TITANIUM DIOXIDE

Chemical and Technical Assessment

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1. Summary

Titanium dioxide (INS no. 171; CAS no. 13463-67-7) is produced either in the anatase or rutile crystal form. Most titanium dioxide in the anatase form is produced as a white powder, whereas various rutile grades are often off-white and can even exhibit a slight colour, depending on the physical form, which affects light reflectance. Titanium dioxide may be coated with small amounts of alumina and silica to improve technological properties.

Commercial titanium dioxide pigment is produced by either the sulfate process or the chloride process. The principal raw materials for manufacturing titanium dioxide include ilmenite (FeO/TiO_2), naturally occurring rutile, or titanium slag. Both anatase and rutile forms of titanium dioxide can be produced by the sulfate process, whereas the chloride process yields the rutile form.

Titanium dioxide can be prepared at a high level of purity. Specifications for food use currently contain a minimum purity assay of 99.0%.

Titanium dioxide is the most widely used white pigment in products such as paints, coatings, plastics, paper, inks, fibres, and food and cosmetics because of its brightness and high refractive index (> 2.4), which determines the degree of opacity that a material confers to the host matrix. When combined with other colours, soft pastel shades can be achieved. The high refractive index, surpassed by few other materials, allows titanium dioxide to be used at relatively low levels to achieve its technical effect.

The food applications of titanium dioxide are broad. US regulations authorize its use as a colour additive in foods in general at levels not to exceed 1%. The European Union also permits its use in foods, in general, with some specified exceptions, at *quantum satis* levels. India restricts its uses to chewing gum and bubble gum at not more than 1% and to powdered concentrate mixes for fruit beverage drinks not to exceed 100 mg/kg. Japan lists its use as a food colour without limitation, other than specifying certain foods in which it is not permitted. Finally, titanium dioxide is listed in Table 3 of the Codex General Standard for Food Additives, which lists additives that may be used in food, in general, unless otherwise specified, in accordance with GMP.

2. Description

Titanium dioxide or Titanium (IV) oxide (TiO_2, Formula Weight 79.88).

> CAS no. 13463-67-7.
> Synonyms: INS no. 171; Titania; CI Pigment White 6; CI (1975), no. 77891.

Natural titanium dioxide exists in nature in one of three crystalline forms, the two most important of which are anatase (CAS no. 1317-70-0) and rutile (CAS no. 1317-80-2), the third being brookite (12188-41-9). Although these minerals are essentially pure titanium dioxide, they do not appear white, because of the presence of impurities, such as iron, chromium, or vanadium, which darken them. Rutile is the thermodynamically stable form of titanium dioxide;

anatase rapidly transforms to rutile above 700°. Rutile melts between 1830° and 1850° (Kirk-Othmer, 1997; Kirk-Othmer, 2006).

Commercial titanium dioxide is generally marketed as a white to slightly coloured amorphous powder. A platelet form is also manufactured. Most titanium dioxide in the anatase form is produced as a white powder, whereas various rutile grades are often off-white and can even exhibit a slight colour, depending on the physical form affecting light reflectance. Titanium dioxide may be coated with small amounts of alumina and silica to improve technological properties. Such coatings can prevent possible reactions between the highly reactive surfaces of the extremely fine titanium dioxide crystals and the matrix in which the pigment is dispersed and they can improve the dispersion of the titanium dioxide in the host matrix (Kirk-Othmer, 2006).

Titanium dioxide is insoluble in water, hydrochloric acid, dilute sulfuric acid, and organic solvents. It dissolves slowly in hydrofluoric acid and hot concentrated sulfuric acid. It is almost insoluble in aqueous alkaline media (Kirk-Othmer, 1997).

3. Method of manufacture

Commercial titanium dioxide pigment is produced by either the sulfate process or the chloride process. Because of significant environmental and cost issues associated with the sulfate process, most new manufacturing capacity is based on the chloride process. Older manufacturing plants that used the sulfate process have had to modify their processes to accommodate stricter environmental requirements by recycling waste acids and roasting metal sulfates to recover sulfur trioxide (Kirk-Othmer, 1997; DeMerlis, 2005).

The principal raw materials for manufacturing titanium dioxide include ilmenite (FeO/TiO_2), naturally occurring rutile, and titanium slag. The last is produced by removing the iron from ilmenite by reduction with coke at 1200-1600°. At these temperatures, the iron oxide is reduced to the metal, which melts and separates from the formed titanium-containing slag, which is 70-75% titanium dioxide (Kirk-Othmer, 2006).

<u>Sulfate process (Kirk-Othmer, 1997; Kirk-Othmer, 2006; DeMerlis, 2005)</u>
Both anatase and rutile grades of titanium dioxide can be produced by the sulfate process, depending on particular processing conditions. Briefly, ilmenite or ilmenite and titanium slag is digested with sulfuric acid and the product is diluted with water or dilute acid. Most of the titanium dioxide from the ore is solubilized as a titanium oxo-sulfate and iron is present in its +II oxidation state. The resulting liquor is clarified by sedimentation to remove insoluble residues such as silica. Iron is removed by crystallization as its sulfate salt ($FeSO_4 \cdot 7H_2O$), followed by filtration.

To produce the anatase form of the titanium dioxide, a small portion of the clarified liquor is neutralized with alkali to produce anatase microcrystals. These microcrystals are then introduced into the mother liquor, which is then hydrolysed under carefully controlled conditions to produce crystals of anatase. These are subsequently filtered, washed, calcined, and micronized. During calcination, the final temperature reaches about 800-850°.

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. Formed crystals are filtered, washed and calcined at temperatures between 900 and 930°, and micronized.

Chloride process (Kirk-Othmer, 1997; Kirk-Othmer, 2006; DeMerlis, 2005)
The chloride process yields the rutile form of titanium dioxide. At temperatures between 800 and 1200°, chlorine is reacted in a fluidized bed reactor with a titanium-containing mineral, e.g., mineral rutile (which is not readily attacked by sulfuric acid), under reducing conditions (presence of coke) to form anhydrous titanium (IV) chloride. Purification of the anhydrous tetrachloride requires separation by fractional condensation. Conversion of the tetrachloride to titanium dioxide may be accomplished by either direct thermal oxidation or reaction with steam in the vapour phase at temperatures in the range of 900-1400°. A minor amount of aluminium chloride is generally added to promote formation of the rutile form. The titanium dioxide is washed, calcined, and packaged.

Alternatively, the titanium-containing mineral can be reacted with concentrated hydrochloric acid to form solutions of titanium (IV) chloride which are then further purified. Hydrolysis of the tetrachloride will yield the dioxide which is filtered off, washed, calcined, and packaged (DeMerlis, 2005).

Titanium dioxide/platelet form (EFSA, 2004)
A platelet form of titanium dioxide (rutile) can be produced by first coating the surface of mica (i.e., potassium aluminum silicate) platelets, which act as templates, with the titanium dioxide (rutile). The titanium dioxide-coated mica nacreous pigment is then subjected to an extractive dissolution in acid followed by an extractive dissolution in alkali. All of the mica is removed during this process and the resulting product is a platelet form of rutile titanium dioxide. This product cannot be obtained from anatase titanium dioxide as a starting material.

The specific properties of the pigment are determined by controlling the thickness of the titanium dioxide layer and the coating process used to coat the mica substrate. The thickness of the rutile titanium dioxide coated on the mica determines the interference colour of the final product. The resulting platelet titanium dioxide contains low levels of impurities comparable to other standard pigment grades of titanium dioxide typically used in the food industry.

4. Characterization

4.1 Composition
Titanium dioxide can be prepared at a high level of purity. Specifications for food use currently contain a minimum purity assay of 99.0% (FCC, 2003; Japan, 2000; JECFA, 2006). Maximum limits for Loss on Drying (Japan, 2000; JECFA, 2006) and Loss on Ignition (FCC, 2003; Japan, 2000; JECFA, 2006) have also been established.

4.2 Possible impurities
The possible impurities in titanium dioxide arise from the impurities in the ores and solvents used in the manufacturing process. The following Table indicates the maximum limits specified in the JECFA and Food Chemicals Codex (FCC) monographs for various impurities.

Maximum Specified Limits for Impurities in Titanium Oxide

Impurity	JECFA (2006)	FCC (2003)	Japan (2000)
Aluminium oxide/silicon dioxide	2%	2.0%	---
Acid-soluble substances	0.5% (1.5% for products containing alumina or silica)	0.5%	0.50%
Water-soluble matter	0.5%	0.3%	0.25%
Antimony	2 mg/kg	1 mg/kg	(a)
Arsenic	1 mg/kg	2 mg/kg	1.3 mg/kg as As_2O_3
Cadmium	1 mg/kg	---	(a)
Lead	10 mg/kg	10 mg/kg	(a)
Mercury	1 mg/kg	1 mg/kg	(a)

(a) 10 mg/kg total Heavy metals (as lead).

4.3 Analytical methods

The FCC, Japanese, and JECFA specifications monographs for titanium dioxide (FCC, 2003; Japan, 2000; JECFA, 2006), as well as the volume on general methods in the *Combined Compendium of Specifications* (JECFA, 2006a), provide analytical methods for all tests indicated.

5.Functional uses

Titanium dioxide is the most widely used white pigment in products such as paints, coatings, plastics, paper, inks, fibres, and food and cosmetics because of its brightness and high refractive index (> 2.4), which determines the degree of opacity that a material confers to the host matrix. The high refractive index, surpassed by few other materials, allows titanium dioxide to be used at relatively low levels to achieve its technical effect (CERAM, 2006; Wikipedia, 2006)).

Titanium dioxide is highly effective as a whitener for confectionary, baked goods, cheeses, icings, toppings, and food supplements. When combined with other colours, soft pastel shades can be achieved. As titanium dioxide is not water-soluble, applications require dispersion using vehicles such as food oils, propylene glycol, sugar syrup, or water with select thickeners (Gerdes, 2004; Vaughn, 2006).

The Codex General Standard for Food Additives (Table 3 - Additives Permitted for Use in Food in General, Unless Otherwise Specified, in Accordance with GMP) contains a provision for the use of titanium dioxide in food (Codex, 2005). The acceptable food categories of this standard (the GSFA) corresponding to general use are reproduced in ANNEX 1, taken from the GSFA on-line data base (Codex, 2005a). Maximum numerical levels of use are not specified for Table 3 additives. GMP (Good Manufacturing Practices) is understood to mean that levels of use should be no more than necessary to achieve the intended technical effect. (*Caution*: The entries in ANNEX 1 do not mean that titanium dioxide is being used in all the listed food categories.)

The United States Food and Drug Administration (FDA) has authorized the use of titanium dioxide in food, in general, at a limit not to exceed 1% by weight of the food. Silicon dioxide and aluminium oxide may be used with the titanium dioxide as “dispersing aids” at levels not to exceed 2% by weight, singly or in combination, of the titanium dioxide (FDA, 2005). In the USA, actual uses of titanium dioxide in food supplements and hard and soft panned candies have been reported to be as high as 1%. Uses in icings, chewing gums, starch-molded confectionary, and baked goods typically range from 0.02% to 2% and in savory snack foods from 0.05% to 0.4% (Vaughn, 2006).

India restricts the uses of titanium dioxide to chewing gum and bubble gum with a level not to exceed 1% (India, 2004) and to powdered concentrate mixes for fruit beverage drinks not to exceed 100 mg/kg (India 2004a).

Japan lists its use as a food colour without limitation, other than specifying certain foods in which it is not permitted (Japan, 2000).

The European Union lists titanium dioxide for use in colouring food, in general, except for certain specified foodstuffs, at *quantum satis* levels (EU, 1994).

A recent report by the European Food Safety Authority, EFSA, notes that the rutile form of titanium dioxide, as platelets, is currently used in aqueous film coating systems for commercial confectionery products in the United States. EFSA states that the platelet form of the additive is being evaluated by the United States food industry for use in cookies, baked goods, pretzels and other salted snacks, and in confectionery products (EFSA, 2004).

6. Reactions and fate in foods

Given its insolubility in water, hydrochloric acid, dilute sulfuric acid, and organic solvents, titanium dioxide is not expected to react with components of food. Its functionality depends upon its inertness within a food matrix. In fact, in 1969 JECFA (JECFA, 1970) "decided not to establish a limit on intake of titanium dioxide since the evidence indicates that it is free from toxic effects on account of its insolubility and inertness. The intake in food would be limited by good manufacturing practice."

7. References

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ANNEX 1

Provisions for the Use of Titanium Dioxide
According to Table 3 of the Codex General Standard for Food Additives
(CX/STAN 192-1995, rev. 2005)

GSFA Table 3 Provisions

Titanium Dioxide is a food additive that is included in Table 3, and as such **may** be used in the following foods under the conditions of good manufacturing practices (GMP) as outlined in the Preamble of the Codex GSFA. Note that food categories listed in the Annex to Table 3 were excluded accordingly.

Number	Food Category
01.1.2	Dairy-based drinks, flavoured and/or fermented (e.g., chocolate milk, cocoa, eggnog, drinking yoghurt, whey-based drinks)
01.3	Condensed milk and analogues (plain)
01.4.3	Clotted cream (plain)
01.4.4	Cream analogues
01.5	Milk powder and cream powder and powder analogues (plain)
01.6	Cheese and analogues
01.7	Dairy-based desserts (e.g., pudding, fruit or flavoured yoghurt)
01.8	Whey and whey products, excluding whey cheeses
02.2.1.2	Margarine and similar products
02.2.1.3	Blends of butter and margarine
02.2.2	Emulsions containing less than 80% fat
02.3	Fat emulsions maily of type oil-in-water, including mixed and/or flavoured products based on fat emulsions
02.4	Fat-based desserts excluding dairy-based dessert products of food category 01.7
03.0	Edible ices, including sherbet and sorbet
04.1.2	Processed fruit
04.2.2.2	Dried vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweeds, and nuts and seeds
04.2.2.3	Vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera) and seaweeds in vinegar, oil, brine, or soy sauce
04.2.2.4	Canned or bottled (pasteurized) or retort pouch vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), and seaweeds
04.2.2.5	Vegetable (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweed, and nut and seed purees and spreads (e.g., peanut butter)
04.2.2.6	Vegetable (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweed, and nut and seed pulps and preparations (e.g., vegetable desserts and sauces, candied vegetables) other than food category 04.2.2.5
04.2.2.8	Cooked or fried vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), and seaweeds
05.0	Confectionery
06.3	Breakfast cereals, including rolled oats
06.4.3	Pre-cooked pastas and noodles and like products
06.5	Cereal and starch based desserts (e.g., rice pudding, tapioca pudding)
06.6	Batters (e.g., for breading or batters for fish or poultry)
06.7	Pre-cooked or processed rice products, including rice cakes (Oriental type only)
06.8	Soybean products (excluding soybean products of food category 12.9 and fermented soybean products of food category 12.10)
07.0	Bakery wares
08.2	Processed meat, poultry, and game products in whole pieces or cuts
08.3	Processed comminuted meat, poultry, and game products

Number	Food Category
08.4	Edible casings (e.g., sausage casings)
09.3	Semi-preserved fish and fish products, including mollusks, crustaceans, and echinoderms
09.4	Fully preserved, including canned or fermented fish and fish products, including mollusks, crustaceans, and echinoderms
10.2.3	Dried and/or heat coagulated egg products
10.3	Preserved eggs, including alkaline, salted, and canned eggs
10.4	Egg-based desserts (e.g., custard)
11.6	Table-top sweeteners, including those containing high-intensity sweeteners
12.2.2	Seasonings and condiments
12.3	Vinegars
12.4	Mustards
12.5	Soups and broths
12.6	Sauces and like products
12.7	Salads (e.g., macaroni salad, potato salad) and sandwich spreads excluding cocoa- and nut-based spreads of food categories 04.2.2.5 and 05.1.3
12.8	Yeast and like products
12.9	Protein products
12.10	Fermented soybean products
13.3	Dietetic foods intended for special medical purposes (excluding products of food category 13.1)
13.4	Dietetic formulae for slimming purposes and weight reduction
13.5	Dietetic foods (e.g., supplementary foods for dietary use) excluding products of food categories 13.1 - 13.4 and 13.6
13.6	Food supplements
14.1.1.2	Table waters and soda waters
14.1.4	Water-based flavoured drinks, including "sport," "energy," or "electrolyte" drinks and particulated drinks
14.2.1	Beer and malt beverages
14.2.2	Cider and perry
14.2.4	Wines (other than grape)
14.2.5	Mead
14.2.6	Distilled spirituous beverages containing more than 15% alcohol
14.2.7	Aromatized alcoholic beverages (e.g., beer, wine and spirituous cooler-type beverages, low alcoholic refreshers)
15.0	Ready-to-eat savouries
16.0	Composite foods - foods that could not be placed in categories 01 - 15