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Environmental Problems of Finely Dispersed Titanium Dioxide Production

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Abstract—Finely dispersed titanium dioxide is widely used in modern technologies. Proved reserves of titanium ores in Russia are expected to meet industrial needs. However, the available facilities for the manufacture of titanium dioxide from ores are clearly insufficient, which naturally requires new plants to be put into operation. The technologies used for the production of titanium dioxide were developed as early as 1940s, when ecological aspects of the production process were almost not taken into account. The present survey analyzes environmental problems related to the titanium dioxide production according to the sulfate and chloride technologies in comparison with the fluoride process proposed for industrial implementation. The fluoride process has been examined as applied to ilmenite from the Turan deposit in Tomsk oblast, and some actions directed toward improvement of ecological parameters of this process have been proposed.

Keywords: Titanium dioxide, production technology, sulfate process, chloride process, hydrothermal process, fluoride process.

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INTRODUCTION

Titanium dioxide is among most important inorganic compounds used in modern industry [1–10]. Unique properties of titanium dioxide determine the level of technological progress in various fields of World economics. Only 5% of the total produced titanium ore is consumed for the manufacture of titanium metal, whereas the major part of annually produced titanium minerals is used to obtain titanium dioxide. Finely dispersed titanium dioxide is the most needed product in the World market. Its global production is estimated at 4.5 million tonnes.

The main application of titanium dioxide is its use as pigment in paint-and-lacquer industry. It is also used in the manufacture of synthetic rubber, paper, refractory glasses, and construction materials. Titanium dioxide is obtained from titanium-containing ores, such as rutile, anatase, and ilmenite (Fig. 1). Rutile and anatase are most appropriate for the manufacture of titanium dioxide whose concentration in these minerals reaches 92–98 and 90–95%, respectively.

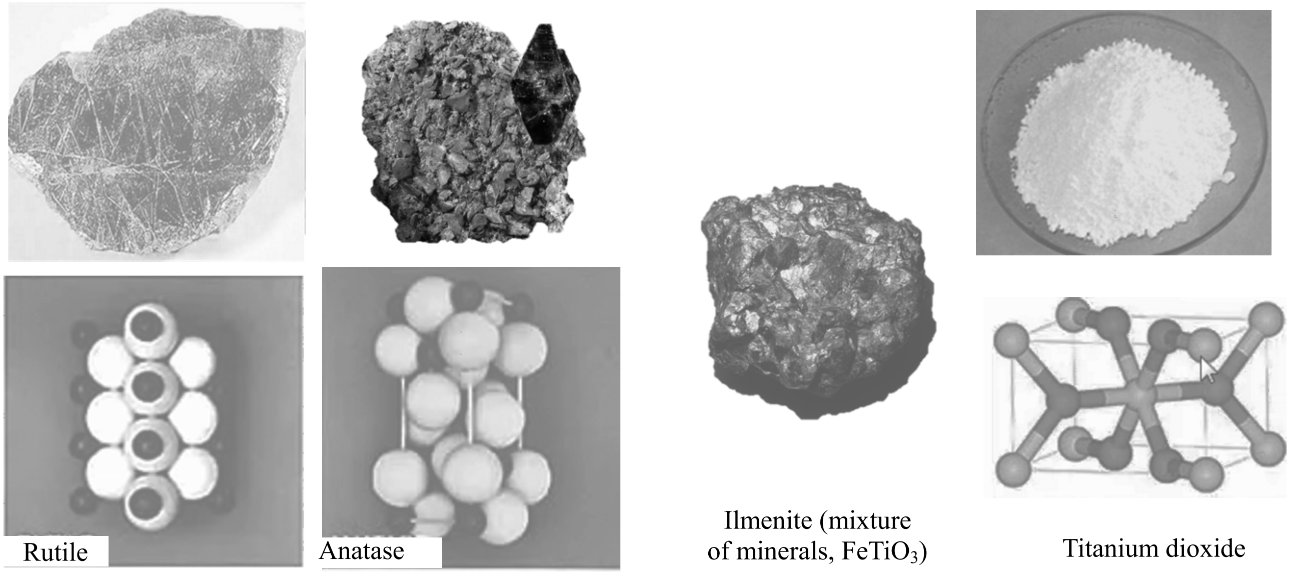
However, only ilmenite deposits are developed in the Russian Federation. From the chemical viewpoint, ilmenite is a mixture of oxides, mainly of titanium and iron oxides. The present article is focused on ecological aspects of titanium dioxide production just from ilmenite.

METHODS OF TITANIUM DIOXIDE PRODUCTION

Titanium dioxide occurs in nature as two minerals, anatase and rutile, and its production from either of these minerals is based on two technological schemes, sulfate and chloride processes.

Sulfate process [11–39]**.** The sulfate technology for the manufacture of titanium dioxide is based on the treatment of ilmenite with sulfuric acid. The sulfate method was put into operation in 1931 for the manufacture of titanium dioxide from anatase, and later (in 1941), from rutile.

Ilmenite is subjected to grinding and drying and then treated with concentrated sulfuric acid. The



Rutile

Anatase

Ilmenite (mixture of minerals, $FeTiO_3$)

Titanium dioxide

Fig. 1. Appearance and structure of titanium ores and titanium dioxide.

resulting molten titanyl sulfate is cooled and dissolved in water to a definite concentration. Iron(III) present in the titanyl sulfate solution is reduced to iron(II). The solution is allowed to settle down and subjected to rough filtration. The filtrate is cooled, and crystalline iron(II) sulfate is separated from the mother liquor by centrifugation. The solution of titanyl sulfate thus obtained is concentrated to a required level and transferred to the hydrolysis step.

In the hydrolysis step, titanium dioxide hydrate separates from the solution in the form of amorphous flakes. The titanium dioxide hydrate pulp is subjected to filtration in two steps, in which it is washed from chromophoric impurities and bleached. After addition of necessary ingredients, the titanium dioxide hydrate paste is calcined in a calcining furnace to remove hydration water and endow the product with pigment properties.

After calcination, the product is ground in two steps and subjected to surface treatment with some chemicals; as a result, pigmentary titanium dioxide acquires required application properties. The treated pigmentary titanium dioxide is dried and subjected to fine grinding. The finished product is packed and stocked. The TiO_2 content of ilmenite does not exceed 43–53%; therefore, its preliminary enrichment is required.

The production of titanium dioxide from ilmenite can be organized as batch or continuous process. The batch technology utilizes concentrated sulfuric acid. High sulfuric acid concentration ensures rapid temperature rise to 190–220°C without additional energy expenditures (via addition of water or recycled waste acid solution). As a result, high rate of the process and high concentrate conversion (96–97%) are achieved. In the continuous process, titanyl sulfate obtained from ilmenite is hydrolyzed directly in the reaction mixture according to the equation:

$$TiOSO_4 + 2H_2O = H_2TiO_3 + H_2SO_4.$$

This reaction produces a large amount of dilute (20–22%) sulfuric acid containing titanium and other metal sulfates. This acid is a waste material. Its possible utilization implies evaporation to a concentration of 55% and subsequent use in the manufacture of superphosphate. After hydrolysis, up to 95–96% of titanium precipitates from the solution, and metatitanic acid (H_2TiO_3) thus formed adsorbs a considerable amount of SO_3. Metatitanic acid is washed, dried, and calcined, so that it initially loses water (at 200–300°C) and then SO_3 (at 500–800°C); at 850–900°C neutral (pH = 7) titanium dioxide is obtained. Iron(II) sulfate heptahydrate formed as by-product is calcined to obtain monohydrate $FeSO_4 \cdot H_2O$, and the latter is ground. The sulfate method requires 4.0–4.5 t of sulfuric acid per metric ton of ilmenite concentrate (TiO_2 content 42%). Figure 2 shows the process scheme for the manufacture of titanium dioxide implemented at the *Krymskii titan* works. The sulfate technology for the titanium dioxide production from ilmenite and

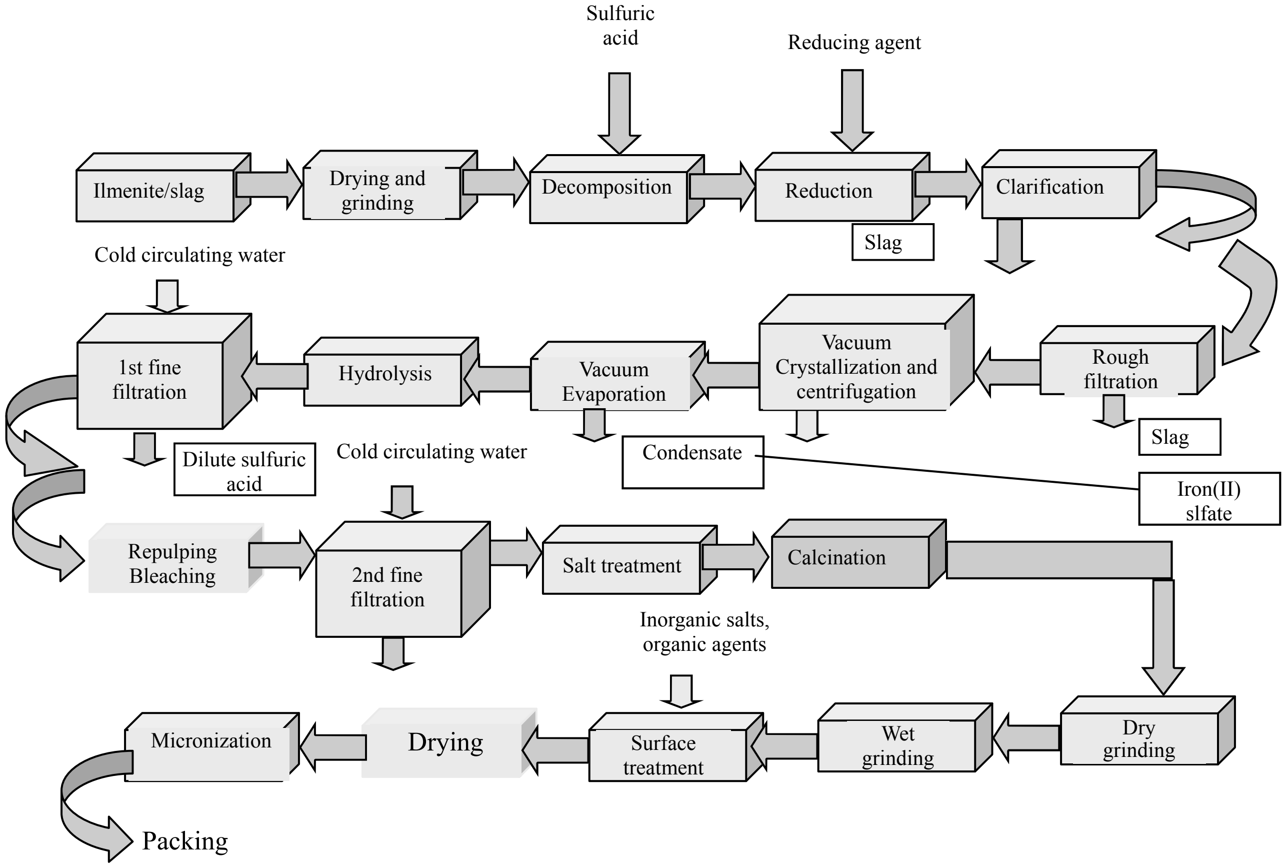


Fig. 2. Technological scheme of the sulfate process for titanium dioxide production (*Krymskii titan*).

titanium slags has a number of essential drawbacks, in particular complex multistep process and high consumption of sulfuric acid a considerable amount of which is unproductively wasted with iron(II) sulfate (more than 3 t of $FeSO_4 \cdot H_2O$ per metric ton of TiO_2) and dilute (20–22%) impure sulfuric acid (after hydrolysis). Therefore, the sulfate technology cannot be regarded as admissible from the viewpoint of up-to-date stringent requirements for environmental safety.

Chloride process [40]**.** The chloride method is more economic and less environmentally harmful. In addition, it is free from the iron(II) sulfate utilization problem, but additional requirements to the quality of titanium concentrates should be met. The chloride process was developed and put into operation in 1948 by DuPont, thus initiating the production of rutile titanium dioxide (Fig. 3).

The process is based on two high-temperature water-free gas-phase reactions. Titanium ore is treated with gaseous chlorine to obtain titanium(IV) chloride and other metal chlorides as by-products which are subsequently removed. After fine purification, $TiCl_4$ is oxidized at high temperature to form intermediate titanium dioxide which is characterized by high brightness. The oxidation step assumes the possibility to rigorously control particle size distribution, as well as their crystalline structure, so that titanium dioxide with excellent covering and bleaching capacities.

$$2FeTiO_3 + 7CI_2 + 3C \rightarrow 2TiCI_4 + 2FeCI_3 + 3CO_2$$
$$TiCl_4 + O_2 \rightarrow TiO_2 + 2CI_2.$$

The most important step in the production of finely dispersed titanium dioxide by the chloride method is oxidation (combustion) of titanium(IV) chloride. This process is carried out at 900–1000°C using specially designed burners which ensure the reaction temperature to be maintained within the required limits and a definite dwell time of the combustion products. The oxidation of titanium(IV) chloride with oxygen follows the reaction equation

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2.$$

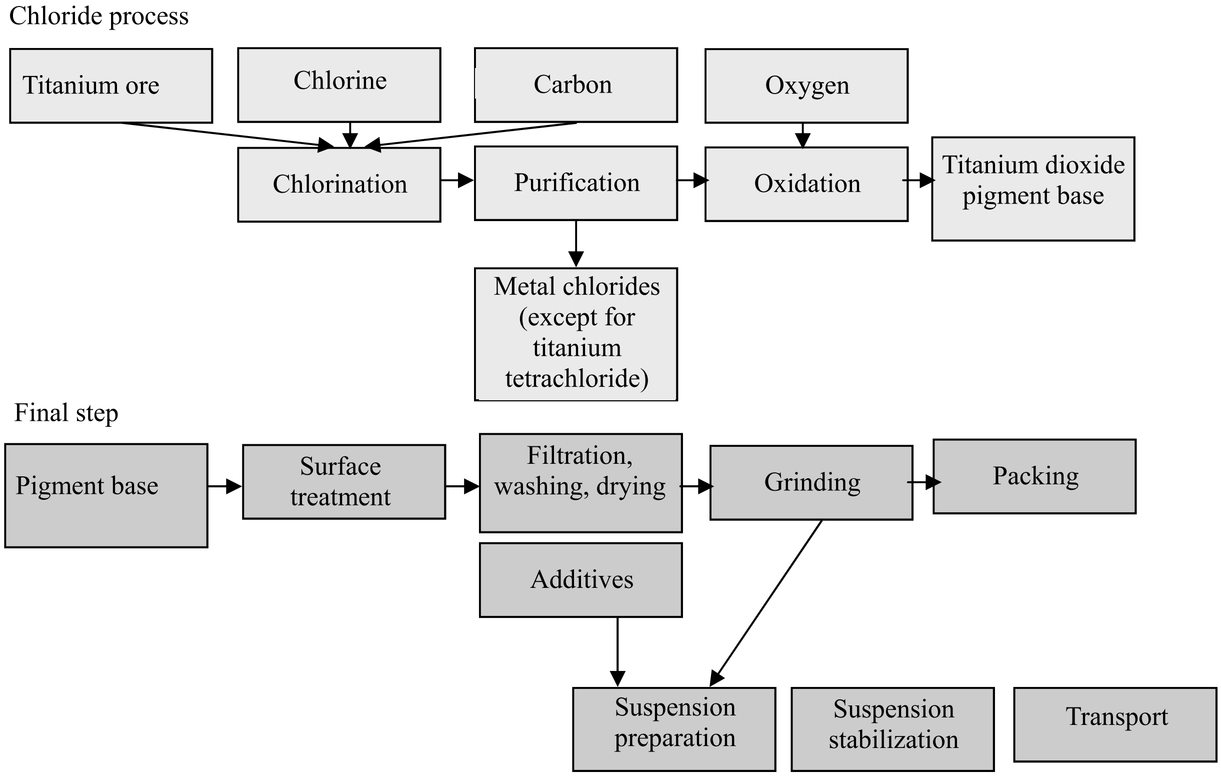


Fig. 3. Technological scheme of the chloride process for titanium dioxide production.

Liberated chlorine can be recycled to the manufacture of titanium(IV) chloride; therefore, the combustion process is already used on an industrial scale.

Titanium dioxide obtained by oxidation of titanium (IV) chloride contains up to 0.6% of adsorbed chlorine, and its aqueous suspension is characterized by a pH value higher than 7. The chlorine content of TiO_2 can be reduced to 0.1% by calcination at 300–900°C. The resulting product has a pH value of aqueous extract of 5–6.8 and is suitable for industrial applications.

Some manufacturers, e.g., DuPont, make use of direct chlorination of ilmenite concentrates. A problem related to this technology is increased discharge of sodium hydroxide (1.1 t of NaOH per metric ton of chlorine). The problem of sodium hydroxide utilization may be solved in part by cooperation with aluminum manufacturers.

The chloride process is more environmentally friendly and perfect than the sulfate method due to the possibility for its implementation in the continuous mode and hence for making it completely automated. However, this process is sensitive to the raw materials, and the use of chlorine and high-temperature conditions require corrosion-resistant equipment.

Hydrothermal process [41, 42]**.** Nanopowders are commonly obtained by high-temperature hydrolysis of various compounds directly in a high-pressure reactor or by hydrothermal treatment of reaction products. Hydrothermal conditions strongly accelerate crystallization of many amorphous phases. In the first case, a high-pressure reactor is charged with an aqueous solution of salt precursors, and in the second, with a suspension of reaction products obtained under conventional conditions. As a rule, there is no need of special equipment and temperature gradient.

Advantages of the hydrothermal method include the possibility for obtaining crystals unstable near the melting point, as well as large high-quality crystals. Among disadvantages, high cost of the equipment and impossibility of visual control over crystal growth.

However, the development of hydrothermal methods for the manufacture of titanium dioxide still remains at the pilot plant level. Their general drawback is unsatisfactorily solved problem of utilization of hydrogen chloride or aqueous HCl formed as a result of hydrolysis, which could not be recycled. Hydrolysis of titanium(IV) chloride with water vapor at 25–75°C on exposure to air gives a viscous liquid which solidified to form a white material on prolonged storage. Gas phase hydrolysis at 1000–1200°C ensures preparation of finely dispersed titanium dioxide. Nevertheless, the problem of hydrogen chloride utilization still restrains large-scale implementation of the hydrothermal technology.

Ecology or economy? Analysis of modern industrial technologies for the production of titanium dioxide allowed us to draw the following conclusions.

The classical sulfate and chloride processes are energy consuming, which increases the cost of the final product. Although the energy intensity of the sulfate process is considerably higher as compared to the chloride process, both these are characterized by approximately equal costs of production of commercial titanium dioxide.

The sulfate method does not allow sulfuric acid to be recycled; therefore, large-scale production of sulfuric acid is necessary. The chloride process is operative only with rutile as raw material, so that this method is inapplicable in Russia, where natural rutile reserves are insignificant.

In addition, analysis of the sulfate and chloride technologies showed that their impacts on the environment are comparable. Ecological problems associated with utilization of hydrogen chloride in the chloride process, large amount of solid wastes from processing of ores with low titanium content, pollution of wastewater, and the necessity of wastewater treatment constitute an important factor retarding the development of titanium dioxide market.

It should be noted that titanium dioxide was initially produced according to the sulfate method. Since the development of the chloride process, the contribution of the sulfate method to the total titanium dioxide production started to decrease. However, over a period of 1998 to 2009 the fraction of titanium dioxide manufactured by the chloride method decreased from 60 to 57%. This reduction resulted from implementation of new facilities for the manufacture of titanium dioxide by the sulfate method in China. Thus we have one more example demonstrating that environmental safety is sacrificed to gain economic profit.

Fluoride process [43–48]**.** Exploitation of new titanium dioxide deposits should be based on innovative technologies with sharply improved economic and ecological parameters. An example of such technologies is a recently developed process which may be referred to as fluoride process. Scientific principles of this process are based on a new line in the chemistry of inorganic fluorides, namely on the use of fluorine-containing oxidants in the chemistry, analysis, and technology of noble metals. The fluoride process was designed for processing of ilmenite concentrate from the Tugansk deposit in Tomsk oblast. While choosing raw material suppliers, the following factors were taken into account:

(1) Conformance of products (raw materials) to the technological requirements (concentration of main components, persistence of composition, etc.);

(2) Cost of finished product (raw materials);

(3) Location;

(4) Industrial potential (production facilities, deposit reserve, etc.).

Table 1 shows the mineral and chemical compositions of the concentrate from the Tugansk deposit in Tomsk oblast.

The technological process for the manufacture of titanium dioxide and iron oxide from the ilmenite concentrate includes the following steps:

(1) Treatment of ilmenite concentrate with ammonium hydrogen difluoride at 150°C to produce ammonium hexafluorotitanate and ammonium pentafluoroferrate(II);

(2) Decomposition of ammonium titanium fluoride and ammonium iron fluoride complexes at 350°C;

(3) Separation of titanium fluoride by sublimation at 550°C;

(4) Desublimation of titanium fluoride by cooling the process gas, its dissolution, and treatment with aqueous ammonia to obtain titanium dioxide hydrate (TDH); isolation of anatase TiO_2 powder from the TDH pulp;

(5) Transformation of anatase TiO_2 into rutile TiO_2 at 800°C;

(6) Transformation of FeF_2 into Fe_2O_3 via pyrohydrolysis;

(7) Absorption of ammonia from the gas phase;

(8) Evaporation of the ammonia mother liquors and crystallization of ammonia dihydrofluoride;

Table 1. Mineral and chemical compositions of the ilmenite concentrate from the Tugansk deposit in Tomsk oblast

Mineral	Concentration in ore, wt %	Chemical composition of mineral	Concentration of oxide in ore, wt %
Ilmenite	95.5	TiO_2	63
		FeO	25.1
Limonite	3	ZrO_2	1.04
Zircon	1	SiO_2	4
Chromite	0.5	Al_2O_3	0.36
Pyrite	Scattered grains	CaO	0.66
Anatase		MgO	0.58
Leucoxene		SO_3	0.1
Rutile		K_2O	0.05
Sphene		P_2O_5	0.1
Pyroxene		Na_2O	0.11
Kyanite		Cr_2O_3	1.5
Sillimanite		MnO	1.4

(9) Treatment with special reagents at the calcination step to endow titanium dioxide with pigment properties.

The chemical processes occurring in the course of preparation of titanium dioxide according to the above operation sequence can be represented by the following equations.

Ilmenite concentrate is subjected to hydrofluorination in molten ammonium fluoride at 150°C in a rotary-drum furnace. As a result, ammonium hexafluorotitanate and ammonium pentafluoroferrate(II) are formed together with gaseous ammonia and water.

$$FeTiO_3 + 5.5NH_4F{\cdot}HF = (NH_4)_2TiF_6 + (NH_4)_3FeF_5 + 0.5NH_3 + 3H_2O.$$

To complete the reaction and ensure maximum extraction from ilmenite, the reactants should be efficiently stirred. The process gas is purified from dust and is supplied to the “Ammonia station.”

$$NH_3 + H_2O = NH_4OH.$$

The ammonium metal fluoride complexes are subjected to thermal decomposition in a furnace at 350°C, where gaseous ammonia, hydrogen fluoride, unreacted ammonium fluoride, and ammonium fluoride silicon compound are removed.

$$(NH_4)_2TiF_6 = NH_4TiF_5 + NH_3 + HF,$$

$$(NH_4)_3FeF_5 = FeF_2 + NH_3 + HF.$$

The process gas is purified from dust and is transmitted to desublimation.

$$NH_3 + HF = NH_4F.$$

Titanium and iron fluorides are separated by sublimation in a furnace at 550°C. Titanium fluoride vaporizes, and the process gas also contains ammonia and hydrogen fluoride. Separation of dust should be avoided (dust containing foreign metal fluorides may contaminate final titanium dioxide). The process gas is subjected to desublimation. The solid phase consists of iron(II) fluoride which is treated with water vapor and atmospheric oxygen at 200°C. This reaction yields iron(III) oxide and gaseous hydrogen fluoride which is used to convert ammonium fluoride into ammonium hydrogen difluoride.

$$2FeF_2 + 0.5O_2 + 2H_2O = Fe_2O_3 + 4HF,$$
$$NH_4F + HF = NH_4F{\cdot}HF.$$

Solid iron(III) oxide is cooled and packed. Desublimed titanium fluoride is dissolved in water and treated with aqueous ammonia to precipitate titanium hydroxide.

$$TiF_4 + NH_4OH = Ti(OH)_4 + NH_4F.$$

Titanium hydroxide is separated from ammonium fluoride solution by filtration, and the precipitate is subjected to repulping with aqueous ammonia (25%) to pH = 12. This procedure removes residual ammonium fluoride, and subsequent filtration yields high-purity titanium hydroxide.

The mother liquors obtained after the first and second filtrations are evaporated at 100°C to recover ammonium fluoride and are then used for the treatment of the next batch of ilmenite concentrate. If necessary, ammonium fluoride is converted into ammonium hydrogen difluoride on heating at 170°C.

$$2NH_4F = NH_4F{\cdot}HF + NH_3.$$

Depending on the required structure of final titanium dioxide pigment, titanium hydroxide paste is heated at 600°C to obtain rutile or at 800°C to obtain anatase.

$$Ti(OH)_4 = TiO_2 + 2H_2O.$$

The process scheme is illustrated by Fig. 4. Ilmenite concentrate and ammonium hydrogen difluoride are loaded into feeder bins A101 and A102 and are supplied at a certain rate to screw mixer with the aid of dosing augers A103 and A104. The screw mixer should be cooled since the heat transferred from the furnace could initiate chemical reaction, which could lead in turn to sticking of the auger shaft with viscous intermediate products. The blend obtained in A105 is supplied at a required rate to rotary drum furnace A106 charged with grinding balls or rods and heated to 150°C. The gas fraction containing ammonia and water is transferred through a pipeline to separator A107 (if the next apparatus is considerably distant from the leaching furnace, the pipeline should be heated to 240°C) where dust is separated, and solid particles are returned to the leaching furnace. The purified process gas passes to aqueous ammonia setup A108. Intermediate product containing ammonium fluoride titanium and iron complexes goes from furnace A106 to bin A109 and is then transferred with the aid of dosing auger A110 to rotary drum furnace A111 heated to 350°C, where the complexes decompose with liberation of gaseous ammonia and hydrogen fluoride.

The process gas is pipelined to dust separator A112, and solid particles are returned to furnace A111. The purified process gas is transmitted to desublimation apparatus A113 where ammonium hydrogen difluoride is separated.

The solid phase containing titanium and iron fluorides is loaded into bin A114 and is supplied therefrom with the aid of dosing auger A115 into sublimation furnace A116 heated to 550°C. Titanium fluoride sublimes, the gas phase also contains ammonia and hydrogen fluoride, and iron fluoride remains in the solid phase.

Table 2. Main toxic chemicals involved in the technological process

Toxic chemical	Maximum allowable concentration in workplace air, mg/m^3	Class of hazard
Ammonium fluoride NH_4F	1.0/0.2	2
Ammonia NH_3	20	4
Hydrogen fluoride (aqueous solution)	0.5	2

The process gas is pipelined to desublimation apparatus A117 (if A117 is remote from the sublimation furnace, the pipeline should be maintained at 300°C) where solid titanium fluoride and ammonium fluoride separate from the gas phase.

Iron fluoride from furnace A116 is transferred (through feeding bin A118 and dosing auger A119) to pyrohydrolysis furnace A120 heated to 200°C. Direct steam from steam generator A136 and preliminarily heated atmospheric air are also supplied to A120. The oxidative hydrolysis yields solid iron(III) oxide and gaseous hydrogen fluoride, and the latter is used to prepare ammonium hydrogen difluoride via saturation of NH_4F in A135. Iron(III) oxide is cooled in cooling auger A137 and packed. Titanium fluoride and ammonium fluoride obtained in A117 are dissolved in water in agitator A121, and the solution is transferred to A122 for precipitation with aqueous ammonia. As a result, hydrated titanium dioxide pulp containing dissolved ammonium fluoride is formed. The pulp is subjected to first filtration in drum vacuum filter A123, followed by washing and final filtration. The solid cake is dried in A126 where it is fed through feeder bin A124 with dosing auger A125.

Titanium hydroxide is dried at 130°C, and the removed water is transferred to the preparation of aqueous ammonia. The filtrate containing ammonium fluoride is evaporated in screw crystallizer A132 at 105°C (or 70°C in a vacuum crystallizer). The water released from A132 is partly consumed for the dissolution of the next titanium fluoride batch in A121, partly for pyrohydrolysis step in A120, and partly for the preparation of aqueous ammonia. If necessary, ammonium fluoride is converted into ammonium hydrogen difluoride in A132 at 170°C, and the liberated ammonia is used for the preparation of aqueous ammonia.

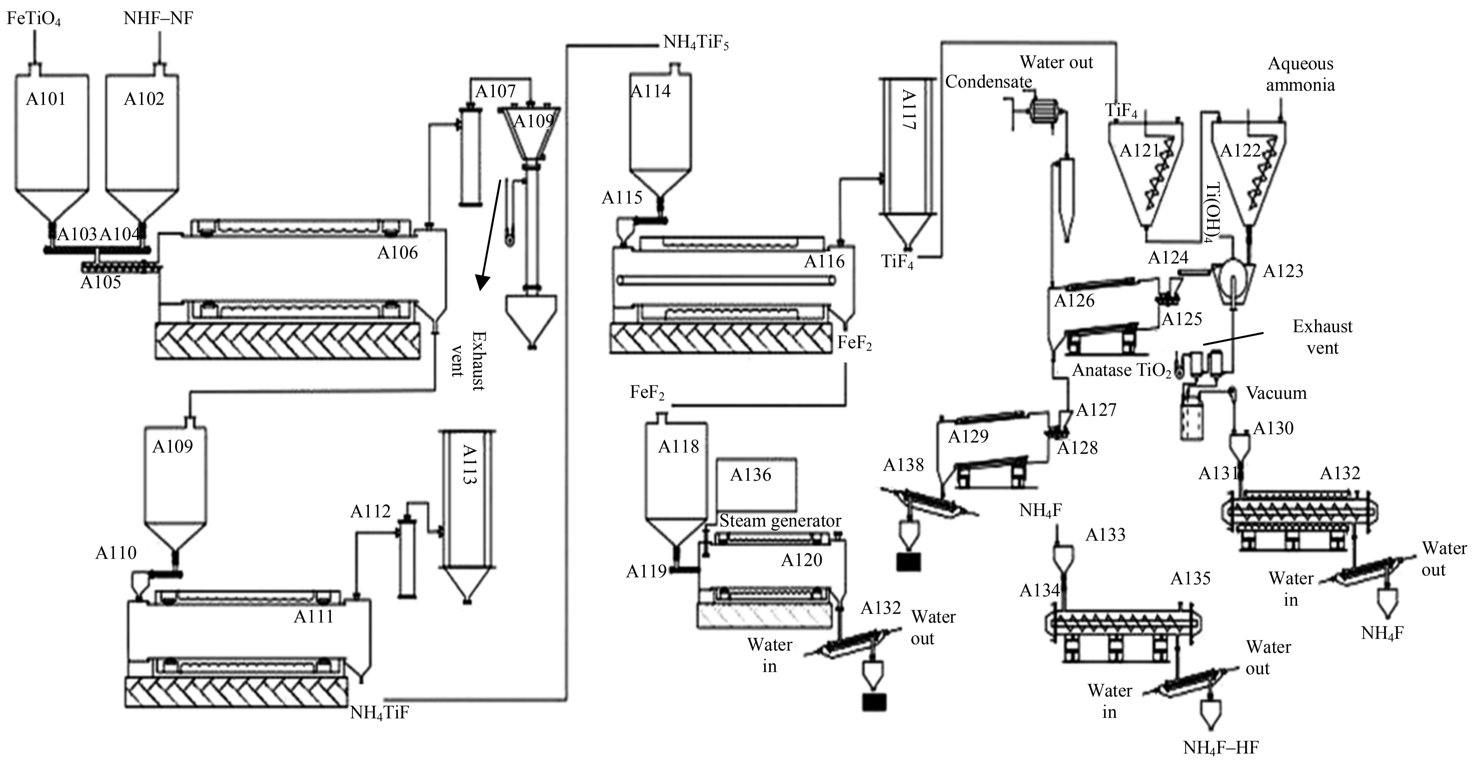


Fig. 4. Process scheme for the production of titanium dioxide and iron oxide from ilmenite concentrate (for comments, see text).

Table 3. Characteristics of different technologies for the production of pigmentary titanium dioxide

Technology	Sulfate	Chloride	Fluoride
Feedstock material	Ilmenite and titanium slag (with addition of rutile, sphene, perovskite)	Rutile (natural or synthetic) and titanium slag containing 55 to 60% of TiO_2	Ilmenite, rutile (SiO_2 <5%, Al_2O_3 and CaO are not limited)
Pre-treatment (leaching)	85–92% H_2SO_4, 40 atm, 200–220°C; passing of pressurized air after melting; maturing for 2–3 h	Desilication, reductive melting at 900–1200°C, magnetic separation, treatment with a solution of iron(III) chloride, chlorination of rutile	Decomposition in melt at 150–200°C, sublimation of titanium tetrafluoride at 500°C
Hydrolysis of intermediate product	Supersaturation of the solution, seeding, double filtration, bleaching purification	Combustion of a mixture of titanium tetrachloride and aluminum trichloride at 1000–1200°C	Precipitation of hydrated titanium dioxide with aqueous ammonia (regeneration of ammonium fluoride after filtration)
Surface treatment	Treatment with inorganic and organic salts	Not required	Not required
Thermal treatment	Rutilizing agents, 900–1000°C	Dry air pulsation under high pressure	700–800°C
Reagent regeneration directly in the production process	No	Chlorine (95%), by combustion of titanium tetrachloride in oxygen	Ammonium fluoride, 97%; aqueous ammonia, 95%
Wastes (by-products) per metric ton of titanium dioxide	Iron(II) sulfate, 3–5 t; dilute sulfuric acid, ≤10 t; polluted wastewater, ≤60 t	10% aqueous HCl, 0.35 t; calcium hypochlorite solution, 0.31 t	Iron oxide pigment, 1 t
Environmental impact	High	Moderate	Low
Class of hazard	Moderate	High	Low
Pigment quality	Medium	High	High
Net cost (kg) at a production level of 2000 t annually	\$1.8–2.0 (strongly depends on the sulfuric acid price)	\$1.6–1.8 (excluding enrichment of titanium slag or synthetic rutile manufacture)	\$1.2–1.3 (excluding commercialization of iron oxide pigment)

Anatase titanium dioxide from A126 is loaded into A127 and is fed with A128 to calcining furnace A129 where it is converted into rutile TiO_2 at 800°C. Rutile TiO_2 is cooled in A138 and packed.

Fluoride process risks. The fluoride technology for the production of titanium dioxide involves some adverse and harmful physical and chemical factors. Harmful chemical factors originate from circulation in the technological process of hazardous chemicals of 2nd to 4th class of hazard according to GOST (State Standard) 12.1.005–88. In order to minimize discharge of hazardous chemicals into occupational air and prevent their impact on the operating personnel, we propose the following technical measures:

(1) Organization of a continuous technological process;

(2) Automatic monitoring of the main process flow parameters and deviation alarm;

(3) Remote control;

(4) Rational process area and equipment layout;

(5) Full-time local and general ventilation of the process areas. Taking into account the possibility for accidental ammonia discharge, the process areas should be equipped with gas analyzers with automatic warning of excess concentration of toxic chemicals;

(6) Pressurization of all equipment, pipelines, and fittings, and isolation of all loading/unloading operations with loose materials;

(7) The use of equipment and service lines made of corrosion-resistant materials and fitting them with built-in or covering local exhausts;

(8) Purging of equipment with an inert gas (nitrogen) before repair works;

(9) Mechanization of assembly, disassembly, and transport of equipment;

(10) Maintenance of safe working environment during repair works;

(11) Monitoring of operation of the gas-cleaning units and discharge of hazardous chemicals into atmosphere;

(12) Provision of personal protective equipment;

(13) The use of pressure suits for repair works.

Harmful physical factors include electric current, elevated temperature of materials and outer surface of equipment, moving parts of equipment.

To protect personnel from harmful physical factors, the following measures should be provided: safety grounding of current-collecting equipment and their enclosure, thermal insulation of hot equipment and pipelines, and enclosure of moving parts of machinery which are potential sources of injury.

In keeping with GOST (State Standard) 12.1.005–88, the job grade in the designed production of high-temperature materials corresponds to 2a and 2b. The production process can be classed as 3a and 3b according to SNiP (Construction Norms and Regulations) 2.09.04-87.

The materials and equipment used are standard for the chemical industry; they conform to the corresponding regulations and hazard and toxicity classes, including those regarding fluorine compounds, ammonia, and dispersed materials. Table 3 compares the existing methods of pigmentary titanium dioxide production with the developed fluoride technology (Table 3). It is seen that the latter offers considerable advantages from the environmental and economic viewpoints. Moreover, the fluoride technology still has not exhausted its possibilities for further improvement of ecological and process parameters. This work is now in progress in *Faktoriya LS*.

For example, it was found that the use of excess ammonium fluoride (5–15 wt %) ensures most complete leaching of ilmenite. The subsequent separation of the titanium-containing component by sublimation is accompanied by evaporation of excess fluorinating agent and decomposition of ammonium metal fluoride complexes. The proposed solution makes it possible to reduce by half the amount of mixture subjected to precipitation. Correspondingly, a smaller amount of ammonia is required, and the energy consumption in the entire production process is reduced by 15–20%. The developed technological scheme is now under laboratory testing.

Implementation of the fluoride technology in Russia is expected to afford efficient utilization of natural resources in our country and increase of the number of jobs without impairment of the environment, in particular in the Tomsk region. Unfortunately, the existing titanium dioxide production facilities designed for the sulfate technology will operate for a long time. Undoubtedly, studies aimed at improving both chemical and technological aspects of the titanium dioxide production process should be continued.

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