Kirk-Othmer Encyclopedia of Chemical Technology.

TITANIUM COMPOUNDS, INORGANIC

Titanium, Ti, atomic number 22, relative atomic mass 47.90, is the ninth most common element (ca 0.6% by weight) and is widely distributed in the earth's crust. It is found particularly in the ores rutile, TiO_2, and ilmenite, $FeTiO_3$.

Titanium is the first member of the *d*-block transition elements. Its electron configuration is [Ar] $4s^2 3d^2$, and successive ionization potentials are 6.83, 13.57, 27.47, and 43.24 eV. Its technologically important chemistry is predominantly that of oxidation states (II), (III), and (IV), in order of increasing importance. Ti(II) and Ti(III) compounds are readily oxidized to the tetravalent state by air, water, and other oxidizing agents. The energy for the removal of four electrons is so high that the Ti^{4+} ion does not itself have a real existence, and compounds of Ti(IV) are generally significantly covalent. Titanium, capable of utilizing the 3*d* shell, forms a large group of addition compounds in which the Ti is coordinated by donor atoms such as oxygen, sulfur, or chlorine.

The titanium compounds of greatest technological importance are titanium dioxide, the predominant white pigment. Global consumption of titanium has grown to 3,707,000 t (expressed as titanium dioxide) in 1996. Approximately 90% of this usage is as a white pigment, placing TiO_2 as the second highest valued inorganic chemical consumed in the world. Titanium esters, eg, titanium isopropoxide, and derived compounds, are used for applications such as structuring agents in paint (qv); titanium metal, which has excellent corrosion resistance and a high strength–weight ratio (see Titanium and titanium alloys); and barium titanate, an important electroceramic (see Advanced ceramics; Ceramics as electrical materials). The general properties and chemistry of titanium are reviewed elsewhere (1–14).

The first recorded use of titanium dioxide as a white pigment was in 1908, when A. J. Rossi, a French metallurgist and chemist, prepared a relatively pure TiO_2, mixed the material with salad oil, and brushed out the mixture. Rossi had come to the United States in the late 1800s and developed methods to produce titanium alloys for the iron-and-steel industry. Work continued on the development of titanium compounds used as pigments, and in 1916, the Titanium Pigment Company was formed in Niagara Falls, New York.

During the same time period, the Norwegian government appointed a commission to investigate the commercial uses of extensive titaniferous magnetites and ilmenite deposits in the southwest coast of Norway. Although initially directed at smelting these ores for iron, the investigations lead to the development of titanium dioxide pigments. By 1912, production of composite pigments was begun at Fredrikstad, Norway.

In 1920, the National Lead Company purchased a substantial interest in the Titanium Pigment Company and in 1927, purchased a controlling interest in the original Norwegian company, Titan Company, A.-S. and a French affiliate, Societe Industrielle du Titane, a sales company.

National Lead constructed a second U.S. pigment plant in St. Louis, Missouri in 1923 and began production at a newly constructed plant in Sayreville, New Jersey in 1935. During the late 1920s to mid-1930's, National Lead and other interests entered into agreements with I. G. Farbenindustrie, A.G. in Germany to build a plant in Leverkusen to supply the European and Asiatic markets, organized the British Titan Products Company Ltd. to manufacture and sell titanium dioxide pigments throughout the British Empire, and formed Titan Kogyo Kabushi Kaisha to build a plant in Kobe to furnish titanium compounds for the Japanese Empire. The

Table 1. Thermal Data for Changes of State of Titanium Compounds

Compound	CAS Registry Number	Change[a]	Temperature, K	ΔH, kJ/mol[b]
$TiCl_4$	[7550-45-0]	mp	249.05	9.966
		bp	408	35.77
$TiCl_3$	[7705-07-9]	sublimation	1103.3	166.15
$TiCl_2$	[10049-06-6]	sublimation	1580.4	248.5
TiI_4	[7720-83-4]	mp	428	19.83 ± 0.63
		bp	651.8	56.48 ± 2.09
TiF_4	[7783-63-3]	sublimation	558.3	97.78 ± 0.42
$TiBr_4$	[7789-68-6]	mp	311.4	12.89
		bp	503.5	45.19
TiO_2	[13463-67-7]	anatase to rutile		ca -12.6
TiN	[25583-20-4]	mp	3220 ± 50	66.9
TiB_2	[12405-63-5]	mp	3193	100.4

[a] Melting and sublimation temperatures are generally based on those given in Ref. 15.
[b] To convert kJ/mol to kcal/mol, divide by 4.1814.

growing success of titanium dioxide as a white pigment during the 1920s and 1930s caused other companies to construct plants in various parts of the world.

Another early development involved Blumenfeld, who devised an improved manufacturing process for which patents were granted in England in 1923 and in the United States in 1924. By 1926, three plants using this process had been built in Europe: one in France by the Fabrique de Produits Chimiques et de Mulhouse, a second in Italy by the Montecatini interests, and a third in Czechoslovakia by the Verein fur Chemische und Metallurgische Produktion.

In 1927, the Commercial Pigments Company constructed a plant in Baltimore, Maryland using the Blumenfeld process. This company was taken over by the Krebs Pigment and Color Corporation in 1932 and in 1943 became the pigment department of E. I. du Pont de Nemours and Company. Du Pont had developed a method of producing composite pigments by blending finished titanium dioxide with calcium sulfate and barium sulfate and built a plant at Edge Moor, Delaware in 1935 to produce these pigments.

Initially, only composite pigments composed of 25% anatase titanium dioxide and 75% barium sulfate were produced. These pigments were commercially successful because they had significantly better opacity than did other available white pigments, mainly white lead and zinc oxide. Pure anatase was first produced in 1923 by Thann et Mulhouse in France via their Blumenfeld sulfate process. Paint using anatase pigments tended to “chalk” when exposed to weather, however. This lead to the development of pigments made from the rutile crystal, a more stable form, which exhibits improved exterior durability. Although rutile pigments were first developed in Czechoslovakia and introduced commercially in 1939, World War II prevented further market penetration in Europe. Work continued in the United States, where rutile pigments were marketed by National Lead and du Pont in the early 1940s.

In 1943, charges were brought by the U.S. Department of Justice against the National Lead Company and E. I. du Pont de Nemours Company for monopolizing the sale and production of titanium pigments in violation of the Sherman Antitrust Act. This was upheld by the U.S. Supreme Court in 1947.

1. Thermochemical Data

Data relating to changes of state of selected titanium compounds are listed in Table 1. Heats of formation, free energy of formation, and entropy of a number of titanium compounds at 298 and 1300 K are collected in Table 2.

Table 2. Thermochemical Data for the Formation of Titanium Compounds[a]

	ΔH_f, kJ/mol[b]		ΔG_f, kJ/mol[b]		S, J/(mol·K)[b]	
Compound[c]	298.15 K	1300 K	298.15 K	1300 K	298.15 K	1300 K
TiO(α)	−542.7	−540.3[d]	−513.3	−427.9[d]	34.8	110.9[d]
anatase	−938.7	−934.1	−883.3	−703.4	49.9	152.2
rutile	−944.7	−940.7	−889.4	−709.2	50.3	151.7
TiB_2	−279.5	−287.5	−275.3	−257.5	28.5	125.3
TiC	−184.1	−188.3	−180.4	−168.8	24.2	92.25
TiN	−337.6	−337.6	−308.9	−214.7	30.2	100.8
$TiCl_2$	−515.5	−504.2	−465.8	−310.2	87.4	204.3
$TiCl_3$	−721.7	−706.5	−654.5	−445.4	139.8	290.9
$TiCl_4$[e]	−804.2	−771.3[f]	−728.1	−573.7[f]	221.9	400.8[f]
$TiCl_4$[g]	−763.2	−765.8	−726.8	−606.3	354.9	507.5
$TiBr_4$	−618	−654.8	−590.7	−347	243.6	440.6
$TiBr_3$	−550.2	−546.5	−525.6	−340.8	176.4	369
TiF_4	−1649.3	−1611	−1559.2	−1289.9	134	338.7
TiI_4	−375.7	−453.3	−370.7	−164.6	246.2	486.6

[a] ΔH_f and ΔG_f refer to the formation of the named substances in the specified states at 298.15 and 1300 K from their elements in the standard states of those elements at these temperatures. Refs. 9 and 15.

[b] To convert J to cal, divide by 4.1814.

[c] In the crystalline state unless otherwise specified.

[d] Values at 1200 K. Above this temperature the α-form of TiO transforms to β.

[e] Liquid.

[f] Values at 1000 K.

[g] Gas.

2. Titanium–Hydrogen System

Titanium metal readily absorbs hydrogen. Absorption rates above 400°C are normally high, but at lower temperatures the rates depend critically on the cleanliness of the surface. There is, for example, significant inhibition by surface oxides. The hydrogen dissociates prior to absorption. Because the absorption is a reversible process, there is thus an equilibrium pressure of hydrogen at each temperature and composition. The limiting stoichiometry of the system is normally accepted as TiH_2, although higher hydrides have been reported under special conditions. For example, TiH_4 has been reported in the products formed when mixtures of titanium tetrachloride and hydrogen were irradiated with uv radiation at 254 nm.

A phase diagram, with notation for the titanium–hydrogen system, is available, as is a review of kinetic data and physical properties (16). The phases may be conveniently described by reference to pure metallic titanium, which at room temperature and pressure has a hexagonal close-packed (hcp) structure (α-titanium). At high temperatures, this converts to a body-centered cubic (bcc) structure (β-titanium). At high pressures, the hcp α-phase converts to a hexagonally distorted bcc structure, ω. In the titanium–hydrogen system, the α-phase, ie, the solid solution of H in hcp titanium, exists up to ca 0.12 atom % at 25°C and up to 7.9 atom % ($TiH_{0.09}$) between 300 and 600°C. Its formation has negligible effect on the titanium's lattice parameters, but whether the hydrogen atoms (radius 41 pm) occupy tetragonal (34 pm) or octahedral (62 pm) interstices within the lattice remains unclear. The region of stability of the β-phase H solution in bcc titanium extends from 0 atom % H at 882°C to ca 50 atom %, ie, a stoichiometry corresponding to TiH, at ca 300°C. In this case, hydrogen solubility expands the β-titanium lattice and the hydrogens have been shown to occupy tetrahedral sites. An fcc †-phase exists as a mixture with the α or β solid solutions over a wide range of hydrogen concentrations, but only as a single phase region between 57 and 64 atom % hydrogen ($TiH_{1.5--1.94}$) at room temperature.

Above 64 atom %, and at relatively low temperatures, variously reported as 20–41°C, transformation from this fcc phase to a tetragonally distorted fcc structure, the ϵ-phase, takes place in near stoichiometric TiH_2. In the ϵ-phase, the H atoms are symmetrically located in tetrahedral interstices. In addition, a metastable γ-phase with a stoichiometry TiH has been identified and is formed when the α-phase containing 1–3 atom % H is cooled. A phase transition from α to the hexagonally distorted bcc ω structure occurs under high pressures of hydrogen, eg, 4 GPa (40 kbar) for $TiH_{0.33}$. By quenching this phase to 90 K, a metastable superconducting phase ($T_c = 4.3$ K) is formed.

Titanium hydrides are grey powders. Their density decreases with increasing hydrogen content from 4410 kg/m^3 for pure titanium metal to ca 3800 kg/m^3 for TiH_2. The applications of titanium hydrides are related to their ability to store hydrogen reversibly (qv). Their possible use as a hydrogen storage medium in hydrogen-fueled vehicles has received particular attention (see Hydrogen energy). Titanium hydrides may also be used to purify cylinder hydrogen or as high purity hydrogen sources for, eg, plasma guns. Suppliers of titanium hydride include Atomergic Chemmetals Corp., Micron Metals, Morton International, and Noah Technologies in the United States, and Hladik-Skalick VOS in Europe.

3. Titanium Borides

Five phases of titanium boride have been reported. TiB_2 [12405-65-35], Ti_2B [12305-68-9], TiB [12007-08-8], Ti_2B_5 [12447-59-5], and TiB_{12} [51311-04-7]. The most important of these is the diboride, TiB_2, which has a hexagonal structure and lattice parameters of $a = 302.8$ pm and $c = 322.8$ pm. Titanium diboride is a gray crystalline solid. It is not attacked by cold concentrated hydrochloric or sulfuric acids, but dissolves slowly at boiling temperatures. It dissolves more readily in nitric acid/hydrogen peroxide or nitric acid/sulfuric acid mixtures. It also decomposes upon fusion with alkali hydroxides, carbonates, or bisulfates.

Research-grade material may be prepared by reaction of pelleted mixtures of titanium dioxide and boron at 1700°C in a vacuum furnace. Under these conditions, the oxygen is eliminated as a volatile boron oxide (17). Technical grade (purity $> 98\%$) material may be made by the carbothermal reduction of titanium dioxide in the presence of boron or boron carbide. The endothermic reaction is carried out by heating briquettes made from a mixture of the reactants in electric furnaces at 2000°C (11, 18, 19).

$$TiO_2 + B_2O_3 + 5\ C \longrightarrow TiB_2 + 5\ CO$$

Titanium diboride, typically 96–98% pure, may also be made by the electrolysis of mineral rutile dissolved in mixed electrolytes, $TiO_2/Na_2CO_3/Na_3AlF_6/NaCl/Na_2B_4O$, at 1050°C (20). Very fine titanium diboride may be made by a gas-phase plasma process in which titanium tetrachloride and boron trichloride are reacted in a hydrogen gas heated by a d-c plasma (21).

$$TiCl_4 + 2\ BCl_3 + 5\ H_2 \longrightarrow TiB_2 + 10\ HCl$$

This reaction, operated at pilot plant scale, has not as of this writing (ca 1997) been commercialized. The same reaction may be used for chemical vapor deposition of titanium boride.

The applications of titanium diboride depend on such properties as its hardness, electrical conductivity, and ability to be wetted by metals. The actual values of these properties attained in sintered bodies depend on the grain structure and degree of densification and, ultimately, on both the fabrication method and the quality of the starting powder (22). Some typical values are given in Table 3. In monolithic form, sintered titanium diboride can be used as a strong but lightweight armor. It is an important constituent of cermets, eg, composites based on TiB_2–TiC–Fe mixtures show excellent performance as cutting tools for aluminum alloys. Titanium diboride also shows excellent wettability and stability in liquid metals, eg, liquid aluminum, and many tons of

Table 3. Physical Properties of Titanium Borides, Carbides, and Nitrides[a]

Compound	Structure	Lattice parameter, pm	Density, kg/m^3	Melting point, °C	Electrical resistivity, 25°C, $\Omega\cdot m \times 10^{-8}$		Hardness, Mohs' scale	Microhardness, GPa
TiB_2	hexagonal							
	a	302.8	4520	2980[b]	10–30	28.4[b]	9	2600[c]
	c	322.8						
TiC	fcc (NaCl)	432.8	4910	3000	50–200	180–250[b]	9–10	3200[d] −31.4
TiN	fcc (NaCl)	423.5	5213	2950	20–50	21.7[b]		1770[c] 15–20

[a] Values are indicative only. Precise values depend on sintering conditions and degree of densification.

[b] Figures based on Ref. 22.

[c] Knoop hardness, 1-*N* load, Kgf/mm.

[d] Vickers hardness.

the powder are used in the production of vacuum metallizing boats, eg, TiB_2, AlN, and BN composites. These are resistance-heated to about 1400°C and used for the continuous evaporation of aluminum to produce thin metal films (see Thin films). The use of titanium diboride as an inert solid cathode, which would replace the molten aluminum cathode in aluminum reduction refining cells, has been proposed.

Suppliers of titanium diboride include Micron Metals, Atomergic Chemmetals, Cerac, and Noah Technologies, in the United States, and Elektroschmelzwerk Kempten, Herman C. Starck, and RTZ Chemicals in Europe.

4. Titanium Carbide

Titanium carbide [12070-08-05], TiC, has the fcc, NaCl structure in which the carbon atoms can be regarded as occupying the octahedral interstices in a slightly expanded cubic close-packed arrangement of titaniums. The system is stable from $TiC_{1.0}$ to $TiC_{0.47}$ (23, 24), ie, ca 50% of the carbon sites can be vacant. As the carbon content is reduced, the lattice parameter (a = 432.8 pm (25)) and density decrease. From $TiC_{0.47}$ to $TiC_{0.08}$, TiC and Ti phases coexist; below $TiC_{0.08}$, only the α-Ti phase is present. Titanium carbide also forms solid solutions with TiO and TiN. Sintered titanium carbide is light gray when fractured but can be polished to a silver gray. The maximum melting point in the Ti–C system is 3067°C for $TiC_{0.8}$, that of $TiC_{1.0}$ is slightly lower. The boiling point of titanium carbide is 4800°C. Representative values of physical properties are given in Table 3.

Titanium carbide is resistant to aqueous alkali except in the presence of oxidizing agents. It is resistant to acids except nitric acid, aqua regia, and mixtures of nitric acid with sulfuric or hydrofluoric acid. In oxygen at 450°C, a nonprotecting anatase coating forms. The reaction

$$3\ CO_2 + TiC \longrightarrow 4\ CO + TiO_2$$

occurs readily at 1200°C, and oxidation by CO also occurs. It is stable to hydrogen to 2400°C, but reacts with nitrogen at 1000°C.

Annual world production of titanium carbide is thousands of metric tons. It is manufactured mainly in-house by cutting-tool manufacturers by the reduction of titanium dioxide with carbon:

$$TiO_2 + 3\ C \longrightarrow TiC + 2\ CO$$

An intimate mixture of titanium dioxide is heated to ca 2000°C in an electric-arc furnace or graphite tube in a hydrogen atmosphere. An important mixed carbide constituent of cemented carbides is made by similarly treating a mixture of tungsten metal, TiO_2, and Ta_2O_5. The product is a carbide powder having a grain size of 1–5 μm, depending on the reaction conditions and starting materials (26, 27). Suppliers of titanium carbide powder include Cerac and Adams Carbide in the United States, London and Scandinavian Metallurgical, Treibacher Chemische Werke, and Herman C. Starck in Europe, and Nippon Soda in Japan (see Carbides, cemented carbides).

A number of high temperature processes for the production of titanium carbide from ores have been reported (28, 29). The aim is to manufacture a titanium carbide that can subsequently be chlorinated to yield titanium tetrachloride. In one process, a titanium-bearing ore is mixed with an alkali-metal chloride and carbonaceous material and heated to 2000°C to yield, ultimately, a highly pure TiC (28). Production of titanium carbide from ores, eg, ilmenite [12168-52-4], $FeTiO_3$, and perovskite [12194-71-7], $CaTiO_3$, has been described (30). A mixture of perovskite and carbon was heated in an arc furnace at ca 2100°C, ground, and then leached with water to decompose the calcium carbide to acetylene. The TiC was then separated from the aqueous slurry by elutriation. Approximately 72% of the titanium was recovered as the purified product. In the case of ilmenite, it was necessary to reduce the ilmenite carbothermally in the presence of lime at ca 1260°C. Molten iron was separated and the remaining $CaTiO_3$ was then processed as perovskite.

Titanium carbide may also be made by the reaction at high temperature of titanium with carbon; titanium tetrachloride with organic compounds such as methane, chloroform, or poly(vinyl chloride); titanium disulfide [12039-13-3] with carbon; organotitanates with carbon precursor polymers (31); and titanium tetrachloride with hydrogen and carbon monoxide. Much of this work is directed toward the production of ultrafine (<1 μm) powders. The reaction of titanium tetrachloride with a hydrocarbon–hydrogen mixture at ca 1000°C is used for the chemical vapor deposition (CVD) of thin carbide films used in wear-resistant coatings.

The primary commercial applications of titanium carbide are in wear-resistant components and cutting tools. Titanium carbide is added to alumina-based cutting tools to give improved thermal conductivity and hence improved resistance to thermal shock, as well as mechanical performance, such as strength, hardness, and toughness, compared with pure alumina ceramics. In cemented carbides, 20–50% of a carbide, typically a mixed TiC–WC–TaC phase, is bonded by a metal, usually a cobalt, a nickel, or an iron alloy. TiC-based cemented carbides bonded with nickel–molybdenum are also used. To reduce tool wear, many cemented carbide tool tips used for steel cutting are coated with a 5–10 μm TiC-containing layer produced by chemical vapor deposition. There is significant research interest in the production of titanium carbide fibers for composite materials. Manufacturers of TiC-based hard material include GTE, Greenleaf, and Kennametal in the United States, Sandvik in Europe, and Kyocera, Mitsubishi Metal, and Nippon Tungsten in Japan.

5. Titanium–Nitrogen Compounds

Nitrogen dissolves in metallic titanium up to a nitrogen content of 20 atom % ($TiN_{0.23}$). Above 30 atom % ($TiN_{0.42}$), a cubic titanium nitride phase is stable.

5.1. Titanium Nitride

Titanium nitride [25583-20-4] has the cubic NaCl structure, but the structure is stable over a wide range of either anion or cation deficiency ($TiN_{0.42}$, $a = 421$ pm; $TiN_{1.0}$, $a = 423.5$ pm). The nitride is a better conductor of electricity than titanium metal. It becomes superconductive at 1.2–1.6 K. Titanium nitride has a density of 5213 kg/m^3 and melts at 2950°C. Thermodynamic data are given in Table 2.

The powder, usually described as chocolate-brown, is actually bluish black when sufficiently fine (32). The ease of sintering depends on particle size. Normal powders require hot pressing at 1800°C or higher, and full density is difficult to achieve. Ultrafine powders ($<0.1\ \mu$m) can be pressureless-sintered at temperatures as low as 1400°C without sintering aids. Sintered titanium nitride is a bronze color and can be polished to a golden lustre. TiN is thermodynamically unstable with respect to the oxide and, under normal conditions, titanium nitride powder is covered by a layer of chemisorbed oxygen. When it is heated in air, oxygen, nitric oxide, or carbon dioxide, it rapidly oxidizes. The susceptibility to oxidation depends on the degree of subdivision. It is resistant to attack by acids except boiling aqua regia, but is decomposed by alkalies with the evolution of ammonia.

Direct synthesis from nitrogen and finely divided titanium metal can be achieved at temperatures of >ca 1200°C (4). Typically, titanium sponge or powder is heated in an ammonia- or nitrogen-filled furnace and the product is subsequently milled and classified.

$$2\ Ti + N_2\ (\text{or}\ NH_3) \longrightarrow 2\ TiN\ (+1.5H_2)$$

A stoichiometric product can be obtained by repeated grinding and reaction. Alternatively, carbothermal reduction of titanium dioxide can be used (33). The reaction is carried out in an inert atmosphere at ca 1600°C.

$$2\ TiO_2 + 4\ C + N_2 \longrightarrow 2\ TiN + 4\ CO$$

The resulting titanium nitride forms a sintered mass, which must be subsequently milled to form a powder having a wide size distribution. The powders produced by these routes are typically 0.5–10 μm, with a wide size distribution. Very fine powders (0.005–0.5 μm) have been prepared at pilot-plant scale by the reaction of $TiCl_4$ with a large excess of gaseous ammonia (32).

$$2\ TiCl_4 + 4\ NH_3 \longrightarrow 2\ TiN + 8\ HCl + N_2 + 2\ H_2$$

The reactants are fed into the tail flame of a d-c nitrogen plasma. The reaction occurs rapidly at temperatures around 1500°C and the HCl reacts with excess ammonia to form ammonium chloride. Similar reactions have been carried out using furnaces, lasers, and r-f plasmas (34) as the source of heat. Other routes using titanium tetrachloride starting material include

$$2\ TiCl_4 + N_2 + 4\ Fe \longrightarrow 2\ TiN + 4\ FeCl_2$$

$$2\ TiCl_4 + N_2 + 4\ H_2 \longrightarrow 2\ TiN + 8\ HCl$$

$$2\ TiCl_4 + N_2 + 8\ Na\ (\text{or}\ 4\ Mg) \longrightarrow 2\ TiN + 8\ NaCl\ (\text{or}\ 4\ MgCl_2)$$

A liquid-phase reaction in which $TiCl_4$ is reacted with liquid ammonia at $-35°C$ to form an adduct that is subsequently calcined at 1000°C has also been proposed (35). Preparation of titanium nitride and titanium carbonitride by the pyrolysis of titanium-containing polymer precursors has also been reported (36).

TiN is used in cutting tools and wear parts, often in conjunction with TiC. Thus, the thermal conductivity, strength, toughness, and hardness of alumina-based cutting tools are improved by adding titanium carbide and titanium nitride at ca 30%. Because of its excellent electrical conductivity, TiN can be used as an additive to confer electrical conductivity on silicon nitride and sialon ceramic components. As a result, these can be shaped by spark erosion instead of by costly diamond grinding. Surface treatment of metals, often by chemical vapor deposition, as well as tungsten carbide cutting inserts, is widely employed to form a wear-resistant, low friction, titanium nitride surface layer.

5.2. Titanium Nitrate

Titanium nitrate [13860-02-1], $Ti(NO_3)_4$, is a white powder, mp 58°C, in which the titanium achieves a coordination number of eight by being surrounded by four bidentate nitrate groups. It is stable in a sealed tube at room temperature, is less sensitive to moisture than titanium tetrachloride, and does not fume in air but reacts vigorously with water, liberating nitrogen oxides. It may be prepared by prolonged reaction of N_2O_5 on titanium tetrachloride at -60 to $-20^\circ C$. This produces an intermediate compound that decomposes on warming in the presence of excess nitrogen dioxide to form NO_2Cl and titanium nitrate.

A more recent patent describes the production of titanyl nitrate by electrolysis of titanium tetrachloride or titanyl chloride (37). Other titanium nitrogen compounds that have been described include titanous amide [15190-25-9], $Ti(NH_2)_3$, titanic amide [15792-80-0], $Ti(NH)_2$, and various products in which amines have reacted with titanium tetrachloride (38).

5.3. Mining and Processing

Hard-rock deposits of ilmenite are typically mined by classical open-pit mining techniques. Extraction of the ore typically includes the steps of (*1*) blasting and crushing the rock, (*2*) grinding the crushed rock into sand, (*3*) magnetically separating out the simultaneously occurring iron-containing minerals such as magnetite, and (*4*) putting the sand through a flotation, or cone and spiral, process to separate the lighter ilmenite fractions, which are then dried and shipped.

Although the theoretical TiO_2 content of ilmenite is 52.7%, in nature the ore always occurs with other minerals; its actual “in the ground” level of TiO_2 ranges in hard-rock deposits from 8 to 37%. The concentration process described in the previous paragraph yields ilmenite ore with a TiO_2 content as high as 50%, depending on the source of the rock and the concentration process used.

Extraction of rutile and ilmenite from heavy mineral sands depends somewhat on the terrain on which the deposit lies. Typically, some type of dredging or scraping of the land surface must be employed to gather the sands. After the sand has been collected, the steps for further processing of the ore consist of (*1*) wet concentration, to remove the lighter minerals such as silica; (*2*) washing, to remove saltwater and/or organic matter and clays, if present; and (*3*) dry separation by magnetic and electrostatic means to split the concentrate into its purified commercially important components: rutile, ilmenite, leucoxene, zircon, and monazite. This concentration process yields rutile with a TiO_2 content of as high as 96%. Ilmenite ore produced from mineral sands generally has a TiO_2 level of 52–62%.

Over the years, TiO_2 pigment producers have increasingly demanded titanium feedstock ores with higher TiO_2 levels to minimize waste disposal costs and maximize capacity of pigment-processing equipment. Using feedstock ore with greater TiO_2 content allows a pigment producer to reduce the amount of by-product iron salts produced in the process. Since neither natural or synthetic rutile will react with sulfuric acid, the demand for high-TiO_2-content sulfate process feedstocks has been met by the production of titaniferous “slags.”

Essentially, a titaniferous slag is beneficiated ilmenite from which a major portion of the iron oxides has been removed by smelting techniques. Feedstocks to slag plants are ilmenite concentrates containing approximately 40–50% TiO_2, depending on the source of the ilmenite. A widely used slag process consists of (*1*) reducing the iron oxide fractions of the ore with coal in an electric arc furnace; (*2*) tapping off the molten, relatively pure iron at the bottom of the furnace; and (*3*) tapping off the molten slag. A second slag process uses a rotating kiln for the reduction step followed by melting the reduced ilmenite charge in an electric furnace, followed by steps *2* and *3* above. In both processes, the slag is cooled, crushed, and shipped. The iron goes through a reheating and desulfurization step, and then is poured into pigs and either shipped or processed further. Slag production is carried out at Rio Tinto's Sorel plant in Quebec, Richards Bay in South Africa, BHP/Tinfos in Norway, and Anglo America's Namakwa Sands in South Africa.

Recently, Rio Tinto has begun operation of facilities at their Sorel, Quebec smelter to produce a new product referred to as (*upgraded slag*) (UGS). This process converts Sorel slag into a higher TiO_2 content product suitable for use in the chloride process. With the exception of one pigment producer, Sorel slag cannot be used in the chloride process because of unacceptable levels of alkaline oxides. With UGS, Rio Tinto will convert a 77% TiO_2 content slag into a 95% TiO_2 slag by means of a selective hydrochloric acid leach and roasting process. The advantages of this product are its high TiO_2 content, a large ilmenite source in a politically stable location (Quebec), and a mine and upgrading facility close to the largest chloride process pigment producing region of the world in the United States.

6. Titanium Oxides

The titanium oxygen-phase diagram has been discussed (4). Metallic α-titanium can dissolve oxygen up to a composition of $TiO_{0.42}$, retaining the hexagonal structure but showing an increase in the lattice parameters. One consequence of the absorption of oxygen is that the transition temperature from α-titanium to the high temperature β-phase increases steeply from ca 900°C at 0 atom % to ca 1750°C at ca 15 atom %. As the oxygen content is increased above $TiO_{0.42}$, titanium oxides of increasing oxygen content are formed. The electronic structure of titanium oxides has been described (39, 40).

6.1. Mining and Processing

Hard-rock deposits of ilmenite are typically minded by classical open-pit mining techniques. Extraction of the ore typically includes the steps of (*1*) blasting and crushing the rock, (*2*) grinding the crushed rock into sand, (*3*) magnetically separating out the simultaneously occurring iron-containing minerals such as magnetite, and (*4*) putting the sand through a flotation, or cone and spiral, process to separate the lighter ilmenite fractions, which are then dried and shipped.

Although the theoretical TiO_2 content of ilmenite is 52.7%, in nature the ore always occurs with other minerals; its actual "in the ground" level of TiO_2 ranges in hard-rock deposits from 8 to 37%. The concentration process described in the previous paragraph yields ilmenite ore with a TiO_2 content as high as 50%, depending on the source of the rock and the concentration process used.

Extraction of rutile and ilmenite from heavy mineral sands depends somewhat on the terrain on which the deposit lies. Typically, some type of dredging or scraping of the land surface must be employed to gather the sands. After the sand has been collected, the steps for further processing of the ore consists of (1) wet concentration, to remove the lighter minerals such as silica; (2) washing, to remove saltwater and/or organic matter and clays, if present; and (3) dry separation by magnetic and electrostatic means to split the concentrate into its purified commercially important components: rutile, ilmenite, leucoxene, zircon, and monazite. This concentration process yields rutile with a TiO_2 content of as high as 96%. Ilmenite ore produced from mineral sands generally has a TiO_2 level of 52–62%

Over the years, TiO_2 pigment producers have increasingly demanded titanium feedstock ores with higher TiO_2 levels to minimize waste disposal costs and maximize capacity of pigment-processing equipment. Using feedstock ore with greater TiO_2 content allows a pigment producer to reduce the amount of by-product iron salts produced in the process. Since neither natural or synthetic rutile will react with sulfuric acid, the demand for high-TiO_2-content sulfate process feedstocks has been met by the production of titaniferous "slags."

Essentially, a titaniferous slag is beneficiated ilmenite from which a major portion of the iron oxides has been removed by smelting techniques. feedstocks to slag plants are ilmenite concentrates containing approximately 40–50% TiO_2, depending on the source of the ilmenite. A widely used slag process consists of

Table 4. Properties of the Lower Oxides of Titanium

Property	TiO	Ti_2O_3	Ti_3O_5
color	golden yellow	violet	blue-black
density, kg/m^3	4888	4486	421(0)
melting point, °C	1737	2127	
structure	fcc	hexagonal	monoclinic
lattice parameters, pm			
a	417	515.5	975.2
b		515.5	380.2
c		1316.2	944.2
solubility			
HF^a	dissolves rapidly	dissolves	
HCl^b	slow attack	no action	
$H_2SO_4{}^b$	slow attack	slow attack	
$HNO_3{}^b$	surface attack	no action	
$NaOH^b$	slow attack	no action	

[a] Hot 40 wt %.
[b] Hot concentrated.

(*1*) reducing the iron oxide fractions of the ore with coal in an electric arc furnace; (*2*) tapping off the molten, relatively pure iron at the bottom of the furnace; and (*3*) tapping of the molten slag. A second slag process uses a rotating kiln for the reduction step followed by melting the reduced ilmenite charge in an electric furnace, followed by steps (*2*) and (*3*) above. In both processes, the slag is cooled, crushed, and shipped. The iron goes through a reheating and desulfurization step, and then is poured into pigs and either shipped or processed further. Slag production is carried out at Rio Tinto's Sorel plant in Quebec, Richards Bay in South Africa, BHP/Tinfos in Norway, and Anglo America's Namakwa Sands in South Africa.

Recently, Rio Tinto has begun operation of facilities at their Sorel, Quebec smelter to produce a new product referred to as *upgraded slag* (UGS). This process converts Sorel slag into a higher TiO_2 content product sitable for use in the chloride process. With the exception of one pigment producer, Sorel slag cannot be used in the chloride process because of unacceptable level of alkaline oxides. With UGS, Rio Tinto will convert a 77% TiO_2 content slag into a 95% TiO_2 slag by means of a selective hydrochloric acid leach and roasting process. The advantages of this product are its high TiO_2 content, a large ilmenite source in a politically stable location (Quebec), and a mine and upgrading facility close to the largest chloride process pigment producing region of the world in the United States.

6.2. Lower Oxides of Titanium

The properties of lower oxides of titanium are summarized in Table 4.

6.2.1. Titanium Monoxide

Titanium monoxide [12137-20-1], TiO, has a rock-salt structure but can exist with both oxygen and titanium vacancies. For stoichiometric TiO, the lattice parameter is 417 pm, but varies from ca 418 pm at 46 atom % to 416_2 pm at 54 atom % oxygen. Apparently, stoichiometric TiO has ca 15% of the Ti and O sites vacant. At high temperatures ($>900°C$), these vacancies are randomly distributed; at low temperatures, they become ordered. Titanium monoxide may be made by heating a stoichiometric mixture of titanium metal and titanium dioxide powders at 1600°C

$$Ti + TiO_2 \longrightarrow 2\ TiO$$

Alternative methods of production include reduction of TiO_2 with magnesium, which yields TiO only. When titanium monoxide is heated in air at 150–200°C, titanium sesquioxide, Ti_2O_3, forms, and at 250–350°C, it changes to Ti_3O_5.

6.2.2. Titanium Sesquioxide

Ti_2O_3 has the corundum structure. At room temperature it behaves as a semiconductor having a small (0.2 eV) band gap. At higher temperatures, however, it becomes metallic. This is associated with marked change in the mean Ti–Ti distance. As with TiO, titanium sesquioxide, Ti_2O_3, may be made by heating a stoichiometric mixture of titanium metal and titanium dioxide powders at 1600°C under vacuum in an aluminum or molybdenum capsule.

$$\mathrm{Ti} + 3\,\mathrm{TiO_2} \longrightarrow 2\,\mathrm{Ti_2O_3}$$

6.2.3. Trititanium Pentoxide

Trititanium pentoxide, Ti_3O_5, may be made by the reduction of titanium dioxide by hydrogen at 1300°C. The low temperature form is monoclinic. Above 177°C, Ti_3O_5 has a distorted pseudobrookite structure, which can be stabilized at lower temperatures by small amounts of iron.

6.2.4. Crystallographic Shear Structures

As with all oxides, the rutile form of titanium dioxide can lose oxygen from the lattice, eg, when heated in vacuum at $>1000°C$. The white oxide becomes first blue-grey and then a very dark blue or blue-black. At all but the very lowest oxygen deficiencies, such as for $x > 0.0005$ in TiO_{2-x}, the resulting point defects (oxygen vacancies) cluster along specific planes in the rutile lattice in such a way that a plane of oxygen atoms is eliminated. The resulting planar defects, which have replaced the point defects, are called crystallographic shear (CS) planes. Low degrees of reduction are accommodated on the $\{132\}$ CS planes and greater degrees of reduction on the $\{121\}$ CS planes. The transition occurs at compositions between $TiO_{1.93}$ and $TiO_{1.90}$. At higher degrees of reduction, these CS planes become ordered to give the oxide series Ti_nO_{2n-1}, sometimes called Magnelli phases, where n is from 4 to 9 or 10. These phases have been extensively studied in both pure rutile and rutile doped with transition metal ions (39, 41–43). At temperatures above 150 K, Ti_4O_7 acts as a metallic conductor, and reduction of rutile to oxides such as Ti_4O_7 gives a conducting ceramic known as Ebonex, which has been proposed as an electrode material in a wide variety of applications (44).

6.3. Hydrated Titanium Oxides

Hydroxides of Ti(II) (black) and Ti(III) (brown) are precipitated when an alkali metal hydroxide is added to a solution of the corresponding salt. These precipitates, though difficult to purify (45), are powerful reducing agents and readily oxidize in air to form a hydrated titanium dioxide.

Hydrolysis of solutions of Ti(IV) salts leads to precipitation of a hydrated titanium dioxide. The composition and properties of this product depend critically on the precipitation conditions, including the reactant concentration, temperature, pH, and choice of the salt (46–49). At room temperature, a voluminous and gelatinous precipitate forms. This has been referred to as orthotitanic acid [20338-08-3] and has been represented by the nominal formula $TiO_2{\cdot}2H_2O$ ($Ti(OH)_4$). The gelatinous precipitate either redissolves or peptizes to a colloidal suspension in dilute hydrochloric or nitric acids. If the suspension is boiled, or if precipitation is from hot solutions, a less-hydrated oxide forms. This has been referred to as metatitanic acid [12026-28-7], nominal formula $TiO_2{\cdot}H_2O$ ($TiO(OH)_2$). The latter precipitate is more difficult to dissolve in acid and is only soluble in concentrated sulfuric acid or hydrofluoric acid.

Precipitation of a hydrated titanium oxide by mixing aqueous solutions of titanium chloride with alkali forms the precipitation seeds, which are used to initiate precipitation in the Mecklenburg (50) variant of

Table 5. Different Forms of Titanium Dioxide

Property	TiO_2 (B)	Anatase	Brookite	Rutile	α-PbO_2 form
crystal structure	monoclinic	tetragonal	orthorhombic	tetragonal	orthorhombic
number of TiO_2/unit cell	8	4	8	2	4
space group		141/amd	Pbca	P42/mnm	Pbcm
lattice parameters, pm					
a	1216.4	378.45	917.4	459.37	455(0)
b	373.5		544.9		547(0)
c	651.3	951.43	513.8	295.87	490(0)
volume per TiO_2, nm^3	0.03527	0.03407	0.03211	0.03122	0.03049
theoretical density, kg/m^3		3895	4133	4250	4350
Ti–O distance, pm		2 at 191, 4 at 195	184–203	4 at 194.4, 2 at 198.8	4 at 191, 2 at 205
hardness, Moh's scale		5.5–6	5.5–6	7–7.5	

the sulfate process for the production of pigmentary titanium dioxide. Hydrolysis of aqueous solutions of titanium chloride is also used for the preparation of high purity ($>99.999\%$) titanium dioxide for electroceramic applications (see Ceramics). In addition, hydrated titanium dioxide is used as a pure starting material for the manufacture of other titanium compounds.

The properties of hydrated titanium dioxide as an ion-exchange (qv) medium have been widely studied (51–55). Separations include those of alkali and alkaline-earth metals, zinc, copper, cobalt, cesium, strontium, and barium. The use of hydrated titanium dioxide to separate uranium from seawater and also for the treatment of radioactive wastes from nuclear-reactor installations has been proposed (56).

6.4. Titanium Dioxide

6.4.1. Physical and Chemical Properties

Titanium dioxide [13463-67-7] occurs in nature in three crystalline forms: anatase [1317-70-0], brookite [12188-41-9], and rutile [1317-80-2]. These crystals are essentially pure titanium dioxide but contain small amounts of impurities, such as iron, chromium, or vanadium, which darken them. Rutile is the thermodynamically stable form at all temperatures and is one of the two most important ores of titanium. Large deposits of anatase-bearing ore occur in Brazil.

Anatase and rutile are produced commercially, whereas brookite has been produced by heating amorphous titanium dioxide, which is prepared from an alkyl titanate or sodium titanate [12034-34-3] with sodium or potassium hydroxide in an autoclave at 200–600°C for several days. Only rutile has been synthesized from melts in the form of large single crystals. More recently (57), a new polymorph of titanium dioxide, TiO_2(B), has been demonstrated, which is formed by hydrolysis of $K_2Ti_4O_9$ to form $H_2Ti_4O_9{\cdot}H_2O$, followed by subsequent calcination/dehydration at 500°C. The relatively open structure may be considered to be formed by the removal of K_2O from $K_2Ti_4O_9$. In addition, a high pressure polymorph, TiO_2(ii), has been made, which possesses the orthorhombic α-PbO_2 structure and has a density about 2.5% greater than that of rutile. A metastable product has been formed from rutile crystals shocked to pressures greater than 330 kbar, or by heating rutile at pressures from 40 to 120 kbar at temperatures of 400–1500°C (58, 59). The phase has also been prepared when Ti_3O_5 is dissolved in sulfuric acid at elevated temperatures (60). The existence of a fluorite or distorted fluorite-type structure at very high pressures, ie, >20 GPa (200 kbar), has also been postulated (61), and structural parameters of rutile and anatase have been reviewed (62). Crystallographic information on the different forms of titanium dioxide is summarized in Table 5.

Table 6. Physical Properties of Anatase and Rutile[a]

Property	Anatase	Rutile
refractive index, 550 nm	2.54[b]	2.75[b]
dielectric constant, static		
static	48[b]	114[b]
parallel to *c* axis		170
perpendicular to *c* axis		86
high frequency		7.37[b]
parallel to *c* axis		8.43
perpendicular to *c* axis		6.84
band gap, eV	3.25	3.05
melting point, °C	converts to rutile	1830–1850
electrical conductivity, S/cm		
30°C, parallel to *c* axis		10^{-13}
227°C, parallel to *c* axis		10^{-6}
30°C, perpendicular to *c* axis		10^{-10}
227°C, perpendicular to *c* axis		10^{-7}
breakdown voltage, mV/m		15.2/17.8
hardness, Mohs' scale	5.5–6	7–7.5

[a] Refs. 5, 7, 65, and 66.

[b] Weighted mean values.

It is accepted that, at normal pressures, rutile is the thermodynamically stable form of titanium dioxide at all temperatures. Calorimetric studies have demonstrated that rutile is more stable than anatase and that brookite and TiO_2(ii) have intermediate stabilities, although the relative stabilities of brookite and TiO_2(ii) have not yet been defined. The transformation of anatase to rutile is exothermic, eg, 12.6 KJ/mol (9), although lower figures have also been reported (63). The rate of transformation is critically dependent on the detailed environment and may be either promoted or retarded by the presence of other substances. For example, phosphorus inhibits the transformation of anatase to rutile (64).

The commercially important anatase and rutile both have tetragonal structures; consequently, the values of physical properties such as refractive index and electrical conductivity depend on whether these are being measured parallel or perpendicular to the principal, ie, *c*, axis. However, in most applications, this distinction is lost because of random orientation of a large number of small crystals. It is thus the mean value that is significant. Representative physical properties are collected in Table 6.

Both anatase and rutile are broad band gap semiconductors in which a filled valence band, derived from the O 2*p* orbitals, is separated from an empty conduction band, derived from the Ti 3*d* orbitals, by a band gap of ca 3 eV. Consequently the electrical conductivity depends critically on the presence of impurities and defects such as oxygen vacancies (7). For very pure thin films, prepared by vacuum evaporation of titanium metal and then oxidation, conductivities of 10^{-13} S/cm have been reported. For both single-crystal and ceramic samples, the electrical conductivity depends on both the state of reduction of the TiO_2 and on dopant levels. At 300 K, a maximum conductivity of 1 S/cm has been reported at an oxygen deficiency of 10^{19} cm^{-3}. Reduction can be brought about by heating under vacuum and is accompanied by a color change through light to dark blue, which is reversed by heating in air. Partial reduction may also be achieved by heating in very low partial pressures of oxygen. Five valent dopants, such as niobium, are able to act as electron donors and increase the conductivity of both single-crystal rutile and rutile ceramic at dopant levels of ca 1%. Factors of between 20 and 1000 have been reported, depending on the measurement temperature and sample type. Dopants such as chromium and aluminum reduce the conductivity by a factor of ca 0.5 (5).

The reactivity of titanium dioxide toward acid is dependent on the temperature to which it has been heated. Freshly precipitated titanium dioxide is soluble in concentrated hydrochloric acid. However, titanium dioxide that has been heated to 900°C is almost insoluble in acids except hot concentrated sulfuric, in which the solubility may be further increased by the addition of ammonium sulfate to raise the boiling point of the acid, and hydrofluoric acid. Similarly, titanium dioxide that has been calcined at 900°C is almost insoluble in aqueous alkalies but dissolves in molten sodium or potassium hydroxide, carbonates, or borates.

6.4.2. Preparation

Normally, the first stage in the preparation of pure titanium dioxide is repeated distillation of titanium tetrachloride. A number of different routes may then be followed, the choice depending on the use for which the titanium dioxide is required.

Hydrolysis in aqueous solution precipitates hydrated titanium dioxide which, after washing and drying, can be calcined at 800°C to remove water and residual Cl. This method has been the basis of producing titanium dioxide of 99.999% purity. If retaining a high specific surface area is important, it may be convenient to reduce the residual Cl content by Sohxlet extraction rather than calcination. For many electroceramic uses, the millability of the product is as important as the absolute purity. A number of process variants designed to modify particulate morphology have been described (67). Titanium dioxide with silica, magnesium, and iron contents as low as 10^{-5} wt % can be achieved by converting the initial hydrous titanium dioxide precipitated from $TiCl_4$ into the double oxalate [10580-02-06] $(NH_4)_2[TiO(C_2O_4)_2]$, recrystallizing this from methanol, and then forming the oxide by calcination (68). Alternatively, the titanium tetrachloride may be converted into an alkoxide, eg, the often-used titanium isopropoxide [546-89-9] (isopropyl titanate), which is then hydrolyzed, washed, and dried. The hydrolysis products have a well-defined spherical morphology but may retain considerable amounts of organic residues (69).

A high purity titanium dioxide of poorly defined crystal form (ca 80% anatase, 20% rutile) is made commercially by flame hydrolysis of titanium tetrachloride. This product is used extensively for academic photocatalytic studies (70). The gas-phase oxidation of titanium tetrachloride, the basis of the chloride process for the production of titanium dioxide pigments, can be used for the production of high purity titanium dioxide, but, as with flame hydrolysis, the product is of poorly defined crystalline form unless special dopants are added to the principal reactants (71).

6.4.3. Nonpigment Uses

Welding electrodes, used in shielded metal-arc welding, consist of a mild steel or stainless-steel core wire coated with a flux layer. The TiO_2 is used as a fluxing agent, slag former, and shade modifier in the electrode, with other minerals performing gas shielding, fluxing, and extrusion aid functions. There are many different types of electrodes produced for different applications. The electrodes are classified by the American Welding Society and other worldwide organizations relating to their strengths and uses. Certain electrodes can be used for flat and horizontal welds and others only for flat-welding applications. The electrodes have special properties and formulations, depending on their applications. Certain fluxes are produced with high sodium and iron oxide levels; others with low potassium or hydrogen levels, or high titanium and sodium mixes. The flux coverings dictate the application of the electrode, its tensile strength, and whether they can be applied with alternating current or direct current. The composition of the electrode flux covering determines the performance of the electrode and the soundness of the weld. A typical electrode may have 12 separate minerals, as detailed in Table 7. The thickness of the flux cover varies from 10 to 55% of the diameter of the electrode. These coverings are usually applied by extrusion of the flux onto the core wire using a blend of sodium and potassium silicate solution as the binder. Stainless-steel core wires require different coverings because of reactivity.

The ultimate formulation, involving the use of different minerals, will produce different arcs. Some yield a semiglobular viscous slag that allows welding of joints with a poor “fit.” Others are used at higher welding currents due to their low cellulose content and high refractory material content, ensuring more specialized

Table 7. The Typical Functions and Composition for Standard Mild Steel Welding Electrodes[a]

Constituent of covering	Function of constituent		Composition range, %
	Primary	Secondary	
cellulose	shielding gas		2–12
calcium carbonate	shielding gas	fluxing agent	0–5
fluorspar	slag former	fluxing agent	
dolomite	shielding gas	fluxing agent	
titanium dioxide (rutile)	slag former	arc stabilizer	30–55
potassium titanate	arc stabilizer	slag former	
feldspar	slag former	stabilizer	0–20
mica	extrusion	stabilizer	0–15
clay	extrusion	slag former	0–5
silica	slag former		
asbestos	slag former	extrusion	
manganese oxide	slag former	alloying	
iron oxide	slag former		
iron powder	deposition rate	contact welding	
ferrosilicon	deoxidizer		
ferromanganese	alloying	deoxidizer	5–10
sodium silicate	binder	fluxing agent	5–10
potassium silicate	arc stabilizer	binder	5–15

[a] IBMA.

welding. Use of electrodes containing more potassium permits the use of low open-circuit voltage, which is a common application for welding sheet materials.

Rutile, or a TiO_2 substitute, is consumed in the flux covering, in the range of 30–55%, depending on the grade. Welding electrode manufacturers prefer natural rutile or leucoxene, because the product is crystalline and contains higher concentrations of TiO_2. Ilmenite and synthetic rutile (SR) are also being considered as a feedstock, but because of the porous nature of the (SR), more silicates are required to ensure effective extrusion of the flux. Also, because natural rutile is in short supply, some specialized welding rod flux coverings contain untreated anatase TiO_2 pigments. Synthetic rutile is also more red in color than natural rutile; therefore, some carbon-black pigment has to be added to match the color of the "natural" electrodes. This is more for cosmetic than physical purposes since the color does not affect the welding properties of the electrode.

Stainless-steel electrodes have different impurity criteria than do mild steel electrodes. Here the Cr and Ni contents are critical. Iron must also be kept under control to prevent a slight "running" problem in vertical down welding. Some adjustments of the flux formulations have to be made to prevent this problem from occurring.

Mild steel electrodes are sensitive to sulfur and phosphorous levels. These will affect the strength of weld metal. In certain applications the sulfur also makes the weld brittle, and phosphorus can cause pitting of the welds. Particle size is important. A uniform, but fine, particle size is required to ensure even covering of the electrode. The stainless industry require a product that is minus 70 Tyler mesh.

The demand worldwide for titanium minerals in the welding electrode industry is approximately 120,000 Te TiO_2 units per year. This is divided between natural rutile, synthetic rutile, and leucoxene, and small amounts of anatase TiO_2 are now used. There are four or five very large consumers, who have grown by consolidation: Esab, Lincoln Electric, Aire Liquid, and Thyssen-Bohler. Approximately 50% of the welding electrodes are produced in Southeast Asia and the Far East.

The traditional ceramic applications of titanium dioxide are in vitreous enamels, thread guides for the fibers industry, and electroceramics. In enamels used on steel and cast iron, titanium dioxide makes up part of the raw-material batch and dissolves during frit smelting. As the enamel cools and fuses to its substrate, the titanium dioxide recrystallizes and confers both improved opacity and acid resistance. To avoid color effects, elements such as tungsten and niobium must be carefully controlled. For ease of handling, it is convenient to use a coarse grade of TiO_2. Thread guides for the fiber industry are made by firing anatase or rutile at ca 1300°C to produce a dense ceramic that can be polished to allow easy drawing of the fiber over the guides during spinning. Friction between the threads and the guides generates static electricity. To dissipate this, the electrical conductivity of the fired pieces is increased by a second firing under reducing conditions. In a separate application area, reduction of rutile to lower oxides such as Ti_4O_7 gives a conducting ceramic known as Ebonex, which has potential as an electrode material (44). The preparation, stability, and properties of titania-based ceramic membranes constitute an area of active research (72).

Titanium dioxide may be used in varistors, electrical circuit elements for which $I = KV^{a}$, where $a > 1$. TiO_2 varistors find particular use for low voltage applications in arc prevention in small motors. Titanium dioxide may also be used as a ceramic sensor for oxygen in automotive exhaust systems. Feedback from the detector controls the air–fuel ratio to minimize pollution. The basis of the device is the sensitivity of the resistance of titania to the oxygen partial pressure, because the removal of oxygen from the titania increases the number of electrons in the conduction band. The rapid response time, about 40 ms, over the full range of oxygen pressures suggests that the measured changes are dominated by surface effects (see Sensors) (73).

The main electroceramic applications of titanium dioxide derive from its high dielectric constant (see Table 6). Rutile itself can be used as a dielectric in multilayer capacitors, but it is much more common to use TiO_2 for the manufacture of alkaline-earth titanates, eg, by the cocalcination of barium carbonate and anatase. The electrical properties of these dielectrics are extremely sensitive to the presence of small (<20 ppm) quantities of impurities, and high performance titanates require consistently pure (eg, $>99.9\%$) TiO_2. Typical products are made by the hydrolysis of high purity titanium tetrachloride.

In the rubber and leather industries, a small quantity of TiO_2 incorporated into the finished product imparts a high degree of whiteness while permitting most of the natural properties of the rubber or leather to be retained.

The fact that TiO_2 is chemically and biologically inert means that it can be used for cosmetics, soap, pharmaceuticals, and certain types of foodstuffs, where whiteness is considered to be important for marketing reasons. TiO_2 is finding increasing use as a uv-A and uv-B absorber in sunscreens (74, 75).

The use of TiO_2 as a catalyst, either as an active agent or as an inert support, is small. On a commercial scale, phthalic anhydride produced by catalytic oxidation of orthoxylene is one of the most important uses of TiO_2 (76, 77). Together with vanadium pentoxide, TiO_2 is ideal for reducing the nitrogen oxides content of exhaust gases by catalytic reduction (78); it is also used as an oxygen sensor for monitoring engine performance, controlling the fuel/air ratio, and thereby minimizing fuel consumption and pollution. TiO_2 impregnated with platinum or nickel is used in the Fischer–Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen and in the photocatalytic splitting of water.

Activity for the removal of hydrogen sulfide and carbon disulfide has been claimed (79). Anatase has received much research interest in the photocatalytic degradation of pollutants, eg, to remove trace amounts of pesticide residues from water (80, 81) (see Photochemical technology, photocatalysis).

TiO_2 is used for the production of various specialized titanium compounds, including titanium carbide and various titanates. Titanium carbide is often made by heating a mixture of TiO_2 (or rutile) with carbon in a vacuum at 1820°C in the presence of hydrogen. Some producers use the *menstruum process*, where a mixture of TiO_2, iron, and carbon is heated to 2670°C by induction heating. Titanium carbide is used to an increasing extent for the tips of cutting tools, either on its own or with tungsten carbide.

Titanates are typically prepared by heating mixtures of TiO_2 with the oxide, carbonate, or hydroxide of the respective metal (barium, strontium, potassium, etc). Potassium hexaflurotitanate (K_2TiF_6) is used for grain-refining aluminum. K_2TiF_6 is currently the largest volume chemical made from TiO_2 Barium titanate has a very high dielectric constant—10,000 at 120°C (its Curie point)—and low dielectric hysteresis; in these respects it is similar to a permanent magnet. It is also piezoelectric and has been used for ceramic transducers for the interconversion of sound and electrical energy. There are good prospects for barium titanate to displace Rochelle salt and quartz for certain applications of ceramic transducers. Strontium titanate has similar electrical properties and has been used for "atomic batteries" for powering navigational lights at offshore oilrig drilling platforms. Potassium titanates in fiber form have been used as thermal insulation, as plastics reinforcing fibers, and in friction-reducing devices. They have also been used for various electrical applications.

TiO_2 can be used as a single-crystal electrode for the electrolysis of water to produce hydrogen, and this may well become the basis for important applications of TiO_2 if hydrogen fuel cells become accepted for powering vehicles, submarines, spacecraft, etc. TiO_2 has also been used in thermistors to measure temperature changes at elevated temperatures or in difficult envrionments (82–84).

6.4.4. Pigmentary Titanium Dioxide

The most important commercial use of titanium dioxide is as a white pigment in a wide range of products, including paint (qv), plastics, paper (qv), and inks (qv) (8, 85, 86). Because of its opacifying properties, TiO_2 is used not just in whites but to opacify colored systems also. Titanium dioxide is the predominant white pigment both because of its high refractive index and because technology has been developed to allow the right size range and the necessary chemical purity.

In order to appear white, a pigment must have minimal optical absorption at visible wavelengths. For titanium dioxide, this in turn requires high chemical purity; in particular, transition-metal impurities must be eliminated as far as possible. Because titanium dioxide pigments do not significantly absorb visible light, their opacity derives from their ability to scatter light. Light scattering by particles depends on their refractive index. A measure of the effect of refractive index on opacity can be achieved by using a simplified form of an equation introduced by Fresnel, which gives the reflectivity, R, of a coating by

$$R = \frac{\left(n_p - n_m\right)^2}{\left(n_p + n_m\right)^2}$$

where n_p is the refractive index of the pigment and n_m the refractive index of the medium in which the pigment is dispersed. This is 1 for air and typically ca 1.5 for an alkyd paint resin. Hence, the higher the value of the pigment refractive index, the higher its potential opacity. Both anatase and rutile are used as white pigments, and scatter light more efficiently than other oxides (Table 8). Because of its higher refractive index, rutile has a higher opacity than anatase and is more widely used. Anatase is, however, used for many specialized applications, eg, in paper and in fibers, where the lower abrasivity of anatase causes less wear on thread guides and other spinning equipment. In order to realize the maximum scattering power, the pigment particles must be of the correct size, ie, light-scattering is a function of d/λ, where d is the diameter of the scattering particle and λ the wavelength in a particular medium of the light. Maximum scattering of visible (400–700 nm) light occurs for pigment particles of ca 300 nm and the scattering efficiency decreases rapidly as the particle size varies from the optimum. This decrease is by about 60% for particles twice the optimum size. Therefore careful control of particle size is necessary. Two further desirable properties are that titanium dioxide is nontoxic and that its density (ca 4000 kg/m^3) is sufficiently low as not to cause excessively rapid settling of the pigment particles in paint. Although titanium dioxide does not absorb visible light, it is a strong absorber of uv radiation. In paints opacified with titanium dioxide, the pigment protects the organic film-forming molecules from photochemical degradation by solar uv. However, absorption of uv by TiO_2 can lead to the generation of hydroxyl radicals, which cause the pigment to act as a photocatalyst. The net effect of the pigments on the uv stability, ie, the durability, of a paint is a balance between the protective and photocatalytic effects. In order to ensure that the actual effect is beneficial, the photocatalytic effect of the pigment is minimized by coating the pigment with hydrous oxides, eg, silica and alumina, during manufacture. This coating treatment is also applied to facilitate

Table 8. Refractive Indexes and Reflectivities of White Pigments

		Reflectivity, R, in air ($n_m = 1$)		Reflectivity, R, in alkyd resin ($n_m = 1.5$)	
Pigment	Refractive index, n_p	$R \times 100$	relative to rutile = 100	$R \times 100$	relative to rutile = 100
rutile	2.72	21.4	100.0	8.36	100.0
anatase	2.55	19.1	89.2	6.72	80.4
antimony oxide	2.20	14.1	65.8	3.58	42.8
zinc oxide	2.01	11.3	52.7	2.11	25.3
lithopone	1.84	8.7	40.9	1.04	12.4
kaolin	1.56	4.8	22.4	0.04	0.5

Table 9. Applications for TiO_2 Pigments, %[a]

Application	North America	Western Europe	Japan	Asia/Pacific	ROW	Total world
surface coatings	50.8	57.0	54.0	59.4	75.2	56.8
plastics	20.3	24.1	13.5	17.2	12.5	19.6
paper	22.3	9.6	11.5	7.5	4.0	13.6
printing inks	2.1	3.1	11.1	2.9	3.1	3.3
fibers	0.8	1.6	3.6	3.7	0.9	1.7
other	3.7	4.6	6.3	9.3	4.3	5.0
Total	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*

[a] IBMA.

good pigment dispersion in the medium of application. Good dispersion ensures that the pigment scatters light efficiently and does not contribute to any surface roughness that would otherwise reduce the gloss of, eg, the final paint.

In every region of the world, the largest single end use for TiO_2 is in surface coatings. However, the percentage of the total amount of TiO_2 going into this end use varies widely by region. Table 9 shows this distribution. Thus the amount of TiO_2 used for surface coatings varies from a high of 75% in the ROW to a low of 51% in North America. The reasons for these skewed distributions arise from a number of economic and technical factors. For example, there is very little paper manufactured in the ROW markets because of the aridness of the region and therefore the percentage of TiO_2 going into surface coatings is greater.

6.5. Surface Coatings

Although white pigments are used in virtually all types of surface coatings, their principal use is in liquid paints (because they are more highly pigmented than most other surface coatings) and to an increasing extent, powder coatings.

Surface coatings in which TiO_2 is used are generally categorized according to their end-use applications. A list of the types of surface coating that make up the major markets for TiO_2 is given in Table 10.

In the United States, TiO_2 pigments for surface coatings are frequently classified according to the ASTM D476-84 standard. This standard defines four types of TiO_2:

Type I: Anatase, free chalking
Type II: Rutile, medium chalk resistance for low-pigment-volume-concentration) (PVC) coatings
Type III: Rutile, medium chalk resistance for medium/high PVC coatings
Type IV: Rutile, highly chalk-resistant

All anatase pigments are classified under Type I and have a minimum of 94% TiO_2. Type II rutile pigments have some degree of surface treatment to enhance their dispersibility and their weatherability. They have a

Table 10. Types of Surface Coating in Which TiO_2 Is Used[a]

architictural	interior	gloss
architectural	interior	semigloss
architectural	interior	flat
architectural	primer	
architectural	exterior	gloss
architectural	exterior	semigloss
architectural	exterior	flat
automotive	topcoat	
automotive	primer/surfacer	
automotive	ED primer	
automotive	refinish	
coil, extrusion, sheet	interior	
coil, extrusion, sheet	exterior	
powder coatings	interior/UV resistant	
powder coatings	interior	
powder coatings	exterior	
appliance		
container		
protective		
marine		
general industrial		
traffic		
polyester–gel		
high solids	interior	
high solids	exterior	

[a] IBMA.

minimum of 92% TiO_2. Types III and IV pigments generally have greater amounts of surface treatments to further improve their weatherability characteristics. Each grade specifies a minimum TiO_2 level of 80%.

In Europe, the grading system is defined by the International Standard ISO 591-1977 (1985), which is somewhat different from the ASTM standard. The ISO standard divides TiO_2 pigments into two Type A anatase grades, and three Type R rutile grades:

Grade	TiO_2
A1	98
A2	92
R1	97
R2	90
R3	80

Grade A1 is uncoated anatase pigment; Grade A2 is the coated type. Grade R1 is basically an uncoated grade, that is, made with little or no posttreatment. Grades R2 and R3 are increasingly surface treated, with the majority of rutile pigment production currently falling into the R2 category.

The Japanese grading system for TiO_2 pigments is JIS K5116-1973 (1979). It is somewhat similar to the ISO standard, except that four grades of rutile are specified, three containing a minimum of 92% TiO_2 and the fourth a minimum of 82%. Also specified are the types of coatings (alumina, silica, and zinc oxide) used in the respective grades.

In most countries of the world, either the ASTM or the ISO standard is used. The Japanese system is utilized in the domestic Japanese market.

Generally, a pigment producer will publish information as to which pigments are recommended, (and sometimes “highly recommended”), for which particular applications. Such recommendations are never cut-and-dried since each paint formulation represents a highly complex compromise of paint performance, paint manufacturing considerations, application considerations, cost and other factors. Each paint manufacturer will have its own product priorities as to which are the relatively more important factors and which are less critical. Thus the paint formulator will take into account the TiO_2 producer’s recommendations, but must overlay his own priorities onto those suggestions. Cost is frequently an overriding consideration, and a manufacturer may produce several lines of paint (usually under separate brand names) that sell in different price ranges. Obviously, in the case of the higher-priced products, the formulator can afford to incorporate superior performance properties.

6.6. Plastics

The plastics industry is the largest user of TiO_2 after the surface coatings industry, consuming approximately 20% of the world’s production of the pigment. TiO_2 itself represents over 65% of the colorants used by the plastics industry.

In their unpigmented state most plastics are either clear or at least somewhat translucent. Except in a few cases, the translucence is due to the various additives incorporated into the pure resins to modify their properties and make them more suitable for their intended end-use applications.

Plastics applications can be divided into two very large and diverse groups: those in which the material is used in a transparent or translucent condition, and those in which complete opacity is required, either for esthetic or practical reasons.

Little or no coloration of plastics is desired in many decorative packaging applications, as well as in certain items of construction such as windows and, architectural partitions. Many applications of plastics, however, require that it be opacified either as a white or a colored material. Even in the case of many colored plastics, a quantity of white pigment is added to enhance the hiding powder of the colorant. Thus, given the tremendous quantity of plastics now used in the world’s economies, the market for white pigments is obviously large and growing.

As in the case of surface coatings, it has long been established that the most cost-effective white pigment for the majority of plastics is TiO_2 because of its many excellent properties. An additional property of TiO_2 pigments—dispersibility—is critically important in plastics because uniform dispersion of the pigment within the plastic matrix is needed to impart maximun opacity without causing a loss of physical or optical properties. Organic surface treatments on the TiO_2 pigments are utilized to facilitate their dispersion in the viscous molten plastic resin. It is believed that TiO_2 currently accounts for over 90% of the inorganic pigments used in plastics. This figure excludes extenders, or fillers, large tonnages of which are used in certain plastics applications, such as flooring, to lower the cost of the final product.

Because of the many pigment properties involved in the use of pigments in plastics, there are a large number of TiO_2 grades marketed for use in the plastics industry. Some TiO_2 producers offer many different grades, covering most possible applications and suggesting more than one grade for many applications to give the formulator a wide degree of flexibility in selecting pigments for specific end-uses. Other producers offer only a few grades to the plastics industry that are designed to cover most plastics applications.

The products offered by the typical TiO_2 producer usually include a number of multipurpose grades that are also recommended for paints, inks, paper coatings, and other applications. However, most pigments producers also offer grades that are explicitly designed for use in plastics. These tend to be products that are highly treated to enhance their dispersibility. Not all plastics grades are recommended for use in all types of resin. Although a good multipurpose pigment can be used in most resins, in some cases, a second grade will have a more optimum set of properties for certain resins. For example, a pigment grade that is designed for used in melt resins may not be as appropriate for a liquid resin as another grade of resin.

Almost all rutile TiO_2 grades recommended for use in plastics will have received an organic posttreatment during production to improve their dispersibility. The high-dispersibility grades receive siloxane or amine posttreatment instead of, or in addition to, their basic organic treatment.

Among the types of pigment offered by the typical TiO_2 producer are grades specifically recommended for exterior use. These may be all-purpose grades that are also recommended for use in, for example, automotive finishes and exterior architectural paints. Or they may be specific plastics grades treated for exterior use. Generally, any TiO_2 grade to be used in exterior applications will have received a posttreatment that included silica in addition to the usual alumina coating.

In many TiO_2 applications today, a blue undertone is highly desirable, often to mask an intrinsic yellowness in the color of the resin or a slight degradation which occurs during the high-temperature processing required to disperse the pigment. Blue undertone pigments are frequently available in weatherable and nonweatherable grades.

Since lacing can be a problem in certain high-temperature fabrication operations, such as extrusion, nonlacing grades of TiO_2 are frequently offered. These are usually chloride process pigment, which have minimum moisture content compared to sulfate process product and can be used at the temperatures required for such operations.

6.7. Paper

In its simplest form, paper is a dried web of randomly oriented vegetable and/or wood fibers in the configuration of a mat. It is formed by layering a slurry of the fibers dispersed in water onto a fine screen, draining the water and drying. Paperboard is fundamentally the same but much thicker, and a perforated cylinder is used to form the fiber mat instead of a screen.

Although modern-day paper, paperboard, and paper laminates, are much more complex products than described above, they are essentially variations on the same basic structure. Today's products also contain, in addition to fibers, a number of chemical additives and usually one or more inorganic fillers.

For many applications, coatings are applied to paper and paperboard variously to improve their appearance, to enhance their printability, and to impart other properties such as high slip and grease resistance. The coatings contain, in addition to various binders, dispersing aids and other additives, large amounts of inorganic fillers.

6.7.1. Paper (Web) Manufacture

Although the use of TiO_2 in paper far exceeds that used in coatings for paper and paperboard, the quantities going into coatings have increased greatly in the late 1990s. In North America, TiO_2 accounts for about 4% of the total tonnage of fillers used; in Europe, the amount is less than 1%. Because TiO_2 costs 10–15 times as much as the other inorganic fillers, the value of the TiO_2 used by the paper industry is roughly equivalent to that of all other fillers combined.

Worldwide, about 12% of TiO_2 production goes into the paper industry. The relative amounts used in various parts of the world, however, differ widely. Per capita TiO_2 consumption for paper manufacture in the United States is four times the West European figure and five times the Japanese figure.

In printing papers, which are derived from highly refined and high-strength pulps, the major criterion for TiO_2 pigments is opacity, especially since double-sided color printing is often used. In writing papers and carton boards, the major criterion is whiteness.

6.7.2. Paper Coatings

Coatings for paper and paperboard are widely and extensively used. Generally a coating consists of a binder, additives, and pigment. Although traditionally, low-cost natural products such as starch and casein were used as binders, synthetic polymeric resins have played an increasing role in their formulation. Additives for paper coatings have much the same function as they do in surface coatings; they are used as levelers, defoamers, rheology modifiers, dispersing aids, and other agents. Fillers often make up as much as 70–90% of the dry weight of the coatings. Most of the filler is kaolin clay and varieties of calcium carbonate. Calcium carbonate is added to impart whiteness to a coating. In coatings for applications in which opacity and brightness of are of prime concern, small amounts of TiO_2 are added to the fillers.

Anatase TiO_2 has traditionally been used in coatings because of its lower cost, and, since it is softer than rutile pigments, anatase pigments may cause less abrasive wear on papermaking machines. In the late 1990s, however, rutile has made major inroads into the coatings market. In those applications in which an optical brightener has been added, however, anatase is preferred.

A broad-ranging development in the paper industry has been the use of aqueous TiO_2 slurries. These are dispersions of TiO_2 in water (with appropriate additives) manufactured by the TiO_2 producers and shipped in various types of bulk containers. They eliminate the need for the paper producer to go through a TiO_2 dispersion process.

Both anatase and rutile TiO_2 are available as slurries in the North American market As much as 80% of the TiO_2 used in paper coating is shipped as slurries. In the early 1990s, the supply of aqueous slurries was extended to the Scandinavian paper industry, but elsewhere in Europe and the rest of the world, this type of TiO_2 product has limited availability.

6.7.3. Paper Laminates

Laminated papers are used to manufacture both high- and low-pressure decorative Formica-type laminates. A high pressure laminate is a construction consisting of 8–10 layers of resin impregnated paper converted by heat and pressure into a plasticlike material. The face is a translucent sheet of textured or untextured melamine resin treated paper. The second layer is the printed pattern (often wood grain) or colored sheet, which is also melamine resin impregnated. The remaining sheets are phenolic resin impregnated kraft filler papers. The sandwich construction is heated to a temperature in excess of 265°C and compressed to pressures as high as 82.6×10^3 Pa (1200 psi) for a period of 60–90 min to convert the sandwich to a printed, textured rigid plastic laminate. High-pressure laminates are typically used for horizontal surfaces experiencing wear and abrasion such as counter tops and furniture wear surfaces.

Low-pressure laminated papers include virtually every other laminated paper used to impart a wood grain, decorative, or solid image to a rigid substrate. Included in this broad category are low basic weight papers, intermediate weight foils and papers, melamine- or polyester-saturated papers that are thermoally fused, vinyl films, and hot-stamped foils.

TiO_2 pigments are used to impart brightness and opacity to the face papers in the laminate construction and often to impart opacity to the entire construction. Pigment loadings will vary considerably according to the base papers used—their color, weight, composition, and other variable factors. The whiter the paper, the greater the loading of pigment. Rutile pigments are used exclusively in paper laminates. Loadings for the whitest face papers can be as much as 50% of the furnish, and as low as 20% for the entire laminate construction.

The pigment is often applied as a dispersion into the wood pulp and saturates it. Sometimes, the pigment is dispersed into the melamine resin mix. Both short- and long-fiber wood pulps are used, and the pulp is considered to be the carrier for the pigment. Above all else, the pigment must provide opacity throughout the laminate and a good printable surface for the printed pattern layer to accurately reproduce complex and realistic wood grain patterns.

Some, but not all, of the pigments used are heat-treated to withstand the laminating process without discoloration.

6.7.4. Available for Paper

Anatase TiO_2 has traditionally been more widely used than rutile for most filler or paper stock applications for opacity, with the exception of resin-bonded laminate papers and waxed papers. The preference for the anatase form grew from the fact that it has a lower specific gravity and is therefore better retained at the wet end of the paper machine and that it imparts a cold blue white appearance instead of the yellow cast imparted by rutile. Also, the anatase crystal is softer than rutile and is less abrasive of rollers, calendars, and other paper-contacting components of papermaking machinery. However, over the years Du Pont has developed applications technology to overcome rutile's shortcomings, and rutile has steadily grown in paper stock because of its superior opacity compared to anatase. Presently, more than half the TiO_2 used in paper stock is rutile.

In coatings, however, rutile is much more widely used because its brightness and opacity is superior to that of anatase in most coatings applications. It is almost always used in conjunction with other fillers such as clays. If, however, the coating or the paper is formulated to contain optical brighteners, anatase may be preferred because it absorbs less uv radiation than rutile, thus leaving more uv available for the optical brighteners. Also, rutile TiO_2 tends to floculate fluorescent whitening agents in some paper-coating formulations. Fluorescent whitening agents are often used as optical brighteners.

6.7.5. Printing Inks

A small but important market for TiO_2 is in printing inks. Although carbon black is the major pigment used in the manufacture of printing inks, decorative printing would be much less vividly rendered and less attractive without the use of TiO_2.

The use of TiO_2 in printing inks has much in common with its use in surface coatings. Thus, printing inks may be considered a highly specific type of surface coating, but with several significant differences. Most of these arise from the fact that ink films are generally much thinner than those of surface coatings.

Although the optical properties of a printing ink film are quite similar to those of a surface-coating film, the thinness of the ink film imposes special requirements on the structure and formulation of the ink. When light strikes the ink film, reflection, refraction, diffraction, and absorption of the incident light all occur. If the film is pigmented with TiO_2, however, absorption is not a major factor because visible light is only slightly absorbed by the white pigment. If, however, the pigment is colored, absorption becomes the dominant mechanism of the interaction of light with the film. Thus, film thickness is much less a consideration in hiding of the substrate in ink films than is the case in surface coatings.

Since ink films are usually thin, a relatively heavy loading of TiO_2 must be used, with a high pigment volume concentration, in order to accomplish effective hiding of the substrate. However, the high pigment volume concentration decreases the efficiency of the pigment because the resultant pigment crowding pushes the pigment particles closer together than the optimum spacing of about one particle diameter. The larger the pigment particle, the more efficient it will be in imparting hiding to the ink. Unfortunately, because of the thinness of the ink film, there will be a tendency for the pigment particles to protrude through the surface of the film, thus degrading gloss. Thus, the formulation of a printing ink to be used for gloss applications requires a judicious balancing of grade of TiO_2, dispersion, pigment loading, and selection of pigment vehicle. If the ink is to have a matte finish, the coarser pigments can be used.

To obtain a glossy ink film surface, a very small particle size TiO_2 must be used. Generally, TiO_2 for high gloss inks will have an average particle diameter of about 0.17 μm. Moreover, excellent dispersion of pigment in the vehicle must be achieved, with flocculation minimized. Pigments for gloss printing inks are generally grades that have been treated to improve dispersibility.

A principal use for TiO_2-pigmented inks is in base coatings for packaging. It has long been known that when clear packaging is printed with colored inks, the printed images are transparent and dull because of the poor hiding power and light-scattering characteristics of the typical color pigment. However, if the clear packaging material is first coated with a TiO_2-containing white ink, and then overprinted with the colored ink, the color of the ink is greatly intensified and brightened. The reason for this is that the TiO_2-pigmented undercoat prevents more of the incident light from reaching the substrate and instead reflects it back up through the colored ink printed on top of it. The result is much more vivid and bright color printing on the packaging material. This type of printing is now used with a large number of clear packaging materials, including cellophane, polyethylene, polypropylene, poly(vinyl chloride) (PVC), and polyester.

Some TiO_2 producers offer a grade of pigment designed explicitly for printing inks. These are a fine particle grade for gloss inks, a highly coated, couarser grade for matte-type inks, and a grade with some degree of weatherability for inks to be used in outdoor applications.

6.7.6. Synthetic Fibers

TiO_2 is widely used as a delusterant for a number of synthetic fibers. Its presence in small amounts (1–2%) helps to diffuse the intrinsic high-gloss appearance of many such fibers. This enables them to take on an appearance more like that of the natural fibers, most of which have a more or less dull surface. The presence of TiO_2 also increases the whiteness and opacity of the fibers and decreases the tendency of some fibers towards translucency.

The type of pigment used is of the anatase type. The chief reason for this is that anatase is much less abrasive than rutile, and synthetic fibers during manufacture and subsequent weaving and knitting into finished goods come into sliding contact with metal guides and similar equipment. Fiber that has been delustered with anatase will exhibit much less wear and tear on the various pieces of equipment through which it passes, and also causes much less fiber breakage than rutile during the fiber forming process.

Since many fibers also contain optical whiteners in addition to TiO_2, anatase is required since rutile will interfere with the mechanism of the optical whitening activity.

Anatase grades recommended for fiber production have usually received organic surface treatments to enhance dispersibility. In addition, two grades are typically available for fibers: one that is dry-milled, that is, has received no inorganic oxide treatment; and one that has been treated with silica and/or alumina. This is a specialized market requiring scrupulous quality control and relatively intensive technical service support.

6.7.7. Ceramics

There are a number of applications for TiO_2 in ceramics. In most of these, TiO_2 is utilized for its chemical properties rather than as a white pigment. In some applications, TiO_2 is used to produce a white hue in a ceramic glaze. In the manufacture of certain types of glass, the high refractive index of TiO_2 is utilized for its effect on the overall refractive index of the glass.

TiO_2 has long been used in the preparation of vitreous (porcelain) enamels for coating glass, aluminum, steel, cast iron, and other materials. In this application, it reacts with the other components of the feedstock mixture, including borax, feldspar, quartz, fluorspar, soda, and metal oxides.

Relatively coarse grades of TiO_2 are made for enameling, and it is important that the concentrations of tungsten and niobium in the feedstock be minimized because even small traces of these elements discolor the enamel. The inclusion of TiO_2 in the feedstock mixture improves its resistance against acid attack and enhances opacity, thus making it possible to use thinner coats of enamel and thereby reducing the risk of flex-induced cracking. Enamels of this type are used for domestic appliances, road signs, sanitarywares, and other applications.

Because of its unique photocatalytic properties, TiO_2 is widely used in electroceramics, such as for the manufacture of miniature ceramic capacitors. For this purpose, high-purity rutile-type TiO_2 is pressed into the required shape, then heated until the particles sinter at 1400–1450°C. On a worldwide basis, growth in electroceramics has more than offset a decline in enameling usage, so that overall there has been slight growth in TiO_2 consumption in the ceramics industry.

The most common grades of TiO_2 recommended for ceramics are a granular form and a dry milled grade that has not received inorganic oxide coating but may have received an organic treatment to enhance dispersibility. Generally, the untreated anatase is used in glazes and glasses, whereas the granular form is used in all types of ceramic frits.

Two pigment production routes are in commercial use. In the sulfate process, the ore is dissolved in sulfuric acid, the solution is hydrolyzed to precipitate a microcrystalline titanium dioxide, which in turn is grown by a process of calcination at temperatures of ca 900–1000°C. In the chloride process, titanium tetrachloride, formed by chlorinating the ore, is purified by distillation and is then oxidized at ca 1400–1600°C to form crystals of the required size. In both cases, the raw products are finished by coating with a layer of hydrous oxides, typically a mixture of silica, alumina, etc.

A hydrochloric acid process for the manufacture of anatase has been proposed but has not been developed. Other routes include fluoride, bromide, nitrate, sulfide, and chloroacetate processes (1). None of these, however, has been used successfully on a commercial scale.

6.7.7.1. Mineral Feedstocks. The titanium-bearing ores ilmenite [12168-52-4], natural rutile, and leucoxene [1358-95-8] used in the production of titanium dioxide pigment occur as mineral sands and massive hard rock in many parts of the world (87). Increasingly, mining companies process these natural ores to extract iron and other minerals to produce slags, or synthetic rutile having higher TiO_2 contents than the original ore. World production of the various types of titanium ore is summarized in Table 11. About 97% of these TiO_2 concentrates were used for pigment production. The choice of ore depends on the production process used. Ilmenites can be attacked by sulfuric acid, the first step in the sulfate process. Ilmenite is ideally ferrous titanate, $FeTiO_3$, having an ideal composition of 52.7% TiO_2 and 47.3% FeO, but usually includes some ferric iron. It can occur either in massive form, for instance, in Norway and Finland, or as a constituent of ancient beach sands, which are not necessarily on the present coast line, for example, in Florida, southern India, and Australia. Ilmenite in sands is often much altered by oxidation and leaching. The ratio of ferric to ferrous iron increases and the total amount of iron falls. Consequently, the amount of titanium dioxide increases. On further weathering, the form of titanium dioxide also changes, passing through leucoxene [1358-95-8] and pseudorutile [1310-39-0] stages to rutile. Typical analyses of TiO_2 process feedstocks are collated in Table 9. Ilmenites from rock deposits typically contain 45% TiO_2, but beach sand ilmenite deposits, because of oxidation/hydrolysis and expulsion of Fe_2O_3, can contain more than 55% TiO_2. These are widely used in the sulfate process, although extreme weathering ($>60\%$ TiO_2) can reduce their reactivity in sulfuric acid, and hence their usefulness. Ores containing high levels of transition-metal impurities are not used because of the deleterious effects of these impurities on color. Strict limits are imposed on thorium and uranium levels for radiological reasons. Neither leucoxene, pseudorutile, nor rutile are attacked by sulfuric acid under the conditions normally used for pigment manufacture.

Although ilmenites and leucoxenes can be used in the chloride process, ores having higher TiO_2 contents, eg, mineral rutile, which is not readily attacked by sulfuric acid, are preferred in order to minimize loss of chlorine in iron chloride by-product.

Both processes also use up-graded ilmenite (slags). About 30% of the world's titanium feedstocks are supplied by titanium slag producers in Canada, South Africa, and Norway. Slags are formed by the high temperature reduction of ilmenites in electric furnaces. Much of the iron oxide content is reduced to metallic iron and separated as a saleable by-product. Magnesium and other impurities may also be incorporated in the following equations.

$$2\ FeTiO_3 + C^0 \longrightarrow FeTi_2O_5 + Fe^0 + CO$$

$$3\ FeTi_2O_5 + 5\ C^0 \longrightarrow 2\ Ti_3O_5 + 3\ Fe^0 + 5\ CO$$

Table 11. Analyses of Titanium Dioxide Process Feedstocks

	Ilmenite			Slag		Rutiles		Synthetic rutiles	
	Massive	Beach sand							
Component, wt %	Norway	West Australia	United States, Florida	Canada	South Africa	West Australia	South Africa	West Australia	West Australia
TiO_2	44.3	54.77	64.7	77.5	85.8	95.5	94.5	93	92.3
FeO	34.8	19.27		10.9	10.5				
Fe_2O_3	11.5	21.2	30				0.8		
Fe metal				0.5	0.1			0.85	
total iron				9	8.3			3	2.48
Cr_2O_3	0.075	0.04	0.17	0.17	0.17	0.15	0.14	0.07	0.12
V_2O_5	0.2	0.14	0.15	0.56	0.44	0.55	0.33	0.3	0.26
SiO_2	2.6	0.78	0.45	3	2.1	0.8	2	0.9	1.14
Al_2O_3	0.6	0.55	0.8	3.5	1.3	0.3	0.6	1.2	1.04
MgO	4.3		0.25	5.3	1	0.03	0.03	0.35	0.46
CaO	0.25	0.01	0.1	0.6	0.15	0.01	0.04	0.01	0.04
MnO	0.3	1.57	1.6	0.25	1.7	0.01	0.01	1	0.87
ZrO_2	0.02	0.08	0.13			0.95	1.1	0.5	0.14
Nb_2O_5	0.01	0.15		0.01		0.35	0.4	0.2	0.25
P_2O_5	0.018	0.04	0.14			0.02	0.04	0.05	0.02
Th^a	<10	100		1.2	16		40		
U^a	<10	10		0.7	2		65		

[a] Values are ppm.

The resultant slag, a complex mixture of titanates, may contain 70–85% TiO_2. The slag route is particularly useful when ilmenite is closely associated with haematite, from which it cannot economically be separated mechanically. Because the iron content of the slag is low, its use reduces the quantity of iron sulfate in the liquid effluent of sulfate process plants. Slag used as a feedstock for $TiCl_4$ production must be low in magnesium and calcium. A variety of other ilmenite beneficiation or synthetic rutile processes have been pursued, primarily to provide alternative chloride process feedstocks. Low grade ilmenite is purified mainly by leaching at high temperatures with either sulfuric or hydrochloric acid to remove iron. Typically, synthetic rutile contains about 94% TiO_2.

6.7.8. Manufacture

Two types of commercial processes are utilized in producing titanium dioxide pigments: the sulfate process and the chloride process. The sulfate process is the older of the two and was used exclusively until 1958, when the DuPont Corporation built the first successful commercial chloride process titanium dioxide pigment plant in Edge Moor, Delaware. Presently, 43% of all titanium dioxide pigments are produced via the sulfate process. However, because of commercial and economic considerations, the chloride process is preferred. In the year 2000, it was estimated that 63% of all pigment production will be via the chloride process.

Other titanium dioxide production processes have been attempted without success. Because of the complex technology, rigorous government regulations controlling effluent discharge, and the extremely high capital cost to construct cost-effective, large-scale pigment plants, no fundamental changes in pigment production processes are anticipated.

6.7.9. Sulfate Process

The sulfate process for manufacturing titanium dioxide pigments (pigments) was the earliest process used, having been first practiced in 1916 in Niagara Falls, New York and in 1915 in Norway. All pigment producers who supplied pigment prior to the late 1950s used SP. Consequently, there are a few variations of the basic sulfate process. Conceptually, the intent is to separate titanium from the host mineral (ilmenite or slag) in the form of a sulfate—titanyl sulfate ($TiOSO_4$)—then to purify it, and convert it to a titanium dioxide hydrate and then calcine the hydrate to a very pure titanium dioxide product.

The sulfate process is a batch, or discontinuous, process utilizing a large number of relatively simple unit operations. In sequence, the primary unit operations are

(1) *Digestion*—reaction of a TiO_2 containing mineral and sulfuric acid. Titanyl sulfate is formed. Digestion can be either batch or continuous in nature.
(2) *Precipitation* of titanium dioxide hydrate.
(3) *Separation and washing* of the hydrate.
(4) *Calcination*—thermal formation of pure TiO_2 crystals.

At this point, the TiO_2 product is chemically, but not physically, suited, to function as a pigment, because of its large calcined particle size and far-from-uniform particle size distribution. Subsequent processing steps are needed to mill or grind the particles and disperse them to a suitable particle size to function as a pigment, and to add chemicals to the surface of the pigment particles that enhance the TiO_2 pigment's optical and physical properties. These processing steps are collectively referred to as *posttreatment* and are similar for both the sulfate and chloride processes.

The key points are

- All sulfate process plants use batch or discontinuous processes, meaning that most operations are separated from upstream and downstream operations. This permits portions of the process to operate independently of the rest, enabling the use of simpler control systems. It also means that maintenance can be performed on an "as available" or "as scheduled" basis and not on an "as needed" basis. One result of this is the use of lower skill-level operators and maintenance personnel than are required for the chloride process. Typically, plants engender a management philosophy oriented toward applying a range of discrete, chemical solutions to plant or process problems. Some experienced operators refer to the sulfate process as a scaled-up laboratory, in which engineers are connected the various pieces of equipment.
- With the exception of calcination, temperatures and pressures encountered in the sulfate process are not high by contemporary chemical processing standards. This permits the use of lead- and rubber-lined equipment and piping instead of exotic alloys and refractory materials used in the more complex chloride process. Therefore, sulfur process plant facilities are easier to erect and maintain, but because of the large number of pieces of equipment, capital cost including waste treatment can be higher for a modern sulfur process plant than for a chloride process plant of the same pigment capacity.
- Generally there is a higher volume of waste products to treat and recycle or dispose of with a sulfur process plant than with a chloride process plant. This relates not only to the fact that lower TiO_2 content minerals are normally used in the sulfate process, but more significantly to the fact that the sulfate ion (and waste sulfuric acid) cannot be easily recovered and recycled whereas much of the chlorine is directly recycled in the chloride process. The sulfate process can have a volume of waste products in the range of 8–12 tons per ton of pigment product versus the chloride process having waste products in the range of 2–5 tons per ton of pigment product.

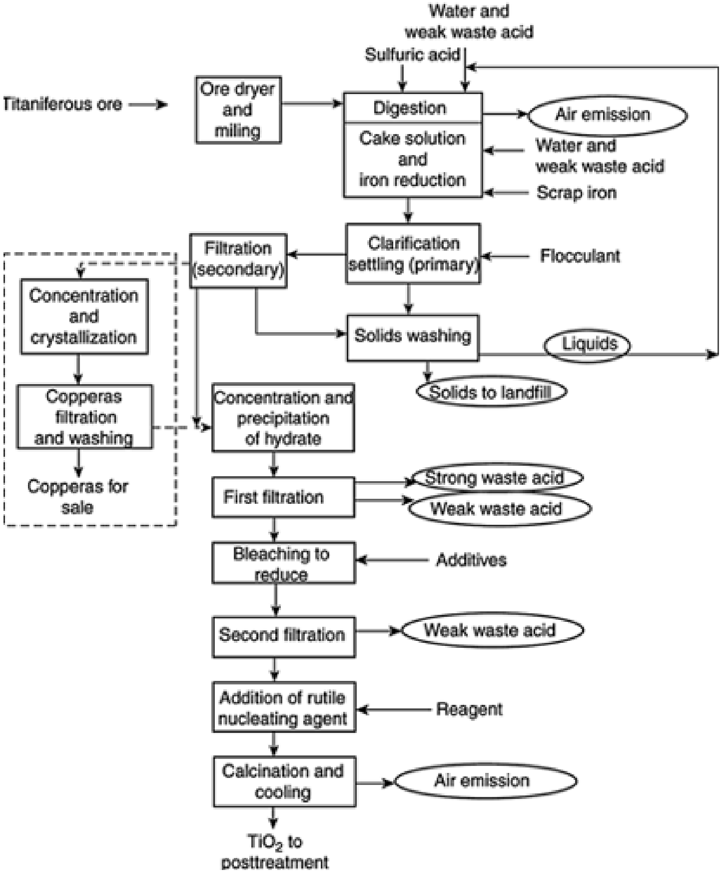

Fig. 1. Schmatic sulfate process.

Figure 1 is a schematic description of a typical sulfate process operating with an ilmenite mineral feed. Operations that can be eliminated using a higher TiO_2 mineral feed are contained within dashed lines.

6.7.10. Chloride Process

The chloride process for producing TiO_2 pigments is newer than the (SP), having been commercialized in 1958 in the United States. Development work on the chloride process route to producing TiO_2 began in the 1930s, but, because of its complexity and demanding requirements for materials of construction, successful, large-scale commercial operation of the chloride process followed the sulfate process by almost 40 years. As with the sulfate process, there are a few variations of the basic elements of the chloride process. The intent of the chloride process is to separate titanium from the host mineral in the form of a chloride—titanium tetrachloride ($TiCl_4$)—purify it, convert it to TiO_2 pigment in an oxidation reactor, and recycle the chlorine.

The chloride process is a modern continuous chemical process utilizing a small number of unit operations, two of which—chlorination and oxidation—are complicated even compared to contemporary chemical unit operations. In sequence, the principal unit operations are

(1) *Chlorination*—reaction of chlorine and a titanium containing mineral under reducing conditions.

(2) *Condensation and purification*—fractional distillation and separation of low-, medium-, and high-boiling chlorides.
(3) *Oxidation*—reaction of titanium tetrachloride with oxygen at elevated temperatures to form titanium dioxide pigment particles.

In contrast to the TiO_2 crystals produced in the calcination operation in the sulfate process, TiO_2 particles from the oxidation reactor are of the correct type and size to function as a pigment.

The key points are

- All chloride process plants are continuous, meaning that the unit operations are interconnected with recycle streams. Although with some chloride processes it is possible for a short time to operate some sections of the process independent from the others, generally speaking, all the unit operations must operate together at one predetermined, designed rate. This requires a good understanding of the process technology, the use of highly skilled and trained operators and maintenance personnel, and good control systems to successfully achieve high on-stream or operating factors. Typically, a chloride process pigment plant must operate more than 90% of the time (based on 24 h per day, 365 days per year) to achieve a satisfactory return on investment. In concert with a high level of operating and maintenance skill, a management philosophy is needed to ensure that operating problems are anticipated and corrective measures implemented before a catastrophic breakdown occurs. As can be expected, maintenance must be performed on a predictive and as-needed basis. Similar to other capital-intensive, large-scale, single-purpose chemical processing operations, operating costs for a chloride process pigment plant closely follow the experience curve. This leads to large-capacity plants with large-sized equipment operating at high rates to achieve low operating costs.
- Some operations in the chloride process generate very high steady-state operating temperatures. The combination of these conditions with corrosive, and toxic, reactants requires the use of costly materials of construction to achieve reliable and safe operation. Chloride process pigment plants are expensive to construct and maintain, but because of the smaller number of pieces of equipment and small footprint of a modern, well-designed chloride process pigment plant, the total capital cost including waste-treatment facilities is less than that for an equivalent sized SP plant with its high-cost waste-treatment facilities.
- As stated earlier in the description of the sulfate process, there can be a markedly lower volume of waste products when operating a chloride process pigment plant. The principal reasons are the internal recycle of most of the chlorine values and the use of higher TiO_2 content minerals.

Figure 2 is a schematic description of a typical chloride process.

6.7.11. Posttreatment

The posttreatment process involves: wet milling the TiO_2 particles to break up agglomerations, and deposition of inorganic chemicals onto the surface of the TiO_2 particle, followed by washing and filtration of the particles. The particles are then dried before being finely ground in a fluid energy mill or micronizer to the desired pigment particle size and size distribution. If organic chemicals are used as a surface treatment, they are normally added during the final milling or micronizing operation where the particles are finely ground. Figure 3 is a schematic description of a typical posttreatment process.

6.7.11.1. Pigment Finishing. Rutile pigments produced by the chloride and sulfate routes are basically similar and require coating for the same reasons, ie, to optimize dispersibility, dispersion stability, opacity, gloss, and durability. The coating techniques are essentially common to sulfate and chloride-route base pigments. Because the treatments are tailored to the requirements of the final application, the details are specific to the needs of the different market sectors, eg, paints, plastics, and paper. Generally, rutile pigments have between 1

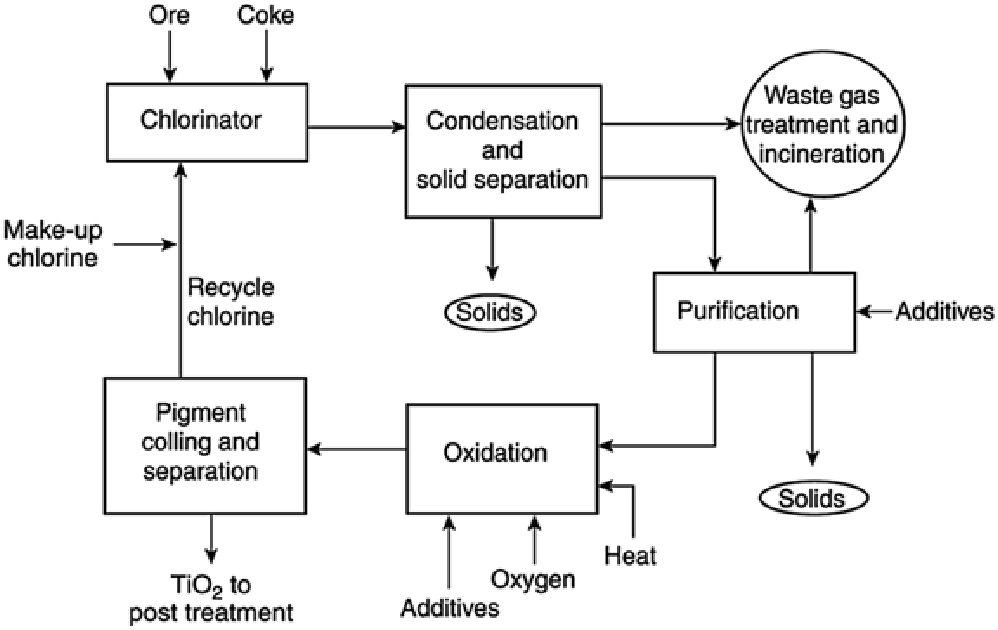

Fig. 2. Schematic chloride process.

and 15% inorganic coating, the higher coating levels typically used for applications such as mat emulsion paints. Anatase pigments generally have lower coating levels of 1 to 5%. The first finishing stage is to disperse the base pigment in water, generally with phosphate, silicate, and/or organic dispersants. The resulting suspensions may then be milled and/or classified to remove oversize particles. The dispersed particles are then coated by selective precipitation of (usually) small quantities of colorless hydrous oxides, eg, P_2O_5, SiO_2, Al_2O_3, TiO_2, and ZrO_2 deposited via controlled changes in pH and temperature. Essentially, the processes are of the type

$$\text{aluminum salt} + \text{alkali} \longrightarrow \text{hydrated aluminum oxide}$$

or

$$\text{silicate} + \text{acid} \longrightarrow \text{hydrated silica}$$

but the detailed chemistry to ensure that deposition occurs on the pigment surface and not as a bulk precipitate is more complex (89) and not completely understood. Specific examples of coating types are available (90, 91). In this way, the pigment surface properties are modified to give the required application properties (92, 93). After the coating stage, the pigment that has, perforce, flocculated during the coating process, is filtered, washed, and dried. It is then milled once more, usually in a steam-fluid-energy mill (micronizer) to break up the flocculates. At the same time, the pigment is additioned with an organic surface treatment, eg, polyol or alkanolamine on pigments designed for use in paints and printing inks or siloxane on pigments for plastics. Finally, the pigment is filtered and packed.

Significant effort has been directed toward encapsulating titanium dioxide using an organic polymer surface layer instead of an inorganic coating. Although there are numerous patents and research papers (94) on this topic, no product has been commercialized as of this writing (1997). Manufacturers produce many grades

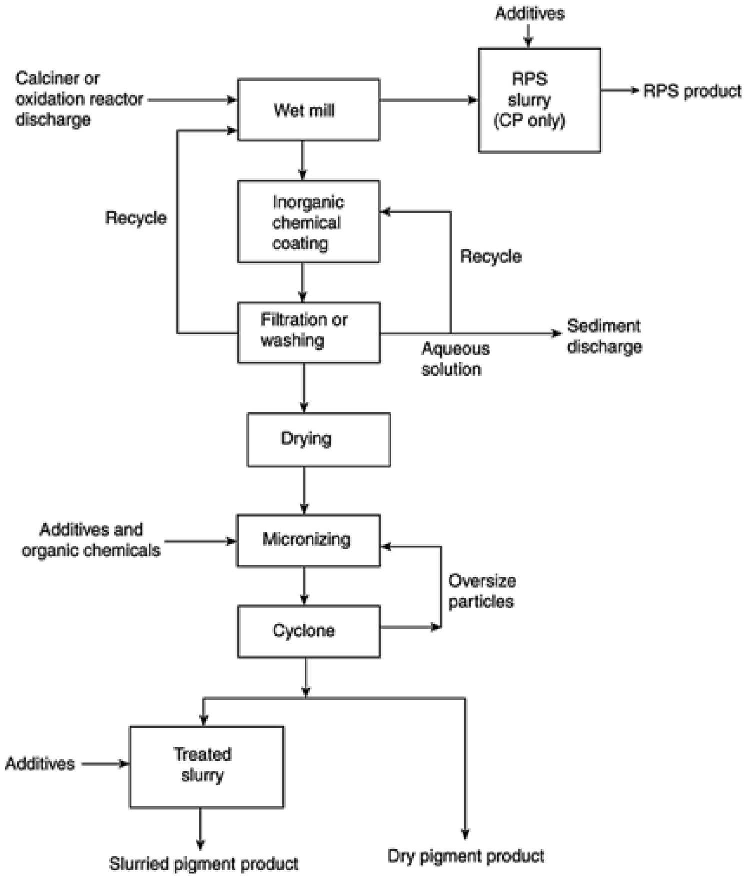

Fig. 3. Posttreatment process.

of titanium dioxide pigments and their literature should be consulted for recommendations on the grade to be used for any particular purpose.

6.7.11.2. Colored Pigments. Colored pigments may be derived from titanium dioxide by substituting some of the titanium in the rutile lattice by small amounts of transition-metal ions. The most important are a yellow pigment formed by introducing nickel ions, and a buff pigment formed by introducing chromium. Of lesser importance are cobalt titanate green and iron titanate brown, both of which have the spinel structure (95, 96).

For rutile-derived pigments, it is important to maintain charge balance. This is accomplished by adding antimony or niobium, both of which can be thought of as forming $5+$ ions to compensate for the charge deficit that would otherwise result from the replacement of Ti^{4+} by either Ni^{2+} or Cr^{3+}. Thus, a typical composition for nickel titanate yellow is $NiO{\cdot}Sb_2O_5{\cdot}20TiO_2$; for chrome titanate buff, $Cr_2O_3{\cdot}Sb_2O_5{\cdot}31TiO_2$. The pigments are made by mixing, either wet or dry, stoichiometric quantities of the oxides, or oxide precursors, calcining at ca 1000°C and then milling. Both pigments have excellent hiding power but poor tinting strength compared to organic alternatives. The principal advantage of these pigments is the excellent light-fastness, which makes them particularly suited for use in vinyl sidings. In this application, they have the additional advantage that deterioration of the plastic by weathering does not cause a change in color. In 1984, world sales of nickel titanate yellows and chrome titanate buffs were ca 1500 and 2000 t/yr, respectively. A number of pearlescent pigments based on mica coated with titanium dioxide have also been manufactured (97).

6.7.11.3. Production and Shipment. A list of the manufacturers of titanium dioxide pigments is given in Table 12, together with capacity information.

Table 12. Titanium Dioxide Pigment Plants Year-End 1996 Capacity with 1997 and 1998 Acquisitions

	Producer	Location		Process[a]	1000 t
1	DuPont	Antioch	United States	C	38
2	DuPont	Umbogintwi	South Africa	S	35
3	DuPont	New Johnsonville	United States	C	320
4	DuPont	Burnie	Australia	S	
5	DuPont	Calais	France	S	100
6	DuPont	Trengganu	Malaysia	S	50
7	DuPont	Huelva	Spain	S	80
8	DuPont	Greatham	United Kingdom	C	76
9	DuPont	Kuan Yin	Taiwan	C	90
10	DuPont	De Lisle	United States	C	280
11	DuPont	Edgemoor	United States	C	129
12	DuPont	TampicoO	Mexico	C	90
13	MIC	Thann	France	S	35
14	MIC	Kemerton	Australia	C	79
15	MIC	Baltimore	United States	S	44
16	MIC	Baltimore	United States	C	51
17	MIC	Ashtabula I	United States	C	104
18	MIC	Ashatubla II	United States	C	86
19	MIC	Stallingboro	United Kingdom	C	109
20	MIC	Le Havre	France	S	110
21	MIC	Arembepe	Brazil	S	55
22	Kronos	Leverkusen	Germany	C	105
23	Kronos	Langerbruge	Belgium	C	55
24	Kronos	Grimsby	United Kingdom	S	83
25	Kronos	Fredrikstad	Norway	S	31
26	Kronos	Varennes	Canada	C	55
27	Kronos	Nordenham	Germany	S	60
28	Kronos	Lake Charles	United States	C	110
29	Kronos	Leverkusen	Germany	S	35
30	Kronos	Varennes	Canada	S	20
31	Kemira	Savannah	United States	C	91
32	Kemira	Savannah	United States	S	54
33	Kemira	Botlek	Netherlands	C	56
34	Kemira	Pori	Finland	S	90
35	Kerr McGee	Hamilton	United States	C	130
36	Kerr McGee	Antwerp	Belgium	S	24
37	Kerr McGee	Uerdingen	Germany	S	105
38	Ishihara	Jurong	Singapore	C	42
39	Ishihara	Yokkaichi	Japan	C	55
40	Ishihara	Yokkaichi	Japan	S	100
41	Crimean PS	Armyansk	Ukraine	S	80
42	Lakokrasa	Chelyabinsk	Ukraine	S	30
43	Agrokhim	Sumy	Ukraine	S	40
44	China Metal	Chin-shin	Taiwan	S	10
45	Hangkook	Inchon	S. Korea	S	36
46	Cinkarna	Celje	Slovenia	S	28
47	Cristal Pigment	Yanbu	Saudi Arabia	C	60
48	Zachem	Police	Poland	S	36

Table 12. ***Continued***

	Producer	Location		Process[a]	1000 t
49	Tohoku Kaga	Akita	Japan	S	30
50	Fuji	Kobe-Hirat	Japan	S	16
51	Furukawa	Osaka	Japan	S	
52	Sakai	Onahama	Japan	S	43
53	Tayca	Saidaiji	Japan	S	60
54	Titan Kogyo	Ube	Japan	S	17
55	Travacore	Trivandrum	India	S	11
56	Kerala Mine	Chavara	India	C	22
57	Sachtleben	Homberb	Germany	S	70
58	Precheza	Prerov	Czech Rep.	S	25
59	Sinochem	Gansu	China	S	15
60	Chem.Works	Shanghai	China	S	50
61	Tiwest	Kwinana	Australia	C	80
Worldwide Total					*4102*

[a] C = chloride, S = sulfate.

Titanium dioxide is traditionally supplied in paper bags containing 25 kg (50 lb) of pigment. Evolutionary developments in packaging have included palletization, the use of multiple bags, and the addition of shrinkwrapping to prevent excessive moisture pickup during transportation. For specialized applications, such as papermaking or plastic masterbatch manufacture, pigment is supplied in bags that can be added directly to the processing machinery without preliminary slitting and emptying. In the United States, titanium dioxide pigment, particularly pigment for paper and latex paints, is often delivered as an aqueous slurry by rail. By contrast, in Europe and particularly in the United Kingdom, the supply of dry pigment by road tanker has become the favored route for the delivery of large quantities of titanium dioxide pigment. At an intermediate (1-t) level, semibulk containers (big bags) constructed from, eg, woven polypropylene, have become increasingly popular in Europe, Japan, and North America.

6.7.12. Economic Aspects

The TiO_2 pigments industry is highly concentrated with six producers expected to hold just over 85% of the worldwide market. In 1997 and 1998 the pigment industry consolidated with the announcement of the following acquisitions. Not all of the acquisitions have been consummated, but the following tables and figures show 1996 data based on the assumption that the announced acquisitions were completed in that time period.

Du Pont to acquire Tioxide's non–North American assets and concurrently to sell the Grimsby (UK) pigment plant to Kronos. U.S. Federal Trade Commission, as of August 5, 1998, had not yet approved this transaction.

Kronos to acquire Tioxide's 50% share in the Lake Charles, La. joint venture (with Kronos) and to acquire from Du Pont (Du Pont's acquisition from Tioxide) the Grimsby (UK) pigment plant. U.S. Federal Trade Commission must approve the Du Pont/Tioxide transaction for the Kronos transaction to be implemented.

Millennium Inorganic Chemicals acquired Thann et Mulhouse and Tibras' TiO_2 pigment operations. Regulatory authorities have approved both transactions.

Kerr McGee Chemical Corporation acquired an 80% interest in Bayer's TiO_2 pigment operations. Regulatory authorities have approved this transaction.

Table 13 summarizes the worldwide sales and capacities for each of these producers in 1996. The major (those producers listed in Table 13) pigment producers' sales by end-use market are given in Table 14. As in Table 13, Table 14 includes shares from 1997 and 1998 acquisitions.

Table 13. Pigment Producers' Sales and Capaceties (Includes 1997 and 1998 Acquisitions)[a]

	1996 sales, 10^3 t	Market share, %		1996 year-end capacity	
		Individual	Cumulative	10^3 t	Share, %
Du Pont	1,146	34.2	34.2	1,369	33.4
MIC	591	17.6	51.8	673	16.4
Kronos	514	15.3	67.1	554	13.5
Kerr McGee	258	7.7	74.8	314	7.7
Kemira	216	6.4	81.2	291	7.1
Ishihara	144	4.3	85.5	197	4.8
Others	485	14.5	100.0	704	17.2
World total	*3356*	*100.0*		*4,102*	*100.0*

[a] IBMA.

Table 14. Principal Pigment Producers' Shares of End-Use Markets, %

	Du Pont	MIC	Kronos	KMCC	Kemira	Ishihara
Paint	57.5	64.0	55.0	64.4	33.9	56.7
Plastics	22.8	17.0	25.8	26.3	8.5	17.8
Paper	15.6	13.2	10.3	3.9	31.2	8.1
Inks	2..4	0.3	1.9	0.7	18.2	9.0
Ceramics	0.2	2.4	1.4	1.8		2.6
Fibers	0.1		2.5		0.9	2.1
Other	1.4	3.2	3.2	2.9	7.3	3.8
Total	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*

IBMA's pigment plant cash cost database for 1996, which includes cash costs for 52 plants throughout the world, shows cash costs ranging from a low of $US 708/t to a high of $US 3,156/t. The average cost of producing pigment in 1996 was $US 1,255/t. There were 17 pigment plants with costs below the average and 35 plants above the average.

6.7.13. Peroxidic Compounds

When hydrogen peroxide is added to a solution of titanium(IV) compounds, an intense, stable, yellow solution is obtained, which forms the basis of a sensitive method for determining small amounts of titanium. The color probably results from the peroxo complex $[Ti(O_2)(OH)(H_2O)_x]^+$, and crystalline salts such as $K_2[Ti(O_2)(SO_4)_2]\cdot nH_2O$ can be isolated from alkaline solutions. The peroxo ligand is bidentate; the two oxygen atoms are equidistant from the titanium (98).

The action of hydrogen peroxide on freshly precipitated hydrated Ti(IV) oxide or the hydrolysis of a peroxide compound such as $K_2[Ti(O_2)(SO_4)_2]$ yields, after drying, a yellow solid, stable below 0°C, of composition $TiO_3{\cdot}2H_2O$. There is one peroxo group per titanium, but the precise structure is not known. The yellow solid loses oxygen and water when heated and liberates chlorine from hydrochloric acid. When freshly prepared, it is stable in acid or alkali, giving peroxy salts.

6.7.14. Inorganic Titanates

Titanium forms a series of mixed oxide compounds with other metals. Only in one of these, Ba_2TiO_4, are there discrete $[TiO_4]^{2-}$ ions (99). Compounds of the general formula $M^+{}_2TiO_3$ or $M^{2+}TiO_3$ are known as metatitanates; those having $M^+{}_4TiO_4$ and $M^{2+}{}_2TiO_4$ are called orthotitanates. Metatitanates of the type $M^{2+}TiO_3$ crystallize with the ilmenite ($Fe^{2+}TiO_3$) structure if M and Ti are of similar size. In the ilmenite structure, the oxygens are octahedrally close-packed. One-third of the octahedral interstices are occupied by M^{2+} ions and a second third by Ti^{4+}. If M is bigger than Ti, the perovskite structure is usually adopted (100).

6.7.14.1. Alkali Metal Titanates. Alkali metatitanates may be prepared by fusion of titanium oxide with the appropriate alkali metal carbonate or hydroxide. Representative alkali metal titanates are listed in Table 15. The alkali metal titanates tend to be more reactive and less stable than the other titanates, eg, they dissolve relatively easily in dilute acids.

Table 15. Alkali Metal and Alkaline-Earth Titanates

Compound	CAS Registry Number	Formula	Density, kg/m^3	Mp, °C
lithium metatitanate	[12031-82-2]	Li_2TiO_3	3418	
lithium dititanate	[12600-48-5]	$Li_2Ti_2O_5$	350(0)	
lithium orthotitanate	[12768-28-4]	Li_4TiO_4		
sodium metatitanate	[12034-34-3]	Na_2TiO_3	319(0)	1030
sodium dititanate	[12164-19-1]	$Na_2Ti_2O_5$		985
sodium trititanate	[12034-36-5]	$Na_2Ti_3O_7$		1128
sodium pentatitanate	[12034-52-5]	$4Na_2O{\cdot}5TiO_2$		
sodium trititanate	[12503-05-8]	$2Na_2O{\cdot}3TiO_2$		
potassium metatitanate	[12030-97-6]	K_2TiO_3		806
potassium dititanate	[12056-46-1]	$K_2Ti_2O_5$		980
potassium polytitanate	[12056-49-4]	$K_2Ti_4O_9$		
potassium polytitanate	[12056-51-8]	$K_2Ti_6O_{13}$		

High temperature hydrogen reduction of sodium metatitanate, Na_2TiO_3, produces nonstoichiometric titanium bronzes, Na_xTiO_2, where x is ca 0.2. These are chemically inert, blue-black metallic in appearance, and electrically conducting. The compounds have the hollandite structure, in which the TiO_6 octahedra are linked via their edges to form square cross-section tunnels. A variable population of cations can occupy these tunnels to give the materials significant composition ranges. Hollandites have received considerable attention as possible host matrices for the storage of radioactive metal ions. The concept involves trapping radioactive ions in barium/aluminium/titanium hollandite tunnels and then encapsulating the matrix in an inert shell (43). Work on this material, Synroc, is being developed mainly in Australia (101).

The crystal structure and properties of potassium titanates $K_2O{\cdot}nTiO_2$ depend on the value of n. Those having high ($n = 2$ or 3) potassium content have a layer structure and show both an intercalation ability and a catalytic activity (102, 103). Those having a low potassium content have a tunnel structure and exhibit high chemical stability and low thermal conductivity (104). The polytitanates, $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$, are of considerable interest because they can be manufactured in fibrous form. The fibers have average diameters of ca 1 μm and may be several millimeters long (105, 106), each fiber being made up of several fibrils that are discrete crystals. They are chemically stable and melt at 1370°C. Production methods include hydrothermal synthesis in which titanium dioxide reacts with aqueous potassium hydroxide at high (ca 20 MPa (200 atm) and 600–700°C) pressure and temperature. Preparation from alkali halide melts and, by slow cooling after calcination, has also been described (106, 107). The product is produced in the form of lumps, which may be broken down under high shear to give a water-dispersed pulp, which in turn may be treated in the same way as paper pulp to give papers, felts, and mats. Potassium titanate has a high refractive index and a low thermal conductivity. Moreover, its size is in the right range to scatter infrared radiation. Thus it has potential use as an insulating and ir-reflective material. Other potential applications of potassium titanate include its use as a filtration medium, a reinforcement material for organic polymers, and an asbestos replacement in friction brakes. Between 1965 and 1972, pigmentary potassium titanate was manufactured in the United States (108).

6.7.14.2. Alkaline-Earth Titanates. Some physical properties of representative alkaline-earth titanates are listed in Table 16. The most important applications of these titanates are in the manufacture of electronic components (109). The most important member of the class is barium titanate, $BaTiO_3$, which owes its significance to its exceptionally high dielectric constant and its piezoelectric and ferroelectric properties. Further, because barium titanate easily forms solid solutions with strontium titanate, lead titanate, zirconium oxide, and tin oxide, the electrical properties can be modified within wide limits. Barium titanate may be made by, eg, cocalcination of barium carbonate and titanium dioxide at ca 1200°C. With the exception of Ba_2TiO_4, barium orthotitanate, titanates do not contain discrete $TiO^{4-}{}_4$ ions but are mixed oxides. Ba_2TiO_4 has the β-K_2SO_4 structure in which distorted tetrahedral $TiO^{4-}{}_4$ ions occur.

Table 16. Properties of Alkaline-Earth Titanates

Name	CAS Registry Number	Formula	Crystal structure	Mean refractive index	Density kg/m^3	Mp, °C
magnesium metatitanate[a]	[1312-99-8]	$MgTiO_3$	hexagonal	2.19	3840	1565
magnesium orthotitanate	[12032-52-9]	Mg_2TiO_4	cubic		3530	1840
magnesium dititanate	[12032-35-8]	Mg_2TiO_5	orthorhombic			1645
calcium titanate[b]	[12049-50-2]	$CaTiO_3$		2.34	4020	1980
barium titanate	[12047-27-7]	$BaTiO_3$	cubic	2.42		1625
bariumtitanate		$BaTiO_3$	tetragonal	2.3	6000	1625
barium titanate		$BaTiO_3$	hexagonal	2.2		1625
strontium titanate	[12060-52-9]	$SrTiO_3$	cubic	2.41	5120	2080

[a] The mineral geikielite.
[b] The mineral perovskite.

Barium titanate [12047-27-7] has five crystalline modifications. Of these, the tetragonal form is the most important. The structure is based on corner-linked oxygen octahedra, within which are located the Ti^{4+} ions. These can be moved from their central positions either spontaneously or in an applied electric field. Each $TiO^{8-}{}_6$ octahedron may then be regarded as an electric dipole. If dipoles within a local region, ie, a domain, are oriented parallel to one another and the orientation of all the dipoles within a domain can be changed by the application of an electric field, the material is said to be ferroelectric. At ca 130°C, the Curie temperature, the barium titanate structure changes to cubic. The dipoles now behave independently, and the material is paraelectric (see Ferroelectrics).

The ease with which the titanium ions may be moved from their central positions in the $TiO_6{}^{8-}$ octahedra results in a very high dielectric constant, the basis of the use of barium titanate in ceramic capacitors. The dielectric constant is ca 1200 at room temperature but can increase tenfold at the Curie temperature. By forming solid solutions of barium titanate with, eg, $SrTiO_3$, the Curie temperature can be lowered to room temperature, and in this way the high dielectric characteristic of the Curie maximum can be exploited. Alternatively, by forming solid solutions with $CaTiO_3$ or rare-earth titanates, capacitors having a lower dielectric constant but greater temperature stability can be made. When ferroelectric materials are polarized, significant changes in dimension can result, eg, ca 1% in $BaTiO_3$. This phenomenon is the basis of piezoelectric actuators. The parent material for such devices is normally a solid solution of lead titanate and lead zirconate.

$BaTiO_3$ is also used for positive temperature coefficient (PTC) resistors, which exploit a large increase of resistivity at the Curie temperature of ferroelectrics (110). The resistance is the result of barrier layers at the grain boundaries in these sintered ceramics, and is not found in single-crystal material. The $BaTiO_3$ is made semiconducting by doping, eg, by substituting some of the Ti^{4+} ions by pentavalent ions, such as Nb^{5+}, and the temperature at which the resistance change occurs is controlled by forming solid solutions, eg, with $SrTiO_3$, to lower the Curie temperature. Applications include self-regulating heaters, power controls, and motor starters.

Other alkaline-earth titanates may be synthesized by heating together stoichiometric amounts of the oxide or by decomposing double salts such as strontium titanium oxalate. The primary use of magnesium, calcium, and strontium titanates is as additives to modify the properties of electroceramic components. Gems cut from strontium titanate boules have good color and brilliance, as well as a refractive index close to that of diamond. Magnesium titanate has also been used as a gemstone (see Gemstones). All three titanates are broad-band-gap (ca 3–4 eV) semiconductors. Strontium titanate absorbs uv wavelengths shorter than ca 395 nm, but magnesium titanate has a band gap of 3.7 eV. Consequently, the absorption of magnesium titanate is sufficiently far into the ultraviolet that the compound can be used as a pigment in uv-cured systems.

6.7.14.3. Other Titanates.

Aluminum Titanate. Aluminum titanate, Al_2TiO_5, a white solid, density 3700 kg/m^3, mp ca 1860°C, has an orthorhombic, pseudobrookite, structure. Al_2TiO_5 may be made by calcination of the stoichiometric amount of oxides at temperatures above 1280°C (111). Below this temperature the compound is thermodynamically unstable and tends to decompose into alumina and titanium dioxide (112). The uses of aluminum titanate are as a low thermal expansion ceramic which has a good thermal shock resistance. The thermal expansion coefficients are markedly anisotropic. The coefficient in the *a* direction is negative. The consequent stresses produced during the cooling of sintered polycrystalline bodies cause extensive microcracking and the application of aluminum titanate relies on the control of the consequent microstructure (113). The material finds applications in thermally insulating exhaust port liners in engine cylinder heads and in burner nozzles and thermocouple sleeves.

Iron Titanates. Ferrous metatitanate [12168-52-4], $FeTiO_3$, mp ca 1470°C, density 472(0), an opaque black solid having a metallic luster, occurs in nature as the mineral ilmenite. This ore is used extensively as a feedstock for the manufacture of titanium dioxide pigments. Artificial ilmenite may be made by heating a mixture of ferrous oxide and titanium oxide for several hours at 1200°C or by reducing a titanium dioxide/ferric oxide mixture at 450°C.

Ferrous orthotitanate [12160-20-2], Fe_2TiO_4, is orthorhombic and opaque. It has been prepared by heating a mixture of ferrous oxide and titanium dioxide. Ferrous dititanate [12160-10-0], $FeTi_2O_5$, is orthorhombic and has been prepared by reducing ilmenite with carbon at 1000°C. The metallic ion formed in the reaction is removed, leaving a composition that is essentially the dititanate. Ferric titanate [1310-39-0] (pseudobrookite), Fe_2TiO_5, is orthorhombic and occurs to a limited state in nature. It has been prepared by heating a mixture of ferric oxide and titanium dioxide in a sealed quartz tube at 1000°C.

Lead Titanate. Lead titanate [12060-00-3], $PbTiO_3$, is a yellow solid having a density of 73(00). It can be made by heating the calculated amounts of the two oxides together at 400°C. It may also be made by sol-gel routes, which may proceed via an intermediate pyrochlore phase, $Pb_2Ti_2O_6$ (114) (see Sol-gel technology). Its former use as a pigment has been superseded (115). Like barium titanate, lead titanate is a ferroelectric and the static dielectric constant shows a strong maximum, at ca 500°C, associated with the phase change from ferroelectric to paraelectric behavior. Lead titanate zirconate [12626-81-2] (PZT) is widely used as a piezoelectric ceramic. A typical composition is $PbZr_{0.6}Ti_{0.4}O_3$. In a typical production process, the oxides, together with minor amounts of modifying additives, are wet-mixed, dried, prereacted at ca 925°C, and then fabricated by pressing and firing at ca 1300°C (116). PZT is also used in pyroelectric detectors (109).

Other Titanates. Nickel titanate [12035-39-1], $NiTiO_3$, is a canary-yellow solid having a density of 73(00). When a mixture of antimony oxide, nickel carbonate, and titanium dioxide is heated at 980°C, nickel antimony titanate [8007-18-9] forms, which is used as a yellow pigment (95).

Zinc orthotitanate [12036-69-0], Zn_2TiO_4, a white solid having a density of 512(0) and a spinel structure, is obtained by heating the calculated amounts of the two oxides at 1000°C. Zinc orthotitanate forms a series of solid solutions with titanium dioxide, extending to the composition $Zn_2TiO_4{\cdot}1.5TiO_2$. These solid solutions begin to dissociate at 775°C with the formation of the rutile form of titanium dioxide. The properties of the rare-earth titanates and their electronic structure are available (117–119).

6.8. Titanium Halides

The most important halides and oxyhalides are shown in Table 17. General introductions to the chemistry of the titanium halides are available (10, 120). Thermodynamic data are given in Tables 1 and 2.

Table 17. Titanium Halides

Titanium oxidation state	Fluoride	Chloride	Bromide	Iodide
Ti(II)	TiF_2	$TiCl_2$	$TiBr_2$	TiI_2
Ti(III)	TiF_3, TiOF	$TiCl_3$, TiOCl	$TiBr_3$	TiI_3
Ti(IV)	TiF_4	$TiCl_4$, $TiOCl_2$	$TiBr_4$, $TiOBr_2$	TiI_4, $TiOI_2$

6.8.1. Titanium Fluorides

6.8.1.1. Titanium Difluoride. Unlike other titanium dihalides, titanium difluoride [13814-20-5] is known only from mass spectra of gases.

6.8.1.2. Titanium Trifluoride. The trifluoride (121) is a blue crystalline solid, density 2980 kg/m^3, in which the titanium atoms are six-coordinate at the center of a slightly distorted octahedron, where the mean Ti–F distance is 197 pm. Titanium trifluoride [13470-08-1] is stable in air at room temperature but decomposes to titanium dioxide when heated to 100°C. It is insoluble in water, dilute acid, and alkalies but decomposes in hot concentrated acids. The compound sublimes under vacuum at ca 900°C but disproportionates to titanium and titanium tetrafluoride [7783-63-3] at higher temperatures.

Titanium trifluoride may be prepared in 90% yield by the reaction of gaseous hydrogen fluoride, in practice in a 1:4 ratio of hydrogen:HF, with either titanium metal or titanium hydride at 900°C.

$$2\ Ti^0 + 6\ HF \longrightarrow 2\ TiF_3 + 3\ H_2$$

The temperature is chosen to maximize reaction rate and to avoid the competitive formation of the tetrafluoride. Alternative preparation methods include the reaction between $TiCl_3$ and gaseous HF,

$$TiCl_3 + 3\ HF \longrightarrow TiF_3 + 3\ HCl$$

as well as the hydrogen reduction of ammonium hexafluorotitanate.

6.8.1.3. Titanium Tetrafluoride. Titanium tetrafluoride [7783-63-3] is a white hygroscopic solid, density 2798 kg/m^3, that sublimes at 284°C. The properties suggest that it is a fluorine-bridged polymer in which the titanium is six-coordinate. The preferred method of preparation is by direct fluorination of titanium sponge at 200°C in a flow system. At this temperature, the product is sufficiently volatile that it does not protect the unreacted sponge and the reaction proceeds to completion. The reaction of titanium tetrachloride with cooled, anhydrous, liquid hydrogen fluoride may be used if pure hydrogen fluoride is available.

$$TiCl_4 + 4\ HF \longrightarrow TiF_4 + 4\ HCl$$

A patent (122) for the production of pigment-grade titanium dioxide describes preparation of titanium tetrafluoride by the reaction of SiF_4 and ilmenite.

$$SiF_4 + TiO_2\,(\text{ilmenite}) \longrightarrow TiF_4 + SiO_2$$

The impure product is dissolved in methanol. Subsequent reaction with ammonium fluoride forms ammonium hexafluorotitanate. This solid, obtained in high purity, reacts with water vapor in a stream of air at 250°C to give anatase.

$$(NH_4)_2\,TiF_6 + 2\ H_2O \longrightarrow TiO_2 + 2\ NH_4F + 4\ HF$$

Other preparative methods include direct synthesis from the elements, reaction between gaseous hydrogen fluoride and titanium tetrachloride, and decomposition of barium hexafluorotitanate [31252-69-6], $BaTiF_6$, or ammonium, $(NH_4)_2TiF_6$.

6.8.1.4. Fluorotitanates. Anhydrous potassium fluorotitanate [23969-67-7], K_2TiF_6, may be prepared by dissolving titanium dioxide in dilute hydrofluoric acid to form a clear solution of H_2TiF_6. The exothermic reaction is carried out in agitated, carbon-tiled, rubber-lined, mild steel vessels. The acid is neutralized with potassium hydroxide solution, through which brilliant white crystals of potassium fluorotitanate are formed (11). Alternatively, titanium dioxide may be fused with potassium fluoride and the melt extracted with water. The anhydrous salt forms sparingly soluble transparent crystals (density 3022 kg/m^3, mp 780°C), which decompose to titanium dioxide and hydrogen fluoride when heated in air at 500°C. The principal use of potassium fluorotitanate is as a grain-refining agent for aluminum and its alloys, ie, to promote the production of a small grain size as the molten metal cools and solidifies. There are minor uses in the preparation of dental fillings and in abrasive grinding wheels.

6.8.2. Titanium Chlorides

6.8.2.1. Titanium Dichloride. Titanium dichloride [10049-06-6] is a black crystalline solid (mp $>$ 1035 at 10°C, bp $>$ 1500 at 40°C, density 31(40) kg/m^3). Initial reports that the titanium atoms occupy alternate layers of octahedral interstices between hexagonally close-packed chlorines (analogous to titanium disulfide) have been disputed (120). $TiCl_2$ reacts vigorously with water to form a solution of titanium trichloride and liberate hydrogen. The dichloride is difficult to obtain pure because it slowly disproportionates.

$$2\ TiCl_2 \longrightarrow Ti^0 + TiCl_4$$

$TiCl_2$ may be prepared either by the disproportionation of $TiCl_3$ at 475°C in vacuum,

$$2\ TiCl_3 \longrightarrow TiCl_2 + TiCl_4$$

or by passing titanium tetrachloride vapor over titanium metal at a temperature of ca 1100°C, slightly above the titanium dichloride melting point.

$$TiCl_4 + Ti^0 \longrightarrow 2\ TiCl_2$$

Alternatively, the $TiCl_4$ may be reduced using hydrogen, sodium, or magnesium. It follows that $TiCl_2$ is the first stage in the Kroll process for the production of titanium metal from titanium tetrachloride. A process for recovery of scrap titanium involving the reaction of scrap metal with titanium tetrachloride at >800°C to form titanium dichloride, collected in a molten salt system, and followed by reaction of the dichloride with magnesium to produce pure titanium metal, has been patented (122, 123).

6.8.2.2. Titanium Trichloride. Titanium trichloride [7705-07-9] exists in four different solid polymorphs that have been much studied because of the importance of $TiCl_3$ as a catalyst for the stereospecific polymerization of olefins (120, 124). The α-, γ-, and †-forms are all violet and have close-packed layers of chlorines. The titaniums occupy the octahedral interstices between the layers. The three forms differ in the arrangement of the titaniums among the available octahedral sites. In α-$TiCl_3$, the chlorine sheets are hexagonally close-packed; in γ-$TiCl_3$, they are cubic close-packed. The brown β-form does not have a layer structure but, instead, consists of linear strands of titaniums, where each titanium is coordinated by three chlorines that act as a bridge to the next Ti. The structural parameters are as follows:

Material	Lattice constants, pm		Ti–Ti distance, pm
	a	*c*	
α-$TiCl_3$	356	587	354
β-$TiCl_3$	627	582	291
γ-$TiCl_3$	614	1740	354

The †-form is produced by grinding either the α or the γ, and the structure is believed to be disordered and intermediate between α and γ.

Titanium trichloride is almost always prepared by the reduction of $TiCl_4$, most commonly by hydrogen. Other reducing agents include titanium, aluminum, and zinc. Reduction begins at temperatures of ca 500°C and under these conditions α-$TiCl_3$ is formed. The product is cooled quickly to below 450°C to avoid disproportionation to the di- and tetrachlorides. β-$TiCl_3$ is prepared by the reduction of titanium tetrachloride with aluminum alkyls at low (80°C) temperatures; whereas γ-$TiCl_3$ is formed if titanium tetrachloride reacts with aluminum alkyls at 150–200°C. At ca 250°C, the β-form converts to α. †-$TiCl_3$ is made by prolonged grinding of the α- or γ-forms.

The primary use of $TiCl_3$ is as a catalyst for the polymerization of hydrocarbons (125–129). In particular, the Ziegler-Natta catalysts used to produce stereoregular polymers of several olefins and dienes, eg, polypropylene, are based on α-$TiCl_3$ and $Al(C_2H_5)_3$. The mechanism of this reaction has been described (130). Suppliers of titanium trichloride include Akzo America and Phillips Petroleum in the United States, and Mitsubishi in Japan.

6.8.2.3. Titanium Trichloride Hexahydrate. Titanium trichloride hexahydrate [19114-57-9] can be prepared by dissolving anhydrous titanium trichloride in water or by reducing a solution of titanium tetrachloride. Evaporation and crystallization of the solution yield violet crystals of the hexahydrate. The hydrated salt has had some commercial application as a stripping or bleaching agent in the dyeing industry, particularly where chlorine must be avoided.

6.8.2.4. Titanium Tetrachloride. Titanium tetrachloride [7550-45-0] is a clear, colorless liquid, normally made by the chlorination of titanium dioxide at ca 1000°C in the presence of a reducing agent.

$$TiO_2 + 2\,Cl_2 + 2\,C^0 \longrightarrow TiCl_4 + 2\,CO$$

It is the most widely studied of the titanium halides both because of its commercial importance and because of its abilities to participate in substitution reactions and form addition compounds with a wide range of donor molecules. Its main uses are in the manufacture of titanium dioxide pigments and titanium metal, as a starting material in the manufacture of a wide range of commercially important titanium organic compounds, which are mostly alkoxides rather than true organometallic compounds, and as a starting material in the production of Ziegler-Natta catalysts. In 1996, world production was ca 6×10^6 t.

Properties. Physical properties of titanium tetrachloride are given in Table 18. In the vapor phase, the titanium tetrachloride molecule is tetrahedral and has a Ti–Cl bond length of 218 pm. The regular tetrahedral coordination is retained in the solid, although each of the chlorines is crystallographically different in the monoclinic lattice (131).

Table 18. Physical Properties of Titanium Tetrachloride

Property	Value
color	none
density, 20°C, g/cm^3	1.7
freezing point, °C	−24.1
heat of fusion, kJ/mol[a]	9.966
boiling point, °C	136.5
vapor pressure, kPa[b]	
20°C	1.33
50°C	5.52
100°C	35.47
heat of vaporization, kJ/mol[a]	
25°C	41.087
135.8°C	35.98
specific heat, 20°C, J/(k·mol)[a]	145.21
critical temperature, °C	370
heat of liquid formation, 25°C, kJ/mol[a]	-804.2 ± 4.2
viscosity, mPa·s(=cP)	0.079
refractive index, n	1.6985
magnetic susceptibility	-0.287×10^{-6}
dielectric constant, 20°C	2.79

[a] To convert kJ to kcal, divide by 4.184.
[b] To convert kPa to psi, multiply by 0.145.

Titanium tetrachloride is completely miscible with chlorine. The dissolution obeys Henry's law, ie, the mole fraction of chlorine in a solution of titanium tetrachloride is proportional to the chlorine partial pressure in the vapor phase. The heat of solution is 16.7 kJ/mol (3.99 kcal/mol). The apparent maximum solubilities of chlorine at 15.45 kPa (116 mm Hg) total pressure follow.

Temperature, °C	Cl_2, mole fraction	Cl_2, in 100-g $TiCl_4$
−10	0.38	23.4
0	0.28	14.3
20	0.155	6.85

The system shows a eutectic that solidifies at $-108°C$ at 87.5 atom % Cl.

Titanium tetrachloride's affinity for water is so high that it acts as a desiccating agent. It is readily hydrolyzed by water and fumes strongly when in contact with moist air. The dense white fumes, consisting of finely divided oxychlorides, are the basis of the use of titanium tetrachloride as white smoke. Hence $TiCl_4$ is used by the military for smoke screen purposes (see Chemicals in war). At room temperature and below, liquid titanium tetrachloride dissolves exothermically in water to form clear mixtures that are acid because of hydrolysis. A series of oxychlorides, and ultimately titanium dioxide, are formed, the precise product depending on conditions of temperature, concentration, and pH. Thus, Raman spectra suggest that complexes of the type $TiO_2Cl^{4-}{}_4$ are formed in hydrochloric acid, whereas the hexachlorotitanate anion is reported to be formed in fuming hydrochloric acid (132).

Titanium tetrachloride is also miscible with other common liquids, including organic solvents such as hydrocarbons, carbon tetrachloride, and chlorinated hydrocarbons. With those containing hydroxyl, carboxyl, or diketone (in the enol form) groups, reaction occurs. Substitution products are formed with the elimination of hydrogen chloride. Thus, with alcohols, alkoxides, also called esters of titanic acid, are formed (see Alkoxides, metal).

$$\mathrm{TiCl_4 + ROH \longrightarrow TiCl_3OR + HCl \longrightarrow TiCl_2\,(OR)_2 + HCl \longrightarrow}$$

$$\mathrm{TiCl\,(OR)_3 + HCl \longrightarrow Ti\,(OR)_4 + HCl}$$

For the reaction to go to completion, it is necessary to remove the liberated hydrogen chloride, eg, by reaction with ammonia.

Addition compounds form with those organics that contain a donor atom, eg, ketonic oxygen, nitrogen, and sulfur. Thus, adducts form with amides, amines, and *N*-heterocycles, as well as acid chlorides and ethers. Addition compounds also form with a number of inorganic compounds, eg, $POCl_3$ (6, 120). In many cases, the addition compounds are dimeric, eg, with ethyl acetate, in titanium tetrachloride-rich systems. By using ammonia, a series of amidodichlorides, $Ti(NH_2)_xCl_{4-x}$, is formed (133).

Titanium tetrachloride is readily reduced. By using sodium, calcium, or magnesium, reduction to the metal occurs. By using hydrogen, on the other hand, complete reduction to the metal only occurs at very high temperatures and the resultant metal sponge takes up hydrogen on cooling. However, at 700°C, titanium trichloride is formed and can be collected as a crystalline solid in a receiver held above the boiling point of the tetrachloride.

Manufacture. Titanium chloride is manufactured by the chlorination of titanium compounds (1, 134–138). The feedstocks usually used are mineral or synthetic rutile, beneficiated ilmenite, and leucoxenes. Because these are all oxygen-containing, it is necessary to add carbon as well as coke from either coal or fuel oil during chlorination to act as a reducing agent. The reaction is normally carried out as a continuous process in a fluid-bed reactor (139). The bed consists of a mixture of the feedstock and coke. These are fluidized by a stream of chlorine introduced at the base (see Fluidization). The amount of heat generated in the TiO_2 chlorination process depends on the relative proportions of CO_2 or CO that are formed (eqs. 1 and 2), and the mechanism that determines this ratio is not well understood.

$$\mathrm{TiO_2 + 2\,Cl_2 + C^0 \longrightarrow TiCl_4 + CO_2} \qquad \begin{aligned} \Delta H &= -217.6\ \mathrm{kJ/mol\ at\ 1100\ K} \\ &= -221.7\ \mathrm{kJ/mol\ at1300\ K} \end{aligned} \qquad (1)$$

$$\mathrm{TiO_2 + 2\,Cl_2 + 2\,C^0 \longrightarrow TiCl_4 + 2\,CO} \qquad \begin{aligned} \Delta H &= -50.1\ \mathrm{kJ/mol\ at\ 1100\ K} \\ &= -54.2\ \mathrm{kJ/mol\ at1300\ K} \end{aligned} \qquad (2)$$

The second reaction (eq. 2) is relatively more favored as the temperature increases ($\Delta G_A = -280$ kJ/mol, $\Delta G_B = -302$ kJ/mol at 1100 K; $\Delta G_A = -290.8$ kJ/mol, $\Delta G_B = -305.7$ kJ/mol at 1300 K). It follows that the chlorinator temperature depends on the proportion of CO_2 and CO generated; it can be adjusted either by coke oxidation, with oxygen in the Cl_2 gas, or by cooling with cold $TiCl_4$.

Under typical chlorination conditions, most elements are chlorinated. Therefore, for every metric ton of titanium tetrachloride produced, lower grade feedstocks require more chlorine. Minor impurities such as alkaline-earths, where the chlorides are relatively involatile, may either inhibit bed-fluidization or cause blockages in the equipment and require particular consideration regarding feedstock specification.

If ores having a lower TiO_2 content, eg, high grade slags, leucoxene, or ilmenites, are used, the majority of metal (mainly iron) oxides are chlorinated and exit with the titanium tetrachloride. The reaction products are condensed and impurities are removed by a sequential process involving a solids separator and a liquid scrubbing system. The crude titanium tetrachloride is further purified by distillation. Vanadium oxychloride that boils at a similar temperature to titanium tetrachloride may be reduced at this stage and converted into a nonvolatile sludge. Many patents relate to the choice of suitable reductants. The final distilled product is extremely pure, a key feature in the subsequent production of pigment having good color.

Alternatives to the fluidized-bed method process include the chlorination of titanium slags in chloride melts, chlorination with hydrogen chloride, and flash chlorination. The last is claimed to be particularly advantageous for minerals having a high impurity content (133–135, 140). The option of chlorinating titanium carbide has also been considered (30).

Producers and Economic Aspects. The main producers of titanium tetrachloride throughout the world are producers of titanium dioxide pigment by the chloride route. These include Bayer, Du Pont, Ishihara Sangyo Kaisha, Kerr McGee, Kronos Titan, Millenium Chemicals, and the Tioxide Group. Other suppliers, not necessarily large-scale producers, include Akzo Nobel Chemicals, Aldrich Chemical, Atomergic Chemetals, Cerac, Janssen Chimica, Noah Technologies, Titanium Metals, and Toth Aluminium.

Hexachlorotitanates. H_2TiCl_6 may be made by dissolving anhydrous hydrogen chlorine in titanium tetrachloride (C13). Ammonium hexachlorotitanate [21439-26-9], potassium hexachlorotitanate [16918-46-0], rubidium hexachlorotitanate [16902-24-2], and cesium hexachlorotitanate [16918-47-1] are light-green to yellow crystalline solids. They may be prepared either by direct interaction of the alkali-metal chloride with titanium tetrachloride or by reaction in fuming HCl. Both the acids and its salts are more susceptible to hydrolysis than the corresponding fluorotitanates. They are also thermally unstable and decompose to the alkali metal chloride and titanium tetrachloride.

Oxychlorides. Hydrolysis of $TiCl_4$ yields a number of products, the composition of which depends on the hydrolysis conditions. In the $TiCl_3$–HCl–H_2O system, species ranging from $Ti(H_2O)^{3+}{}_6$ through $TiCl(H_2O)^{2+}{}_5$ to $TiCl_5(H_2O)^{2-}$, as the acid concentration increases, has been reported (141).

Titanium oxide dichloride [13780-39-8], $TiOCl_2$, is a yellow hygroscopic solid that may be prepared by bubbling ozone or chlorine monoxide through titanium tetrachloride. It is insoluble in nonpolar solvents but forms a large number of adducts with oxygen donors, eg, ether. It decomposes to titanium tetrachloride and titanium dioxide at temperatures of ca 180°C (136).

A titanium monoxychloride, TiOCl, may be prepared by the action of TiO_2, Fe_2O_3, or oxygen on $TiCl_3$ (137). For example, at 650°C,

$$2\,TiCl_3 + TiO_2 \longrightarrow 2\,TiOCl + TiCl_4$$

Titanous oxychloride forms yellow tablets, is inert in mineral acids and water and also stable in air. When heated in air, it gives titanium tetrachloride and titanium dioxide.

6.8.3. Titanium Bromides

6.8.3.1. Titanium Dibromide. Titanium dibromide [13873-04-5], a black crystalline solid, density 4310 kg/m^3, mp 1025°C, has a cadmium iodide-type structure and is readily oxidized to trivalent titanium by water. Spontaneously flammable in air (142), it can be prepared by direct synthesis from the elements, by reaction of the tetrabromide with titanium, or by thermal decomposition of titanium tribromide. This last reaction must be carried out either at or below 400°C, because at higher temperatures the dibromide itself disproportionates.

$$2\ \mathrm{TiBr_3} \longrightarrow \mathrm{TiBr_2} + \mathrm{TiBr_4}$$

6.8.3.2. Titanium Tribromide. Titanium tribromide [13135-31-4] crystallizes in two different habits: hexagonal plates or blue-black needles. It can be prepared by the reaction of $TiBr_4$ with either titanium or hydrogen.

$$3\ \mathrm{TiBr_4} + \mathrm{Ti^0} \longrightarrow 4\ \mathrm{TiBr_3}$$

or

$$2\ \mathrm{TiBr_4} + \mathrm{H_2} \longrightarrow 2\ \mathrm{TiBr_3} + 2\ \mathrm{HBr}$$

A hexahydrate is also known and may be prepared by the electrolytic reduction of the tetrabromide in hydrobromic acid solution.

6.8.3.3. Titanium Tetrabromide. Titanium tetrabromide [7789-68-6] is an amber-yellow, easily hydrolyzed, crystalline solid, having a density of 3250 kg/m^3. The crystal structure depends on temperature. At 20°C, $TiBr_4$ is monoclinic (143) and has $a = 1017$ pm, $b = 709$ pm, $c = 1041$ pm, and $\beta = 101.97^\circ$ (143). It melts at 39°C and may be purified by vacuum sublimation. The liquid boils at 233°C to give a monomeric vapor in which the Ti–Br distance is 231 pm. Titanium tetrabromide is soluble in dry chloroform, carbon tetrachloride, ether, and alcohol. Like titanium tetrachloride, $TiBr_4$ forms a range of adducts with molecules such as ammonia, amines, nitrogen heterocycles, esters, and ethers.

Analogous with titanium tetrachloride, the tetrabromide may be made by the carbothermal bromination of titanium dioxide at ca 700°C,

$$\mathrm{TiO_2} + 2\ \mathrm{Br_2} + \mathrm{C^0} \longrightarrow \mathrm{TiBr_4} + \mathrm{CO_2}$$

and also by direct bromination of titanium at 300–600°C in a flow system. Halogen exchange among titanium tetrachloride, hydrogen bromide, and boron tribromide has also been used.

6.8.4. Titanium Iodides

6.8.4.1. Titanium Diiodide. Titanium diiodide is a black solid ($\rho = 499(0)$ kg/m^3) that has the cadmium iodide structure. Titaniums occupy octahedral sites in hexagonally close-packed iodine layers, where $a = 411$ pm and $c = 682$ pm (144). Magnetic studies indicate extensive Ti–Ti bonding. TiI_2 reacts rapidly with water to form a solution of titanous iodide, TiI_3.

Titanium diiodide may be prepared by direct combination of the elements, the reaction mixture being heated to 440°C to remove the tri- and tetraiodides (145). It can also be made by either reaction of solid potassium iodide with titanium tetrachloride or reduction of TiI_4 with silver or mercury.

6.8.4.2. Titanium Triiodide. Titanium triiodide is a violet crystalline solid having a hexagonal unit cell (146). The crystals oxidize rapidly in air but are stable under vacuum up to 300°C; above that temperature, disproportionation to the diiodide and tetraiodide begins (147).

Titanium triiodide can be made by direct combination of the elements or by reducing the tetraiodide with aluminum at 280°C in a sealed tube. TiI_3 reacts with nitrogen, oxygen, and sulfur donor ligands to give the corresponding adducts (148).

6.8.4.3. Titanium Tetraiodide. Titanium tetraiodide [7720-83-4] forms reddish-brown crystals, cubic at room temperature, having reported lattice parameter of either 1200 (149) or 1221 (150) pm. TiI_4 melts at 150°C, boils at 377°C, and has a density of 440(0) kg/m^3. It forms adducts with a number of donor molecules and undergoes substitution reactions (151). It also hydrolyzes in water and is readily soluble in nonpolar organic solvents.

Titanium tetraiodide can be prepared by direct combination of the elements at 150–200°C; it can be made by reaction of gaseous hydrogen iodide with a solution of titanium tetrachloride in a suitable solvent; and it can be purified by vacuum sublimation at 200°C. In the van Arkel method for the preparation of pure titanium metal, the sublimed tetraiodide is decomposed on a tungsten or titanium filament held at ca 1300°C (152). There are frequent literature references to its use as a catalyst, eg, for the production of ethylene glycol from acetylene (153).

6.9. Titanium Silicon Compounds

6.9.1. Titanium Silicides

The titanium–silicon system includes Ti_3Si, Ti_5Si_3, TiSi, and $TiSi_2$ (154). Physical properties are summarized in Table 19. Direct synthesis by heating the elements *in vacuo* or in a protective atmosphere is possible. In the latter case, it is convenient to use titanium hydride instead of titanium metal. Other preparative methods include high temperature electrolysis of molten salt baths containing titanium dioxide and alkalifluorosilicate (155); reaction of $TiCl_4$, $SiCl_4$, and H_2 at ca 1150°C, using appropriate reactant quantities for both TiSi and $TiSi_2$ (156); and, for Ti_5Si_3, reaction between titanium dioxide and calcium silicide at ca 1200°C, followed by dissolution of excess lime and calcium silicate in acetic acid.

Table 19. Structure and Physical Constants of Titanium Silicides[a]

Property	$TiSi_2$	TiSi	Ti_5Si_3	Ti_3Si
CAS Registry Number	[12039-83-7]	[12039-70-2]	[12067-57-1]	
Ti, atomic	33	50	62.5	75
structure	orthorhombic	rhombic	hexagonal	
lattice parameters, nm[b]				
a	0.8253	0.654(4)	0.7448	1.039
b	0.4783	0.363(8)		
c	0.854	0.499(7)	0.5114	0.517
density, kg/m^{3b}	439(0)	434(0)	431(0)	
mp, °C	ca 1540	1760	2120	
hardness, 100-g load, kg/mm	850	1050	1000	
resistivity, $\mu\Omega\cdot$cm	123			

[a] Ref. 153.
[b] Numbers in parentheses are fourth digit of reduced accuracy.

Titanium disilicide [12039-83-7] is a silvery-gray, crystalline material that oxidizes slowly in air when heated to 700–800°C. It is resistant both to mineral acids (except hydrofluoric) and to aqueous solutions of alkalies, but reacts with fused borax, sodium hydroxide, and potassium hydroxide. It reacts explosively with chlorine at high temperatures.

Titanium silicides are used in the preparation of abrasion- and heat-resistant refractories. Compositions based on mixtures of Ti_5Si_3, TiC, and diamond have been claimed to make wear-resistant cutting-tool tips (157). Titanium silicide can be used as an electric–resistant material, in electrically conducting ceramics (158), and in pressure-sensitive elastic resistors, the electric resistance of which varies with pressure (159).

6.9.2. Titanium Silicates

A number of titanium silicate minerals are known (160); examples are listed in Table 20. In most cases, it is convenient to classify these on the basis of the connectivity of the SiO_4 building blocks, eg, isolated tetrahedra, chains, and rings, that are typical of silicates in general. In some cases, the SiO_4 units may be replaced, even if only to a limited extent by TiO_4. For example, up to 6% of the SiO_4 in the garnet schorlomite can be replaced by TiO_4. In general, replacement of SiO_4 by TiO_4 building blocks increases the refractive indices of these minerals. Ti has also replaced Si in the framework of various zeolites. In addition, the catalytic activity of both titanium-substituted ZSM-5 (TS-1) and ZSM-11 (TS-2) has received attention (161), eg, the selective oxidation of phenol, with hydrogen peroxide, to hydroquinone and catechol over TS-1 has been operated at the 10,000 t/yr scale in Italy (162).

Table 20. Silicate Minerals

Mineral	Chemical formula	Crystal form, lattice parameters, pm	Structural unit
natisite	Na_2TiSiO_5	tetragonal; $a = 650$, $c = 507$	isolated SiO_4 tetrahedra
titanite (or sphene)	$CaTiSiO_5$	monoclinic; $a = 706.6$, $b = 870.5$, $c = 656.1$	isolated SiO_4 tetrahedra
benitoite	$BaTiSi_3O_9$	hexagonal	hexagonal rings of three SiO_4 tetrahedra
schorlomite	$Ca_3(Fe,Ti)_2(Si,Ti)_3O_{12}$	cubic; $a = 1212.8$	garnet structure, isolated SiO_4 tetrahedra
lorenzenite	$Na_2TiSi_2O_9$	orthorhombic; $a = 1449$, $b = 870$, $c = 523$	SiO chains
davanite	$K_2TiSi_6O_{15}$	triclinic; $a = 714$, $b = 753$, $c = 693$	silicate layers

6.10. Titanium Phosphorus Compounds

6.10.1. Titanium Phosphides

The titanium phosphides (154) include Ti_3P [12037-66-0], Ti_5P_3, and TiP (163). Titanium monophosphide [12037-65-9], TiP, can be prepared by heating phosphine with titanium tetrachloride or titanium sponge. Alternatively, titanium metal may be heated with phosphorus in a sealed tube. The gray metallic TiP is slightly phosphorus-deficient ($TiP_{0.95}$), has a density of 408(0) kg/m^3, and displays considerable mechanical hardness (700 kg/mm^2). It is oxidized on heating in air but is stable when heated to 1100°C in either vacuum or a protective atmosphere; it is resistant to concentrated acid (except aqua regia) and alkalies; and it is reported to act as a catalyst in polycondensation reactions.

6.10.2. Titanium Phosphates

Titanium(III) phosphate [24704-65-2] (titanous phosphate) is a purple solid, soluble in dilute acid, giving relatively stable solutions. It can be prepared by adding a soluble phosphate to titanous chloride or sulfate solution and raising the pH until precipitation occurs.

Titanium(IV) phosphate gel [17017-60-6] may be prepared by adding an alkali phosphate to titanium(IV) sulfate or chloride solution, followed by filtering, leaching, and drying the derived gel. The product is insoluble in dilute sulfuric acid. Titanium phosphate prepared in this way has been used in the dyeing and leather (qv) tanning industries. Polymeric titanium phosphate compositions for metal activation prior to phosphating have also been claimed (164). A process for the recovery of titanium phosphate pigment from wastes from the TiO_2–sulfate process has been proposed (165, 166).

The α-form of titanium(IV) bis(hydrogen phosphate) dihydrate has a layer structure similar to that of the analogous zirconium compound (167, 168). It is prepared by refluxing the gels in phosphoric acid for long (400 h or more) periods. The degree of crystallinity achieved depends on the acid concentration and treatment times. The derived compounds can act as ion-exchange materials. The catalytic activity of these compounds for alcohol dehydration, oxidative dehydrogenation, oxidation, and polymerization has been reviewed (169). Under special conditions, a second, γ, form may be prepared (168). The interlayer distance in the γ-form is significantly larger than that in the α, which makes γ-forms of greater potential use as ion exchangers. Processes for the removal of K^+ from seawater, $^{42}K^+$ and $^{37}Cs^+$ from strong mineral acids, and $NH^+{}_4$ and NH_3 from waste solutions have been described (170–172).

Titanium pyrophosphate [13470-09-2], TiP_2O_7, a possible uv reflecting pigment, is a white powder that crystallizes in the cubic system and has a theoretical density of 3106 kg/m^3. It is insoluble in water and can be prepared by heating a stoichiometric mixture of hydrous titania and phosphoric acid at 900°C.

6.11. Titanium Sulfur Compounds

6.11.1. Titanium Sulfides

The titanium sulfur system has been summarized (4). Titanium subsulfide [1203-08-6], Ti_2S, forms as a gray solid of density 4600 kg/m^3 when titanium monosulfide [12039-07-5], TiS, is heated at 1000°C with titanium in a sealed tube. It can also be formed by heating a mixture of the two elements at 800–1000°C. The sulfide, although soluble in concentrated hydrochloric and sulfuric acids, is insoluble in alkalies.

The structures of titanium monosulfide and titanium disulfide [12039-13-3], TiS_2, are both made up of layers of hexagonally stacked sulfur atoms (43). In TiS, all the octahedral sites between each layer are filled by titanium; in the disulfide, only the sites in alternate layers are filled. Partial occupation of the remaining octahedral sites in titanium disulfide then results in a series of nonstoichiometric phases, where the nominal formula varies from Ti_8S_9 through Ti_4S_5 to titanium sesquisulfide [12039-16-6], Ti_2S_3, and in which the ordering of the additional titaniums depends on the preparation conditions. Because the outer electrons are delocalized to an appreciable extent, the compounds have pseudometallic properties. TiS is a dark-brown solid (density 4050 kg/m^3), Ti_2S_3 is a black crystalline solid (density 3520 kg/m^3), and TiS_2 is a bronze-colored solid (density 3220 kg/m^3). Each can be prepared by direct combination of the elements. Other methods of preparation are also similar:

$$TiS_2 + H_2 \longrightarrow TiS + H_2S$$

$$2\ TiS_2 + H_2 \longrightarrow Ti_2S_3 + H_2S$$

Titanium disulfide can also be made by pyrolysis of titanium trisulfide at 550°C. A continuous process based on the reaction between titanium tetrachloride vapor and dry, oxygen-free hydrogen sulfide has been developed at pilot scale (173). The preheated reactants are fed into a tubular reactor at approximately 500°C. The product particles comprise orthogonally intersecting hexagonal plates or plate segments and have a relatively high surface area ($>$4 m^2/g), quite different from the flat platelets produced from the reaction between titanium metal and sulfur vapor. The powder, reported to be stable to storage for long periods under dry air or nitrogen at or below 20°C, is not attacked by hydrochloric acid but is soluble in both hot and cold sulfuric acid and also, unlike the other sulfides, in hot sodium hydroxide solution.

Titanium trisulfide [12423-80-2], TiS_3, a black crystalline solid having a monoclinic structure and a theoretical density of 3230 kg/m^3, can be prepared by reaction between titanium tetrachloride vapor and H_2S at 480–540°C. The reaction product is then mixed with sulfur and heated to 600°C in a sealed tube to remove residual chlorine. Sublimation may be used to separate the trisulfide (390°C) from the disulfide (500°C). Titanium trisulfide, insoluble in hydrochloric acid but soluble in both hot and cold sulfuric acid, reacts with concentrated nitric acid to form titanium dioxide.

The principal use of titanium sulfides is as a cathode material in high efficiency batteries (11). In these applications, the titanium disulfide acts as a host material for various alkali or alkaline-earth elements.

$$x\,Li^+ + x\,e^- + TiS_2 \longrightarrow Li_xTiS_2$$

The titanium sulfide is able to act as a lithium reservoir. On intercalation with lithium, the titanium lattice expands from ca 570 to 620 pm as the intercalation proceeds to completion on formation of $TiLiS_2$. Small button cells have been developed, incorporating lithium perchlorate in propylene carbonate electrolyte, for use in watches and pocket calculators (see Batteries).

Titanium disulfide has been proposed as a solid lubricant. The coefficient of friction between steel surfaces is 0.3, compared to only 0.2 for molybdenum disulfide. However, because it does not adhere strongly to metal surfaces, TiS_2 is generally less effective than molybdenum sulfide.

6.11.2. Titanium Sulfates

Solutions of titanous sulfate [10343-61-0] are readily made by reduction of titanium(IV) sulfate in sulfuric acid solution by electrolytic or chemical means, eg, by reduction with zinc, zinc amalgam, or chromium(II) chloride. The reaction is the basis of the most used titrimetric procedure for the determination of titanium. Titanous sulfate solutions are violet and, unless protected, can slowly oxidize in contact with the atmosphere. If all the titanium has been reduced to the trivalent form and the solution is then evaporated, crystals of an acid sulfate $3\ Ti_2(SO_4)_3{\cdot}H_2SO_4{\cdot}25H_2O$ [10343-61-0] are produced. This purple salt, stable in air at normal temperatures, dissolves in water to give a stable violet solution. When heated in air, it decomposes to TiO_2, water, sulfuric acid, and sulfur dioxide.

If a solution of the acid sulfate in dilute sulfuric acid is evaporated at 200°C, green crystals of the anhydrous neutral salt form. The anhydrous salt is insoluble in water, alcohol, and concentrated sulfuric acid, but dissolves in dilute sulfuric or hydrochloric acid to give a violet solution. The salt is isomorphous with chromic sulfate and is used commercially as a reducing agent.

Titanium(IV) sulfate can be prepared by the reaction of titanium tetrachloride with sulfur trioxide dissolved in sulfuryl chloride.

$$TiCl_4 + 6\ SO_3 \longrightarrow Ti\,(SO_4)_2 + 2\ S_2O_5Cl_2$$

It is readily hydrolyzed by moisture and, when heated, changes first to titanyl sulfate [13825-74-6], $TiOSO_4$, and then to TiO_2. Because of the high charge/radius ratio, normal salts of Ti^{4+} cannot be prepared from aqueous solutions. Instead, these hydrolyze to form a titanyl species normally written as $[TiO]^{2+}$. Ion-exchange studies on aqueous solutions of Ti(IV) in perchloric acid are consistent with the existence of monomeric, doubly charged cationic species, although it is not clear whether these are $[TiO]^{2+}$ or $[Ti(OH)_2]^{2+}$ (174, 175). Titanyl sulfate is the best known of the derived salts because of its importance as an intermediate in the manufacture of titanium dioxide pigments by the sulfate process. The white, needle-like powder of the hydrate [58428-64-1], $TiOSO_4{\cdot}H_2O$, is formed when solutions of TiO_2 in sulfuric acid are evaporated. However, there is no evidence for the existence of the $[TiO]^{2+}$ ion in the solid. Rather, it is believed to contain –Ti–O–Ti–O– chains, where each Ti is octahedrally coordinated by the two bridging oxygens (Ti–O distance ca 180 pm), a water molecule, and one oxygen from each of the three sulfates. In addition to its role as an intermediate in the production of titanium dioxide, titanyl sulfate is used for treatment of metals and in the dyeing industry for the preparation of titanous sulfate. Titanyl sulfate may also be used as a tanning agent for the production of leather (176). In this application, it is often complexed, ie, masked, with, eg, sodium gluconate to prevent unwanted precipitation of hydrous titania (177). Various double sulfates have also been described. For example, $(NH_4)_2[TiO(SO_4)_2]$, which can be prepared from sulfate liquors of titanium by precipitation with ammonium sulfate and sulfuric acid, is also used as a tanning agent (178).

6.12. Analytical Methods

The analytical chemistry of titanium has been reviewed (179–181). Titanium ores can be dissolved by fusion with potassium pyrosulfate, followed by dissolution of the cooled melt in dilute sulfuric acid. For some ores, even if all of the titanium is dissolved, a small amount of residue may still remain. If a full analysis is required, the residue may be treated by moistening with sulfuric and hydrofluoric acids and evaporating, to remove silica, and then fused in a sodium carbonate–borate mixture. Alternatively, fusion in sodium carbonate–borate mixture can be used for ores and a boiling mixture of concentrated sulfuric acid and ammonium sulfate for titanium dioxide pigments. For trace-element determinations, the preferred method is dissolution in a mixture of hydrofluoric and hydrochloric acids.

Titrimetric methods based on dissolution of the sample, reduction of the Ti(IV) to Ti(III), and reoxidation to Ti(IV) using a standard oxidizing agent are widely employed for the determination of significant levels of titanium. Reduction may be by means of either a solution of chromium(II) chloride, Nakozono, Jones reductors, or aluminum metal. In all cases, the reduced solutions, which must be protected from reoxidation by atmospheric oxidation, can be titrated using standard ferric iron solutions. Chromium chloride reduction followed by a potentiometric titration is preferred because it is not subject to interference by chromium or vanadium. For reductions using Nakozono, Jones reductors, or aluminum metal, the end points can be determined either potentiometrically or by using a potassium thiocyanate indicator but chromium and vanadium interfere. Gravimetric procedures for the determination of titanium are not widely employed, although precipitation with cupferron from an ammonium acetate-buffered solution containing ethylenediamine tetraacetic acid (EDTA) can be used.

Wavelength dispersive x-ray fluorescence spectrometric (xrf) methods using the titanium K_α line at 0.2570 nm may be employed for the determination of significant levels of titanium only by careful matrix-matching. However, xrf methods can also be used for semiquantitative determination of titanium in a variety of products, eg, plastics. Xrf is also widely used for the determination of minor components, such as those present in the surface coating, in titanium dioxide pigments.

Minor levels of titanium are conveniently measured by spectrophotometry, eg, by the 410-nm absorbance of the yellow-orange peroxide complex that develops when hydrogen peroxide is added to acidic solutions of titanium.

For trace levels, instrumental methods of analysis are normally used. Flame atomic absorption spectrometry using a reducing nitrous oxide–acetylene flame typically gives a sensitivity of 2 mg/L for 1% absorption at 364.3 nm. Much greater sensitivity (ca 1 μg/L) can be obtained using electrothermal atomic absorption spectrometry using Zeeman background correction, but many interfering elements can lead to the formation of stable titanium complexes in the furnace. Inductively coupled plasma–atomic emission spectrometry atomizes the titanium more effectively. For the 334.941-nm line, detection limits of 0.5 μg/L have been reported. Finally, inductively coupled plasma–mass spectrometry can be used to monitor the titanium isotopes of mass 46, 47, 48, 49, and 50, achieving detection limits in the range of 0.001–0.01 μg/L for the principal ($\sim$75% abundance) mass 48.

6.13. Health and Safety Aspects

The following discussion on health and safety aspects of titanium compounds is concerned only with the behavior of the titanium present in inorganic compounds and not with the effects of the compounds themselves. For example, titanium tetrachloride must be treated with care because of the effects of the hydrochloric acid and heat produced when it reacts with water, not because of the possible toxicity of titanium. Apart from very few exceptions, the inorganic compounds of titanium are generally regarded as having low toxicity. Because of the ubiquitous nature of the element and its compounds, average concentrations of titanium in blood have been determined at 130–160 μg/L (182–184), with a typical value of 10 μg/L in urine (185).

Titanium metal is frequently used as a surgical implant, and several titanium compounds have been used in medical, food, food-contact, and cosmetic products. In the human body, the highest concentrations of titanium are found in the lung (182, 186, 187), resulting from the slow clearance of insoluble inhaled particles that accumulate with time. Such particles are typically oxides or complex silicates. Exposures during occupational activities have been shown to increase the lung burden. For example, miners have reported values of 119 μg/g dry weight titanium in lung, compared with 19 μg/g dry weight for nonoccupationally exposed people (188).

Much work has been carried out on the toxicology of titanium, mainly as a result of the widespread use of titanium dioxide pigments. Animal experiments have demonstrated that titanium dioxide is not carcinogenic by the oral route (189), whereas inhalation experiments have demonstrated that an excess of tumors is formed on high exposure in rats, but not in other species, such as mice (190, 191). It is considered that the tumors in rats are an exaggerated response to lung-overload effects, associated with any insoluble, low toxicity dust, which may be rat-specific. This is corroborated by the fact that an epidemiological study of pigment production workers did not demonstrate any excess of tumors (192).

Titanium dioxide, because of its insolubility and low toxicity, has been allocated occupational exposure limits by the ACGIH of 10-mg/m^3 total dust, or 3-mg/m^3 respirable dust averaged over an eight-hour exposure period (193). Guidance on the precautions to be taken while handling titanium dioxide pigments includes the avoidance of the generation of inhalable dust, preferably by engineering controls or, when necessary, by respiratory protection (194). Because titanium dioxide has the ability to dry and defat the skin by adsorption, prolonged skin contact should be avoided.

6.14. Environmental Concerns

This section discusses the sources and typical quantities of by-product and waste materials that arise during TiO_2 pigment manufacture.

The difference between a waste material and a by-product is principally semantic. Sometimes a wastestream can be treated or modified in such a way that a useful product is developed for which there is a market. This product then becomes a by-product. Sales values of by-products may generate a positive margin, or a negative margin that may nevertheless represent a net reduction in the cost of waste disposal.

By-products and wastes arising from the sulfate process, the chloride process, and posttreatment operations are described here.

6.14.1. Sulfate Process Wastes

6.14.1.1. Air Emissions. Numerous air emissions from the sulfate process must be controlled to permitted levels and, in some instances, neutralized before disposal. The principal particulate emissions are listed below.

- *Ore drying and milling*—fine-particle-size ore dust is recovered in a dry form, usually with bag filters or electrostatic precipitators and returned to the digestion process. Recoveries are very high, and, typically, there are no air emission or pollution problems if the air-cleaning equipment is maintained and operated properly.

- *Digestion*—this is the major source of air emissions and pollution in the sulfate process. Large quantities of SO_2, SO_3, H_2SO_4 mist, steam, and unreacted ore in the form of dust are emitted during the very short digestion or reaction cycle. Large air scrubbing and neutralization systems are utilized to capture and neutralize these pollutants, and most producers are able to reduce them to acceptable limits. However, most air-emission permits allow the use of an averaging time period greater than the time period of the reaction of the titaniferous ore with sulfuric acid. This means that these systems can operate satisfactorily with the very large volume of pollutants emitted in a brief time period. Some sulfate process producers are now using innovative acid mist and particulate scrubbing equipment that will meet newer, more rigorous, point-source instantaneous air-emission standards.

Miscellaneous acidic gaseous emissions from processing operations up to the calcination operation must be captured and neutralized. This is generally accomplished by a central scrubbing-and-neutralization system. Quantities of these miscellaneous air emissions are difficult to estimate but represent less than 1% of the total air emissions from a sulfate process plant.

Air emissions from the calcination operation are significant and can comprise as much as 25% of the total air emissions from the sulfate process. The hot counterflow gas stream in the calciner absorbs the free and strongly absorbed water while converting the TiO_2 hydrate to a dry oxide. The SO_3 and sulfuric acid bound up in the TiO_2 hydrate (typically 10% of the total waste acid) are also absorbed in the gas stream together with some TiO_2 particles. This acidic gaseous solution is washed in scrubbers to remove the SO_3 and TiO_2 particles. The free sulfuric acid and that formed from the SO_3 absorption must be neutralized, and the neutral solids landfilled. Techniques are employed by some pigment producers to recover the lost TiO_2, recycle it to the calcinator, and also recover the thermal energy contained in the gas stream.

Quantities of particulate TiO_2 emissions from the calciner generally constitute 1–2% of the TiO_2 units fed to the calciner. Neutral solids from the calciner off gas scrubbing are significant and are in the range of 0.1 tons of neutral solids per ton of pigment produced.

6.14.1.2. Liquid Wastes. Liquid wastes from the sulfate process are numerous and particularly troublesome.

Waste acid formed in the filtration of the TiO_2 hydrate is the largest SP liquid effluent stream. This strong acid stream is typically segregated as 23% strength H_2SO_4 and contains most of the non-TiO_2 metal sulfates that are in a soluble form. Most of the weak-acid stream is generated in the second washing operation (begun with clean water) and is collected as a 0.5% strength H_2SO_4. These streams can be combined with other acidic streams and recycled back to the digestion reactor to dissolve the digest cake, to wet the ore prior to digestion, or to dilute the strong sulfuric acid stream prior to the digestion reaction, thus creating the setoff charge in the reactor. Some of the waste acid can also be used in posttreatment to adjust pH of the treatment solution to precipitate the inorganic surface treatment on the TiO_2 particle. The weak acid stream eventually generated contains 0.5% H_2SO_4 and can be discharged directly. The strong-acid stream (23% H_2SO_4) is also isolated, and is either neutralized, and the neutral solids landfilled, or this strong-acid stream is concentrated, and the recovered acid recycled back to digestion.

6.14.1.3. Solid Wastes. Some solid wastes from the sulfate process can be a source of value-added by-products.

The solid residues from the digestion reaction consist of inert solid materials, unreacted and insoluble ore (natural rutile), and undissolved digest cake. These solids are washed with waste acid to recover any acid-soluble ore and digest cake. The residual solid material is further washed with water to remove any contained acid, and then the neutral solid waste is landfilled.

Typical quantities of landfilled solids from the clarified digest solution are in the range of 0.1–0.2 tons per ton of pigment produced.

Quantities of precipitated copperas vary depending the iron content of the ore and the type of hydrolysis process used. Some SP producers use a hydrolysis process that allows precipitation of TiO_2 hydrate from an unconcentrated titanyl sulfate solution.

Another source of copperas is from waste acid concentration (WAC) processes, which concentrate the 23% strength waste acid and recycle it back to the digestion reactor. Markets for copperas to treat wastewater and as a soil conditioner are large and growing, and most copperas is sold readily.

6.14.2. Chloride Process Wastes

The volumes of air, liquid, and solid wastes generated are significantly lower than those generated by the sulfate process. Because the chloride process is continuous, all wastestream flow rates and their compositions are more readily monitored and controlled than with the discontinuous or batch-type sulfate process.

6.14.2.1. Air Emissions. Air emissions from chloride process derive from the low-boiling compounds formed in the chlorinator and from hydrogen chloride formed in the oxidation reactor. The gaseous components typically comprise CO, CO_2, COS, N_2, Cl_2 and HCl. CO and COS are converted to CO_2 in a waste-gas incinerator. The CO_2 is discharged and SO_x absorbed in water and neutralized. HCl is generally recovered and sold as muriatic acid.

6.14.2.2. Liquid Wastes. Liquid wastes from the chloride process consist principally of HCl that is generated by absorbing free chlorine in water in the waste-gas cleaning system and in some processes it is generated in the oxidation reactor. The liquid-waste stream formed when the solid metal chlorides are dissolved in HCl, neutralized, and separated is generally suitable for direct discharge into surface water with only minor purification needed. Typically, the dilute HCl in the wastestream is at a strength of about 1% HCl.

6.14.2.3. Solid Wastes. Solid wastes from the chloride process consist of high-boiling chlorides and some altered medium-boiling chlorides. Since all the metallic impurities present in the ore are removed, small quantities of metal oxides are also present in the solid waste.

High-boiling chlorides are mainly $FeCl_2$ and $FeCl_3$ with small amounts of alkaline materials that may be blown out of the chlorinator as liquids; $MnCl_2$, $CaCl_2$, and $MgCl_2$. Altered medium-boiling chlorides are $AlCl_3$ and $VOCl_3$, which are converted to high boiling chlorides and removed with the $FeCl_3$.

Another source of solid waste is the chlorinator fluidized bed material that occasionally must be removed because its reactivity has declined or because of a chlorinator refractory lining failure. This material is often referred to as *bed purge*. Disposal of bed purge material is becoming a problem if ore with elevated levels of radioactivity is used because the radioactive elements in the ore accumulate and concentrate in the chlorinator fluidized bed, thus making its disposal in a solid-waste landfill site more expensive.

6.14.3. Posttreatment Process Wastes

Quantities of waste products from the posttreatment operations are very small when compared to the sulfate and chloride processes. However, gaseous emissions and liquid wastes do arise at this step and must be properly handled.

6.14.4. Air Emissions

Air emissions from posttreatment operations consist principally of airborne TiO_2 particles. This represents more of an economic issue than an environmental one.

TiO_2 particulate emissions first occur at the spray-drier or belt-drier and continue through the posttreatment operations to packaging. These particulate emissions are adequately controlled by bag filters, but good maintenance and operating procedures are needed to keep fugitive losses to a reasonable level. A well-designed and- operated posttreatment process typically could experience TiO_2 losses of 0.1%. Losses as high as 10 times this are possible if the equipment is not operated and maintained properly.

6.14.4.1. Liquid Wastes. Liquid effluent in posttreatment comes from the eventual discharge of aqueous treatment solutions containing principally inorganic hydroxides. The pH of these solutions is almost always suitable for direct discharge into local surface waters. However, the presence of inorganic hydroxides may require the pH of the solution be adjusted to eliminate the possibility that gypsum could precipitate in a body of freshwater. Consequently, the optimum location for a pigment plant is adjacent to brackish water where these hydroxides remain in solution when discharged to surface waters.

6.14.5. Waste Treatment Processes

6.14.5.1. Air Emissions. Process technology used to treat air emissions such as particulates, SO_x, and acid mist are well known. Technology and equipment designed to enable TiO_2 producers to comply with air-quality standards are available from a variety of suppliers as a process package, and some innovative technology is being applied to control and remove emissions from sulfur process digestor stacks.

6.14.5.2. Solid Wastes. Process technology to treat solid wastes consist of techniques to upgrade iron salts to salable by-products and solid-waste neutralization processes. Solid-waste dry neutralization processes have been tried by a number of pigment producers with generally unsatisfactory results. The solid metal chlorides generated in the chloride process and the unwashed digestion solids from the sulfate process clarification operations are solid waste streams most suited to dry solid neutralization techniques. Neutralization typically consists of a simple mixing of solid lime or caustic with the acidic solid residues. The resultant neutral solid mixture can then be pelletized, with the addition of small amounts of water and directly landfilled. The process typically creates severe air-emission problems, as a large amount of acidic particles can be emitted to the atmosphere during the mixing, material handling, and disposal processes. Consequently, dry solid neutralization techniques are rarely used. In their place, the solid materials are either thoroughly washed (in the case of the sulfur process digestion solids) or are dissolved and neutralized in a liquid state (chloride process solid metal chlorides).

6.14.5.3. Liquid Wastes. Processes to treat liquid wastes are relatively new and are being modified as regulations change and new technology and improved materials of construction become available. Because liquid waste streams represent the largest volume of sulfur process and chloride process wastes to be treated, different processes have been developed to handle pigment plant acidic liquid wastes.

Chloride Process:	Underground deep-well injection of acidic liquid wastes
	Neutralization and solids landfilling
Sulfate process:	Waste acid neutralization
	Waste acid concentration

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