized bed. Fine titanium ore and coke are injected into the middle of a large refractory-lined vessel that operates near 1,000°C. These particles are fluidized by chlorine in the presence of coke (major reactions given as Equations 3 through 5) and immediately begin reacting. Most of the species in the ore will form gaseous metal chlorides at these temperatures, predominantly titanium tetrachloride ($TiCl_4$), ferric chloride ($FeCl_3$), and ferrous chloride ($FeCl_2$); melting and boiling points for species of interest can

Table 2 Phase transition temperatures for relevant chlorides

Species	Melting Point, °C	Boiling Point, °C
$AlCl_3$	193	180
$AsCl_3$	–16	130
$CaCl_2$	775	1,935
HCl	–114	–85
$FeCl_2$	677	1,023
$FeCl_3$	308	316
$MgCl_2$	714	1,412
$MnCl_2$	650	1,190
$NbCl_5$	206	247
PCl_5	167	160
$POCl_3$	1	106
$SbCl_5$	3	92
$SiCl_4$	–70	58
$SnCl_4$	–33	114
$ThCl_4$	770	921
$TiCl_4$	–24	136
VCl_4	–28	149
$VOCl_3$	–79	127
$VOCl_2$	380	Unknown
$ZrCl_4$	437	331

Source: Grant et al. 2004; Helberg 2011; Lynch 2002

be seen in Table 2. These gaseous species (along with some fines carryover) exit the top of the chlorinator into a long piping system. Left behind in the bed are less-reactive species, typically some Si-containing compounds, as well as Zr, U, and Th (Gázquez et al. 2014; McCoy et al. 2011). Because liquids can cause loss of fluidization in this type of reactor, it is clear why operators prefer low levels of species such as Mn, Mg, and Ca in their ore feeds.

$$2TiO_2 + 3C + 4Cl_2 \rightarrow 2TiCl_4 + 2CO + CO_2 \quad \textbf{(EQ 3)}$$

$$FeO + C + Cl_2 \rightarrow FeCl_2 + CO \quad \textbf{(EQ 4)}$$

$$2FeO + 2C + 3Cl_2 \rightarrow 2FeCl_3 + 2CO \quad \textbf{(EQ 5)}$$

Cooling operations begin just downstream of the chlorinator, where recycled liquid $TiCl_4$ begins to cool the hot off-gases toward the $TiCl_4$ condensation temperature, 136°C. Along the way are one or more separation points for blowover solids from the chlorinator and condensed metal chlorides. By the time it is cool enough for $TiCl_4$ to condense, there is little else in the gas but noncondensable species such as HCl, Cl_2, CO_2, N_2, and COS. However, the condensed $TiCl_4$ product contains enough impurity chlorides that it is known as *crude* $TiCl_4$. Crude $TiCl_4$ must be purified to remove species such as arsenic, phosphorus, and tin, but mainly vanadium (V), which would lead to discolored pigment if not reduced to low limits (Lynch 2002). These impurities are removed by the addition of species that preferentially react with them, such as copper, hydrogen sulfide, or fatty acids (Helberg 2011), preferably without removing titanium from the liquid as well. The result is *pure* $TiCl_4$ (Henry et al. 1987). Crude $TiCl_4$ can contain up to 2,000 ppm V (Lynch 2002), with the product often below 5 ppm (Buxbaum and Pfaff 2005). Approximately 1% of the $TiCl_4$ is lost with the vanadium in the fatty acid stream (Lynch 2002).

Pure $TiCl_4$ is reacted with pure oxygen at high temperature to create fine TiO_2, with Cl_2 recycled back to the chlorinator (Equation 6). Different pigment grades can be made by controlling how the oxidation occurs.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \quad \textbf{(EQ 6)}$$

The waste produced in the chloride process is less than that of the sulfate process; how much less depends on the ore used. Chlorine consumption per metric ton of product ranges from 0.1 t for some high-grade ores to 0.9 t for ilmenite; impurity production is 0.7 t (mainly iron chlorides) for high-grade ores. TiO_2 recovery is typically around 89% (Henry et al. 1987). Purification yields 0.4–0.9 t of by-products.

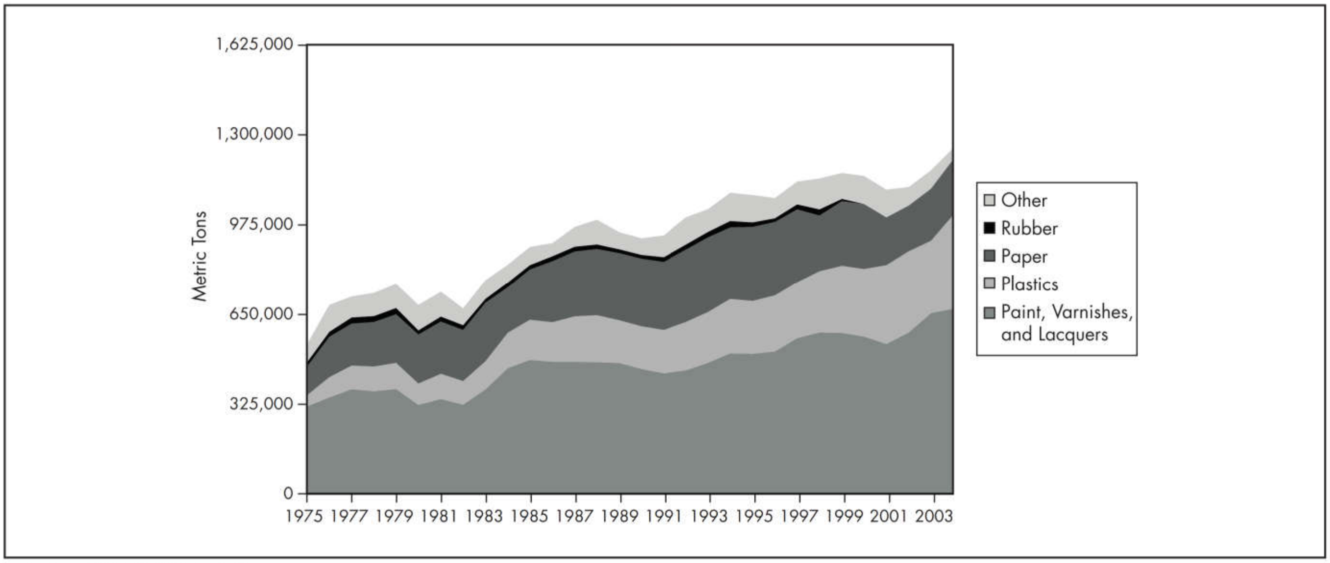
FINISHING STEPS

Equation 6 defines the main reaction in the oxidation of titanium tetrachloride, converting it to titanium dioxide and chlorine, which can be recycled. However, pure TiO_2 is not used in most applications, and the particle size of the product is critical. Alterations to pure TiO_2 take place during the oxidation (chloride process) and calcination (sulfate process) steps to prepare the product for the last production stage, often called *finishing*. Conditions are adjusted before finishing to make sure the desired phase structure is present (e.g., aluminum chloride can be added during oxidation to ensure formation of rutile, not anatase, in the chloride process; calcining temperature does the same for sulfate product [Tian 2016]). Finishing operations ensure the development of the desired particle size distribution, which may include fine grinding (micronizing). Additives to coat the surface of the pigment particles can also be included to impart desired physical properties. When processing is complete, TiO_2 is often shipped in bulk bags, typically containing 1 or 2 t. A common product, particularly in the paper industry, is a slurry containing up to 75% TiO_2, which is stabilized to minimize settling, even over significant periods of time (Elsner 2010).

APPLICATIONS

As mentioned earlier, properties of treated TiO_2 pigments include a high refractive index, good thermal stability, resistance to chemical attack, and resistance to degradation by UV light (Gázquez et al. 2014; Elsner 2010). These properties allow for its use in a myriad of applications (as discussed in detail by Iluka 2014; Gázquez et al. 2014). The major application has always been coatings, followed by plastics and paper; sales in these areas trend with a country's gross domestic product. Major uses of titanium dioxide in the United States over time can be seen in Figure 5 (USGS 1975–2006). Minor applications include inks, enamel, and rubber, with lesser applications including "catalysts, ceramics, coated fabrics and textiles, floor coverings, printing ink, and roofing granules" (USGS 1975–2006).

> Approximately 80% of end applications can use either chloride or sulphate pigment. Some of the applications that need chloride pigment specifically are specialty heat treated coatings, including automotive paint and some industrial coatings, while fibres and cosmetic applications need sulphate pigment. (Iluka 2014)



Data from USGS 1975–2006

Figure 5 Major uses of titanium dioxide pigment in the United States, 1975–2005

FUTURE

Work continues on the processing of titanium ores to make high-quality pigment process feeds and for the pigment processes to handle a wider variety of ores, yet still produce quality product with reduced waste streams (Battle et al. 1993). Relatively little research has been conducted on new TiO_2 production technologies. But every few years, a new technology is unveiled, most recently by Argex Titanium (n.d.).

The biggest changes in the industry pertain to the location of pigment plants and the potential markets for it. Figure 2 clearly shows that the center of pigment production has shifted from North America to China, whose pigment quality has been increasing such that many grades are considered roughly equal to the traditional suppliers (Barlow 2015), and new pigment grades continue to be developed (Cappelle and de Backer 2015).

Perhaps the biggest potential change in the industry is the addition of new major applications for TiO_2. This includes possible use in solar cells, water treatment, cancer treatments, cement with self-cleaning properties, catalysis, and air purification (Gázquez et al. 2014). Along with increasing needs in developing nations for paint, plastics, and paper that require white pigment for their functionality, the TiO_2 market is expected to continue expanding.

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