TiO2 Introduction

Titanium dioxide (TiO2) was discovered in 1791 by the clergyman and mineralogist William Gregor who produced a white metal oxide by calcining black magnetic sands from Menachan in Cornwall (England). TiO2 naturally occurs mainly as anatase and rutile phases, and rarely as brookite. Usually, natural rutile crystals are impure and, therefore, the first research was limited to ceramic samples, but later (around the year 1950), a single colorless, large synthetic rutile crystal was obtained with the Boule technique. TiO2 is a nontoxic, biocompatible, and inexpensive material with very high dielectric constant and chemical stability. It is a semiconductor with a bandgap ranging from 3.0 to 3.2 eV corresponding to a light absorption edge of c. 387 nm. Depending on its chemical composition, this oxide could present various values of electrical conductivity mainly due to the presence of oxygen defects, while the contribution of intrinsic free carriers is negligible even at high temperatures. As a UV light absorber, TiO2 is a white pigment widely used in paints since the 1920s, when it replaced the most important white pigment known until then, namely lead white. Moreover, the high stability to corrosion, the low-cost production, and the nontoxicity makes it a good candidate as food additive. Due to its electronic properties, TiO2 has been largely studied and employed as photocatalyst for environmental and green-synthesis purposes. In this contest, it can be used as an additive in building surfaces because of its air detoxification and self-cleaning features. In the form of nanoparticles, TiO2 has unique electronic properties and is a good candidate for use in dye-sensitized solar cells, a photovoltaic technology that converts sunlight into electricity. In addition, by taking into account all of the abovementioned properties and outstanding mechanical and rheological behavior, TiO2 is up today one of the most important components of cosmetic products such as UV sunscreen. A large number of efforts have been made to synthesize TiO2 materials with different methods to tune its physicochemical properties and to extend its use. In this chapter, we summarize the most important properties of TiO2 underlying the wide range of applications of this material.

TiO2 as white pigment and valorization of the waste coming from its production

In 1791 William Gregor (1761-1817), a British clergyman and mineralogist, discovered titanium while studying the black magnetic sands from Menachan in Cornwall (England). Shortly after, in 1795, German chemist Martin Heinrich Klaproth (1743-1814) managed to isolate TiO2 from the mineral rutile, which he called titanium, after Τιταν ("Titan" in Greek). This name was explained by Klaproth as follows: "Whenever no mane can be found for a new fossil which indicates its peculiar and characteristic properties (in which situation I find myself at present), I think it best to choose such a denomination as means nothing of itself, and thus can give no rise to any erroneous ideas. In consequence of this, as I did in the case of Uranium, I shall borrow the name for this metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this new metallic genus TITANIUM; of which this titanium, is, indeed the first, but perhaps not the only species as is made probable by the following essay" (from Analytical Essays Towards Promoting the Chemical Knowledge of Mineral Substances). Thirty years later, in 1825, Jo¨ns Jacob Berzelius (1779-1848), considered one of the founders of modern chemistry, was the first person to isolate titanium. In addition, the first pigments (in the anatase form) were produced by mixing ilmenite (FeTiO3) with sulfuric acid, carrying out a hydrolysis process by adding calcium or barium sulfate. Thus, in 1916, the Titanium Pigment Corporation of Niagara Falls, New York, and the Titan Co. AS, Norway, simultaneously began the commercial production of titanium dioxide pigments. Later, in the 1940s, titanium pigments (in the rutile form) were obtained by using sulfuric acid. Then, in the 1950s, following the chloride route (developed by DuPont), this pigment was manufactured also in the rutile form, beginning the widespread use of the pigment. Finally, the manufacture of Ti metal also started in the 1950 decade, mainly due to the considerable advance of the aircraft industry.

Titanium minerals

Titanium, symbol Ti and atomic number 22, is one of the transition metals in Group IVB of the periodic table, with relative atomic mass 47.867. Its main valence state is 41 , although can be 31 and 21 , which are less stable. Titanium is the ninth most abundant element in the Earth's crust (with 0.64 w/w%) and the fourth most widely used metal after aluminum, iron, and magnesium, with an abundance of around 5 times smaller than iron and 100 times greater than copper. Titanium is not free in nature and must be extracted by several processes. The titanium ores that are mined are ilmenite [mixed oxide of titanium and iron ($FeTiO_3$ or FeO TiO_2)], rutile, anatase, and brookite, which have the same formula (titanium dioxide TiO_2) and different crystalline structures. Other less common titanium oxide-bearing minerals are pseudobrookite (Fe_2TiO_5), perovskite ($CaTiO_3$), geikielite [(Mg, Fe)TiO_3], pyrophanite ($MnTiO_3$), sphene or titanite ($CaTiSiO_5$), and leucoxene (Fe_2O_3 TiO_2) . The properties of these titanium minerals are listed in Table 9.1. Leucoxene is not a true mineral, but a finely crystalline aggregate of rutile, anatase, or brookite with a percentage of TiO_2 above 70%, which is the result of the weathering of ilmenite .

The most economically important titanium oxide is ilmenite, usually associated with magnetite, and is found in rocks and certain beach sands. In some cases, the quality of ilmenite can decrease due to the substitution of titanium with aluminum, calcium, chromium, copper, magnesium, manganese, silicon, vanadium, and zinc in the ilmenite crystal structure . Rutile is usually associated with sedimentary, igneous, and metamorphic rocks. Other titanium minerals, such as anatase and brookite, are closely related to the deposit of rutile . While it is true that all these minerals are too widely dispersed, the main commercially important deposits are low and limited to certain locations of Canada, China, the United States, South America, Norway, and South of Australia. As we can see in Table 9.2, around 93.6% of the world's titanium resources correspond to the mineral ilmenite; the remaining percentage is mainly from rutile and, to a lesser degree, leucoxene. In addition, it is important to note that the production capacity of titanium dioxide pigments corresponds to around 1.3 Mt in both the United States and Europe, 3.2 Mt in China, and 5.7 Mt in the rest of the world.

Titanium ore purification

Ilmenite and rutile are the most important mineral sources of titanium dioxide pigments; however, it is important to note that these minerals contain other metals in addition to titanium. Depending on the deposits, titanium minerals can contain impurities that must be removed before carrying out the industrial process to obtain titanium dioxide pigment. Nowadays, TiO_2 pigment producers are requested to use titanium feedstock ores with higher TiO_2 levels, with the aim of minimizing waste disposal costs and maximizing the capacity of pigment-processing equipment. When titanium dioxide pigment is produced by the sulfate route, the use of ilmenite mineral as raw material is needed, since rutile cannot be dissolved using sulfuric acid, as is detailed in Section 9.2. Typically, this mineral contains 30%-70% of TiO_2, with the rest being mainly iron, which must be removed during the manufacturing process in order to guarantee the quality of the final product. Thus, large amounts of by-product iron salts are produced. Therefore, the demand for feedstock with high concentration of titanium dioxide has been met by the production of titaniferous "slags." These titaniferous slags are coproducts of smelting processes where iron is removed from the ilmenite ore. Typically, the feedstock for slag manufacture is ilmenite with a concentration of titanium dioxide below 50%, finally containing about 85% TiO_2; however, through high-pressure acid leaching, titanium slag can be enriched to about 95% TiO_2. On the other hand, high-grade TiO_2 feedstocks, that is, with high percentage of TiO_2, are necessary in chloride process plants. Thus, while ilmenite sand can be directly used in the sulfate or chloride routes for manufacturing titanium dioxide, rutile and leucoxene cannot be attacked with sulfuric acid and only can be used directly in the chloride process. Therefore, upgraded feedstocks, such as synthetic rutile (obtained by two basic processes, i.e., the Becher process and the Benilite process), synthetic rutile enhancement process (SREP) (modification of the Becher process involving the addition of a flux at the thermal treatment stage), and upgraded slag, can only be used in the chloride process . Synthetic rutile (classified in thermal reduction, selective chlorination, and selective leaching) is produced by removing iron from ilmenite, which increases the TiO_2 content to nearly 95% from about 50%. Synthetic rutile can be used as a substitute for natural rutile.

Routes for the manufacture of titanium dioxide pigments (Pigment White 6)

About 93% of the titanium extracted in the world is used in the manufacture of TiO_2 for pigment production. Currently, commercial titanium dioxide pigment can be produced by two different routes: the sulfate process (about 40% of total TiO_2 production) and the chloride process (about 60%). The anatase and rutile forms can be obtained by the sulfate route, while the chloride route can only yield the rutile form. The sulfate process employs simpler technology compared to the chloride route, and it can use lower grade, cheaper ores; however, due to the acid treatment involved, a sulfate plant is more expensive to build than a chloride plant. In addition, the general perception is that the sulfate route is less environment-friendly; however, in the last decades the recycling and valorization of the wastes produced can make it as clean as the chloride route, where the amounts of generated wastes are lower. Nevertheless, due to such belief, the chloride process has dominated the pigment industry for the last few years. The choice between the two processes is based on several factors, such as the availability of specific raw materials, waste disposal costs, and requirements of final titanium dioxide grade. For example, the chloride process is the favorite form for use in coating and plastics, the two most common end-use markets, while the pigment from the sulfate process is preferred to use in selected paper products, manmade fibers, food products, pharmaceuticals, and cosmetics. Another aspect to consider is that the sulfate process can produce a volume of waste in the range of 8-12 t per ton of pigment, whereas the chloride process generates waste products in the range of 2-5 t per ton of pigment.

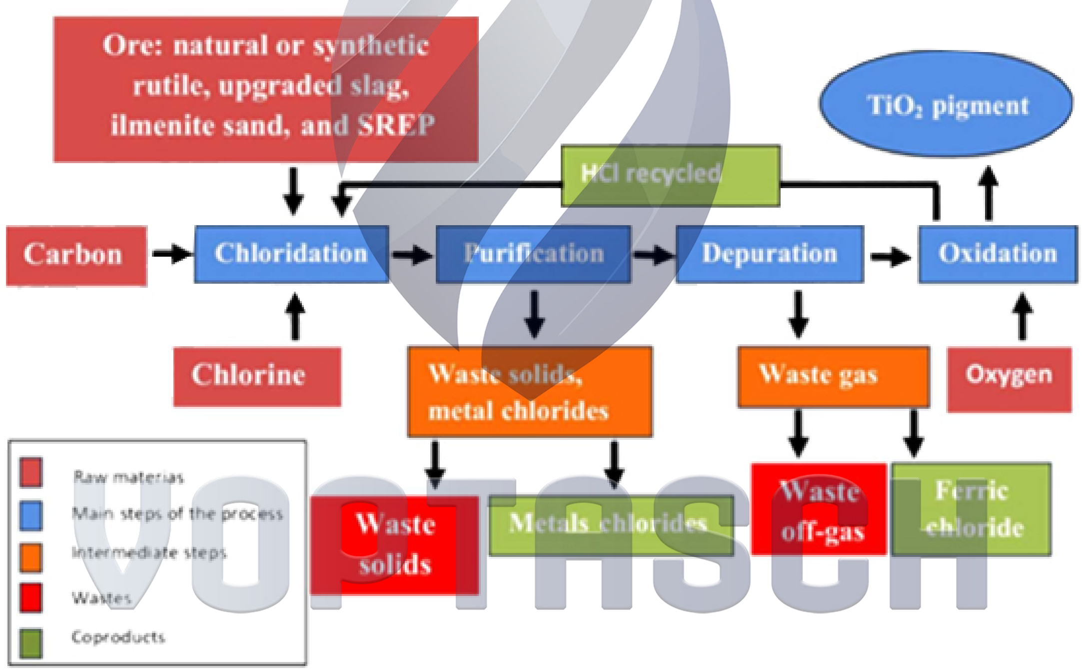
The chloride process

The development of the chloride process started in the 1940s. The first chloride plant, owned and run by DuPont, began to produce in the early 1950s, and there are currently 23 chloride process plants operating in North America, Europe, Asia, and Australia. The chloride process route accounts for 55%-60% of the 5.5 million tons/per year of pigment production worldwide, involving the use of gaseous chlorine to produce $TiCl_4$, which is then converted to titanium dioxide by oxidation. The chloride process includes a wide range of titaniferous feedstocks containing high-grade titanium dioxide, such as ilmenite sand, rutile, synthetic rutile, SREP, and upgraded slag. The selection of feedstock depends on the presence and percentage of heavy metal impurities, as they can influence the quality of the final product (e.g., whiteness and brightness). The chloride process is carried out in two main steps: first, the conversion of ore to titanium(IV) chloride and, second, the oxidation of titanium(IV) chloride. The process begins with the conversion of feedstock to titanium tetrachloride (vapor form) by chlorination in a fluidized bed reactor at 900 C-1000 C, using petroleum coke as a reducing agent. The main reactions are the following.

$$2TiO_2(s) + 3C(s) + 4Cl_2(g) \rightarrow 2TiCl_4(g) + 2CO(g) + CO_2(g)$$

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$$

In the ores, oxygen is reacted with carbon to form carbon monoxide and dioxide. The titanium chloride vapor obtained is cooled down and recollected in its liquid form, which is possible thanks to the fact that its boiling point is higher than that of other metal chlorides. Then, it is boiled again and distilled to produce a purer product. At this stage, the nonvolatile chlorides and the unreacted coke and feedstock solids are removed from the gas stream and from the bottom of the chlorinator. For example, high boiling point chlorides such as CaCl2 and MgCl2 tend to remain in the bed in their liquid form, while SiO2 and ZrO2 tend not to chlorinate and accumulate in the bed in their solid form.



(Diagram of chloride process)

Next, the liquid titanium chloride is transferred to an oxidation reactor, where it is mixed with oxygen at around 1500 C (in a plasma arc furnace or toluene-fired furnace), forming titanium dioxide and chlorine gas, as expressed by diagram. This chlorine is recycled again in the first steps of the industrial process. The residual chlorine attached to the solid TiO2 is removed by hydrolysis and, finally, the pure titanium dioxide is taken through a conditioning step, where it is subjected to chemical surface treatments, milling, and drying. Currently, about 1 t of chlorine is required to produce 5-6 t of titanium dioxide pigment (depending on the percentage of impurities in the feedstock used).

Sulfate process

The sulfate process was the first commercialized technology to obtain titanium dioxide pigment in 1916. The sulfate route represents 40%-45% of the total TiO2 production, and it involves the use of concentrated sulfuric acid. The feedstocks of this route are mainly ilmenite and titanium slag . The sulfate process can be divided into three main steps: feedstock digestion with ore dissolution, formation of hydrated titanium dioxide, and, finally, formation of anhydrous titanium dioxide. The sulfate process begins with the acid digestion step of ilmenite or titanium slag (or a carefully controlled blend) with concentrated sulfuric acid (around 95%), water (to activate the reaction), and recycled acid (around 65%)

The result of this step is a liquid effluent containing titanyl sulfate (TiOSO4) and iron sulfate (FeSO4)

$$FeTiO_3(s) + 2H_2SO_4(aq) \rightarrow TiOSO_4(aq) + 2H_2O(l) + FeSO_4(aq)$$

To ensure that all Fe is in dissolution, the liquor is passed through scrap metal to convert Fe31 to Fe21, which is called the “reduction step.” At this point, the resulting liquor is sent to a clarification tank, where the undissolved solids (mud) are separated from the solution by flocculation (decantation) and filtration. The titanium liquor is concentrated and hydrolyzed with steam in order to produce the precipitation of hydrated titanium dioxide .

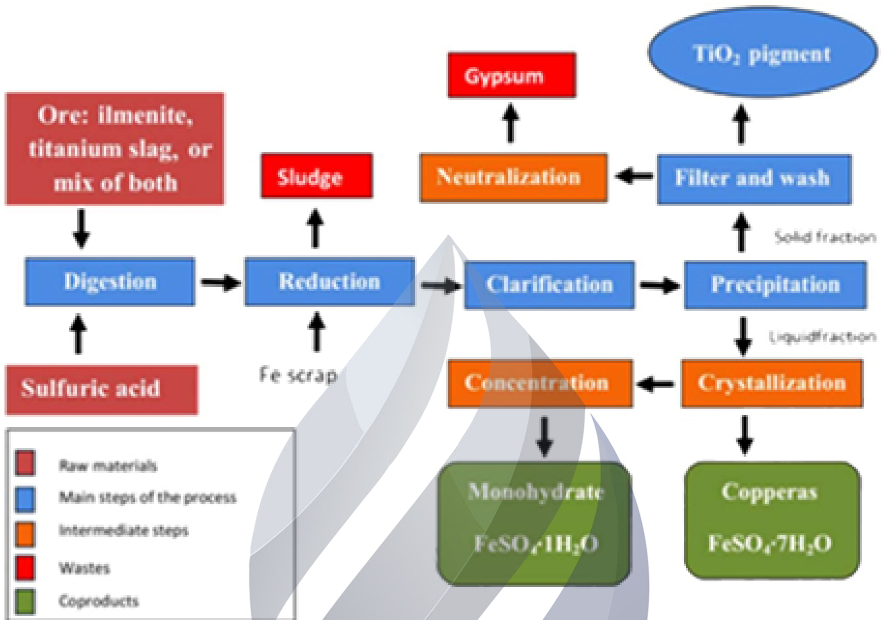
$$TiOSO_4(aq) + (n+1)H_2O(l) \rightarrow TiO_2 n \cdot H_2O(s) + H_2SO_4(aq)$$

After boiling for several hours, the liquor is cooled down to around 60 C, in order to precipitate the hydrated titanium dioxide. This step is essential for the control of the final crystal size and form (anatase or rutile) of the titanium dioxide, which is achieved through the addition of titanium-containing seed nuclei. Then, the titanium dioxide hydrate is separated from the liquor (commonly referred to as “strong” acid, 20%-25% H2SO4) through filtration using vacuum filters (known as Moore filters). The quantity of strong acid generated is more important when the iron content of the ilmenite ore is high. After filtration, the filtered TiO2 cake is washed with water to remove the remaining impurities, obtaining a solid phase containing TiO2 and a liquid phase usually called “weak acid solution.” Then, the hydrated titanium dioxide is sent to a calciner, where the titanium dioxide crystals grow to their final crystalline size, and the residual water and H2SO4 are removed.

$$TiO_2 n \cdot H_2O(s) \rightarrow TiO_2(s) + n \cdot H_2O(g)$$

The dried titanium dioxide is sent to pigment finishing, involving any required milling and or chemical treatment, such as surface coating with silica or alumina. The milling process is carried out in two different steps. In the first step the particle is reduced to 75-100 µm and, after the second step, the final size is 0.2-0.4 µm, which is the optimal size for use as pigment. In addition, the coating steps are very important, as they improve both pigment durability and dispersibility. To produce the anatase form of the titanium dioxide, a small portion of the clarified liquor is neutralized with alkali to produce anatase microcrystals. Then, these microcrystals are introduced into the mother liquor, which is then hydrolyzed under carefully controlled conditions to produce anatase crystals. To produce the rutile form of the titanium dioxide, the clarified liquor is hydrolyzed in the presence of a specially prepared rutile seeding agent obtained by neutralizing a small portion of the mother liquor in the presence of hydrochloric acid or some other monohydric acid.

Finally, both crystals formed are filtered, washed, calcined, and micronized. About 1 ton of feedstock (ilmenite or ilmenite 1 slag) is required to produce 0.5 tons of titanium dioxide pigment.



(Diagram of Sulphate process)

TiO2 applications

Titanium dioxide is the most versatile white pigment (usually called PW6 or CI 77891), as it is used in a wide range of applications, especially in paints and coatings (57%-58%), plastics and rubber (24%-25%), paper (12%), inks (6%); the remaining 3% correspond to synthetic fibers and the food, pharmaceutical, and cosmetic industries. Due to the relatively low price of the raw material and its processing, titanium dioxide has been steadily gaining importance in the manufacturing processes over recent decades. The following sections describe all of these uses.

- **Coatings, plastics, and paints**

This section describes how the use of TiO2 is essential for opaque paints, coatings, and plastics. The success of this pigment lies in its excellent light-scattering capability, making its opacity unbeatable. In addition, it is important to note that TiO2 is not only present in white paint, as it is also added to color shades. Due to its light-scattering properties, anatase (pigment with lower quality than rutile) is mainly used in the manufacture of paints and, more specifically, indoor paints, since quality is less important for this use . On the other hand, rutile is preferred to paints and plastics, especially those exposed to outdoor conditions. Rutile and anatase pigments can be made more resistant to photodegradation by coating the pigment particles with, for example, alumina, silica, zirconia, or a combination of these. Usually, rutile pigments contain 1%-15% coating and anatase pigments contain 1%-5%, with the higher levels of the coating being used for applications such as flat (low-gloss) paints. According to the American Society for Testing and Materials (ASTM)-D476-84 standard, there are four different types of titanium dioxide pigment for surface coating, which are as follows:

- Type I (containing at least 94% titanium dioxide) is a titanium dioxideanatase pigment used in white interior and exterior house paints.
- Type II (containing at least 92% titanium dioxide) is a titanium dioxiderutile pigment mainly used in all types of interior paints, enamels, and lacquers.
- Type III (containing at least 80% titanium dioxide) is also a titanium dioxiderutile pigment used mostly in alkyd and emulsion flat-wall paints.
- Type IV (containing at least 80% titanium dioxide) is another titanium dioxiderutile used in exterior paints due to its excellent durability and gloss retention.

In Europe the grading system is defined by the International Standard ISO 591-1, which is different from the classification given by the ASTM standard. Depending on the type and percentage of titanium dioxide, titanium pigments are classified into the following grades: Type A (anatase grades: A1 and A2) and Type R (rutile grades: R1, R2, and R3). A1 (uncoated anatase pigment) and A2 (coated anatase pigment) contain 98% and 92% TiO_2, respectively, and R1 (uncoated), R2 (coated), and R3 (coated) contain 97%, 90%, and 80% TiO_2, respectively. In most countries of the world, either the ASTM or the ISO standard is used. A third system, that is, the Japanese grading system (JIS K5116-1973), specifies four grades of titanium dioxide rutile, three of which contain at least 92% titanium dioxide and the fourth contains a minimum of 82% . Many researchers have studied the use of titanium dioxide as coating in several applications, based on its photocatalytic properties, discovered by Fujishima in 1967. For example, Lo et al. tested its application as anode material in secondary lithium-ion batteries, Zhong et al. used coated TiO_2 in air filters to retain volatile organic compounds, and Yemmireddy and Hung used it as antimicrobial coating on stainless steel surfaces where food is processed. In addition, TiO_2-based photocatalyst shows great potential in the disinfection/inactivation of several harmful pathogens (e.g., Escherichia coli) in aqueous media . On the other hand, and taking into account its antibacterial properties, titanium dioxide is also employed as coating in the acrylic resin used as a denture base material in order to minimize the adhesion of food , bacteria, and fungi. Titanium dioxide pigment is used to increase the opacity of plastic materials. The plastic industry, which consumes around 25% of the global TiO_2 production, is the second largest user after the coating industry, which represents over 65% of the pigment used in the plastic industry. Plastic applications are divided into two groups. In the first group of applications, titanium dioxide is used in a transparent or translucent condition, whereas in the second group the opacity is fully necessary. In addition, the use of TiO_2 in plastics minimizes the fragility and surface cracking that may occur with prolonged exposure to light. It is the most important pigment used in the manufacture of outdoor polyvinyl chloride (PVC) plastic products, conferring UV protection to the material. In this case the best crystalline form is rutile, which shall be under a surface coating formed by zirconium, silica, or aluminum, in order to minimize the photocatalytic effect of TiO_2 in PVC degradation.

- **Printing inks and paper**

Titanium dioxide pigment is used in a wide variety of products, such as paper (direct addition to whiten and opacify the paper stock, and paper coatings), and as the main component of inks (letterpress, gravure, and lithographic printing). Titanium dioxide is extremely lightfast and has a high refractive index and a very high light-scattering and hiding capacity. It also has the highest opacity of all white pigments and an excellent brightening capacity. In addition, titanium dioxide is thermally stable, noncombustible, nearly insoluble in water, and resistant to weather and UV light. Therefore, in the applications related to the manufacture of printing inks and paper, it is very difficult to find an alternative product with similar properties. In the manufacture of paper and paperboard, the end properties and quality mainly depend upon the resistance of the fiber net and the extent to which it is intertwined. In addition, the spaces between the fibers of cellulose must be filled with nonfibrous materials (inorganic additives), usually called pigments. One of the most widely used inorganic additives is titanium dioxide, as wet end filler, which is commonly employed to increase the opacity and the brightness of the final product. Therefore, titanium dioxide pigment is widely used in the production of several types of paper, including lamination paper (decorative use), filled paper, and coated paper, to provide whiteness, brightness, and opacity as main properties. Thus, for example, in lamination paper (used as a substitute for wood and tile in countertops, furniture, and wallboards, among others), TiO2 is used in the first layer, mixed with plastic resin, where the decorative patterns are printed. One of the main roles of pigments is to prevent the decoloration of the product after prolonged exposure to sunlight and other environmental agents. In this sense, in order to ensure that the titanium dioxide pigment sticks to the fibers, flocculating agents and retention aides are added. Moreover, up to 6 wt.% of titanium dioxides can be added without decreasing the strength of the paper . The paper sector accounts for approximately 12% of TiO2 consumption, which is around 130 kt annually, with lamination paper being especially relevant, representing around 80% of the total titanium dioxide consumption of the sector. In addition, TiO2 has been used in toners, inks, and backings for inkjet printing substrates, improving the opacity and hiding power of printing inks and allowing to achieve very high print quality, with low abrasion and high printing speed. Thus, for example, white inks for packaging can be used as surface print or last layer on flexible packaging in plastic or aluminum films, obtaining optimal opacity. On the other hand, the hiding power of titanium dioxide is also crucial for uses which require a perfect contrast, such as barcode scanning. Moreover, titanium dioxide is used in labels (self-adhesive labels, wrap-around labels, lidding, shrink sleeve, in-mold labeling, etc.), due to its high opacity, toners, where it confers free flow and charge control, writing materials (colored pencils, finger paints, school tempera paints, modeling clays, etc.), and inks for leather, where titanium dioxide pigments are used as opacifier to helping printed textiles stand out. Finally, the usual concentrations of TiO2 in inks and related products are, for example, 50%-60% in white printing inks, 5%-10% in shaded inks, 3%-35% in pencils and similar products (3%-35%, up to 50% in correction fluids, 1-5% in toners, and up to 100% in artistic and recreation colors) .

Another field in which titanium dioxide is widely used is flexible packaging, since the consistency and performance of white ink are crucial to the quality of the printed image. White ink should give enough hiding power to allow high-quality color printing, thus it is used in surface printing, reverse printing, and lamination structures. Furthermore, TiO2 pigments are suitable for use in various solvent-, water-, and oil-based inks and also in UV curable inks.

- **Pharmaceutical and cosmetic industries**

In the pharmaceutical industry, TiO2 meets all the safety requirements of medicines, including those set by the European, Japanese, and US pharmacopoeias, and its additive number (E-171) is also found in the food industry, since pharmaceutical manufacturers adhere to the same food additive standards governed by the European Food Standards Agency. In this industry, titanium dioxide pigment can be used in different ways: as a basic pigment (to increase whiteness), as coating (protection for photosensitive ingredients and also ingredients that may be vulnerable to UV light degradation), and in packaging (routinely incorporated in the packaging of medicines to extend shelf life and to prevent any premature degradation from moisture, heat, or light). For this type of application, nanometric particle size (less than 100 nm) is required. In addition, in recent years, the use of titanium dioxide in medical applications has been studied, showing an important role in the improvement of health care, especially cancer treatment, due to its excellent photocatalytic activity. In addition, it is well known that sunlight may decompose active substances and excipients in pharmaceuticals, generating numerous formulation problems for the pharmaceutical compounds. For that reason, titanium dioxide pigment is widely used in packaging to protect against light transmission. Furthermore, titanium dioxide has also been tested to evaluate the protection of photolabile substances in photodecomposition processes. Thus, for example, this property of titanium dioxide has been analyzed in a photolabile nonsteroidal anti inflammatory drug substance called ketoprofen, which is a drug for transdermal delivery used in clinical practice to relieve pain in acute and chronic conditions. This drug has been involved in adverse photosensitivity reactions due to its instability under sunlight. Therefore, titanium dioxide has been tested on the photostability of ketoprofen, demonstrating that it can photostabilize this drug. In the cosmetic sectors, TiO_2 or CI 77891 (as it is known in this market) is currently listed in Annex IV of the Cosmetics Regulation EC 1223/2009 (list of colorants allowed in cosmetic products) and Annex VI (list of UV filters allowed). Currently, only two mineral UV filters are allowed in cosmetics, that is, TiO_2 and ZnO. Therefore, the addition of titanium dioxide provides makeup with a sun protection factor, although relatively low (around 15), which can confer the sun protection upon a "side effect." Sunburn is caused by sun radiation, known as UV radiation. Although UV radiation does not exceed 5% of the total energy that comes from the sun, its impact on organic molecules is very important, as they cause both photoaging and sun damage.

This radiation is produced in three different wavelengths, called UV-A, UV-B, and UV-C, which have different wavelength ranges. UV-C is in the range of 190-290 nm, which is only transmitted in the air. On the other hand, UV-A and -B can generate different types of damage. UV-A, with longer wavelengths (320-400 nm), can cause cell damage, since it penetrates the skin, producing premature aging, skin decoloration, and wrinkles, whereas the effects of UV-B (290-320 nm) are visible on the skin surface, causing freckles, moles, sunburn, and cancer. In the cosmetic industry, sunscreens are usually classified into categories: chemical and physical (or mineral). Chemical sunscreens are composed of different chemical compounds that are combined to block the UV-A and UV-B rays, transforming UV rays into heat, which is subsequently released by the skin. On the other hand, physical sunscreens are manufactured with natural compounds, which settle on the skin, absorbing and deflecting UV radiation from the sun. The most obvious example of this natural compound is titanium dioxide pigment. For example, as a curiosity, due to the high reflection power of titanium dioxide pigment, it is recommended not to apply makeup during a photo session, since it can make it difficult to control the brightness generated by it. Thus, considering the previously described properties of titanium dioxide, it is important to note that TiO_2 is widely used as a protector that absorbs and scatters both UV-A and UV-B radiation to protect the skin. Therefore titanium dioxide nanoparticles (particle size: 1-100 nm) are currently approved to be used as a UV filter in sunscreens. Coating titanium dioxide with silicon dioxide and aluminum (3.5 wt.%) can increase the photostability of titanium dioxide, reducing its photocatalytic activity by 99%. Due to the extensive use of nanoparticles and considering their small size, the safety of titanium dioxide nanoparticles has been reevaluated in some studies where their use in cosmetic preparations or sunscreens is considered negligible . In addition, and in view of all the evidence, the Scientific Committee on Consumer Safety demonstrated that titanium dioxide nanoparticles, used at a concentration of up to 25% as a UV filter in sunscreens, can be considered nonharmful for humans after application on a healthy, intact, or sunburnt skin.

- **Textiles**

For several years, great effort has been made to immobilize TiO2 nanoparticles onto textile materials with the aim of producing smart textiles with multifunctional properties, such as UV protection, self-cleaning , enhanced durability , and antibacterial activity . The antibacterial activity of titanium dioxide nanoparticles in textiles is based on the degradation of organic materials by photocatalytic reaction. Thus, the antibacterial power of titanium dioxide nanoparticles is higher than other antimicrobial agents, such as silver, which makes it safer for the human skin.

Wool is the most important natural animal fiber used in the textile industry, mainly due to its excellent properties, which are basically determined by the configuration of the fabric. However, wool shows low photostability, high decomposition derived from insect action, and photo-yellowing, among other drawbacks. Most of these problems can be solved by coating the fiber with TiO2. Cotton is a very comfortable fabric to wear, easy to care, absorbs water and "breathes." Thus when the body perspires, cotton fibers absorb the moisture and release it to the surface of the fabric, where it evaporates. On the other hand, it also shows some negatives aspects, such as sensitivity to mildew, and prolonged exposure to sunlight can damage it, apart from the fact that it easily becomes wrinkly and spotty. Cotton fiber can be blended with synthetic fibers, with the most common being the cotton/polyester blend, which reduces the appearance of wrinkles. In addition, anti-UV finish is also demanded in the manufacture of cotton fabric. As was previously described, titanium dioxide can reflect, scatter, or absorb UV rays. Therefore TiO2 has been tested in several studies with the aim of evaluating the behavior of the anti-UV ray finish of cotton . The results obtained in treated fabric surfaces in these studies showed an exceptional anti-UV performance. Regarding synthetic fibers, there is an important parameter that provides information about the reflected light called "shine." This parameter is mainly controlled by the concentration of TiO2 used in their manufacture. Thus, a synthetic fiber is considered to be bright when the concentration of titanium dioxide is around 0.06%, semiopaque with a concentration of 0.3%, and opaque when the concentration is around 2%. Another fundamental aspect related to fiber products is the static electricity generated by friction, which can cause skin damage. This problem can be solved by adding titanium dioxide nanoparticles with a concentration of 0.1%0.5% to fiber resin; the resistance value is around 108 109 Ω cm .

- **Food industry**

Although titanium is not an essential element for humans beings, titanium dioxide is approved by the US Food and Drug Administration and FAO/WHO Codex Alimentarius as colorant E-171 in the United States and Europe , with the condition that the additive should not exceed 1 wt.% of the food and without the need to include it on the ingredient label. In the United States, it is used in the manufacture of candies, cookies, sweets, gum, yogurt, cottage cheese, milk, ice cream, etc. For example, the concentrations of up to 1% have been reported in food supplements and hard and soft panned candies, 0.02%-2% in icings, chewing gums, starch-molded confectionery and baked goods, and 0.05%-0.4% in savory snack foods. Titanium dioxide provides certain optical properties, such as brightness and whitening, improving food presentation, for example, skimmed milk and codfish. It is poorly soluble and not readily absorbed by the body, and to date, its use in the food industry has not been shown to have negative health effects.

Despite the aforementioned, in May 2016, the French authorities proposed the classification of TiO2 "as a category 1B (Carc1B) carcinogen." While it is true that the Risk Assessment Committee of the European Chemical Agency concluded that this classification has not been scientifically justified, in September 2017, it was asserted that TiO2 "meets the criteria to be classified as suspected of causing cancer, falling into carcinogen category 2," although specifically linked to the inhalation route (respirable particles). EU legislation regulating the use of and exposure to carcinogens generally does not distinguish between routes of exposure. Therefore, even though the French authorities specifically indicate that titanium dioxide can be considered carcinogenic by inhalation, it is important to note that the EU regulatory framework regulating the use of and exposure to carcinogens generally does not distinguish between routes of exposure. Thus, on April 17th 2019, the French Government announced, following the recommendation of the French Food Safety Agency and the French Agricultural Research Institute, the suspension of the commercialization of foods containing titanium dioxide pigment (E-171). This decision shall come into force between January 1, 2020 and December 2020. The French ban applies to neither nonfood products, such as medications, cosmetics, and toothpastes, nor food contact materials (National Law Review, 2019). It is important to note that, to date, the E-171 colorant is still accepted in the rest of the EU, since, in most cases, TiO2 is used by the end user within a matrix, typically as a pigment, from which exposure to TiO2 via inhalation is highly improbable. Titanium dioxide nano-size is not approved for the food industry; however, the pigments used in foods do not have any specification in terms of particle size. Some researchers have reported that around 15%-36% of titanium dioxide particles are in the nanoscale. Furthermore, in 2015, researchers from the Food and Environment Research Agency in the United Kingdom, the Food Institute at the Tu¨bitak Marmara Research Center in Turkey, and the RIKILT Institute of Food Safety in the Netherlands carried out a study on the oral consumption of nano- and larger particles of TiO2, showing no evidence of important internal exposure of the consumer to nanoparticles . In addition, titanium dioxide pigment is widely used to protect foods, drinks. and supplements from premature degradation caused by the effect of light, thus extending the shelf life of the product. Moreover, TiO2 packaging reduces E. coli contamination on food surfaces. The most important food contact coatings are the following: food packaging adhesives, paper/paperboard in contact with aqueous/fatty foods, and food contact textiles/fibers, which can contain titanium dioxide pigments. TiO2 provides numerous advantages in food contact materials, such as UV protection properties and antibacterial and antimicrobial activities. All this, combined with its low cost and high stability, makes it a perfect additive for this application.