Contemporary methods of production of titania

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Abstract. The article describes various processes of the manufacture of titanium dioxide, or titania, with two methods, viz. chlorination and sulphatization, presented. The detailed description of the features, advantages and existing submethods of the chlorination method and its comparison with the sulphatization method are given. High-frequency induction oxygen plasma submethod has been considered the most prospective in the manufacture of titanium dioxide.

1. Introduction
Titania, or titanium dioxide [1], is a polymorphous pigment found naturally in t crystal modifications: two with tetragonal symmetry crystals, viz. anatase [2,3,4] and rutile [5,6,7], and one with orthorhombic symmetry crystals, viz. brookite [8,9,10]. Titania has high spreading capacity and intensity. Titania forms solid solutions with transition metal oxides hereby distorting its crystal lattice and acquiring a coloured tinge. The phenomena of phototropy and photochemical activity are also inherent in titania.

The disadvantage of titania is chemical inertness and high resistance to the overwhelming majority of reagents and corrosive media; it is completely soluble only in concentrated sulphuric acid with prolonged boiling. The solubility of TiO₂ in sulphuric acid decreases with increasing temperature of calcination.

As is known [11,12,13,14,15,16], titania is obtained from titanium tetrachloride [17] by the following techniques:
1. Hydrolysis of titanium tetrachloride in aqueous solutions.
2. Hydrolysis of titanium tetrachloride in water vapour, or steam-gas technique.
3. Interaction of titanium tetrachloride with oxygen, or oxidation technique.

The first two techniques are not widely used in industry by far, because, firstly, their implementation yields a significant amount of diluted hydrolyzed hydrochloric acid, and secondly, although they enable the obtaining of concentrated hydrochloric acid, a closed cycle for chlorine is not provided.

As for the interaction of titanium tetrachloride with oxygen, or the oxidation technique, it enables the obtaining of both gaseous chlorine and titania, with the latter consequently refed to the production cycle for the purpose of the further chlorination of titaniferous raw materials.

2. Advantages and disadvantages of chlorination of titania
In world practice, titania obtained with the oxidation technique is mainly produced by two methods. The sulphate method [18] is based on the process of sulphatization of titaniferous raw materials with sulphuric acid, and the chloride method [19,20] is based on the process of chlorination of rutile
concentrates and titanium slags, with titanium tetrachloride obtained by chlorination on plasma torches subsequently transformed into titania.

Chlorination has several significant advantages over sulphatization. For example, chlorination has only three technological stages – chlorination of titaniferous raw materials, interaction of titanium tetrachloride with oxygen and surface treatment of titania in order to obtain various grades of titania.

Chlorination, along with being easy-to-handle, provides higher quality pigments. In addition, the production of titania by chlorination yields significantly less waste than that by sulphatization. As of economical estimation, the cost of titania obtained by both methods is equal, while chlorination enables the higher quality of the obtained titania.

3. Chlorination of titania in comparison with sulphatization of titania
Chloride and sulphate grades of titania, when compared by quality, allow us to see the differences in their physicochemical characteristics as well as in the application areas, as is indicated in the table 1.

| Characteristics                  | Sulphate grades | Chloride grades |
|----------------------------------|-----------------|-----------------|
|                                  | Rutile          | Anatase         |
| Whiteness (Conventional unit)    | 94.0…97.6       | 96.0…97.7       | 96.0…97.7       | 97.0…98.0       |
| Bleaching power (Conventional unit) | 1550…1650       | 1200…1250       | 1650…1900       | 1280…1300       |
| Oil absorption (g/10 g of pigment) | 16…19           | 18…25           | 11…30           | 18…20           |
| Hiding power (g/m²)              | 36…40           | 40…43           | 10…30           | 10…20           |
| Dispersibility, (units per wedge) | 20…60           | 15…50           | 10…30           | 10…20           |

As is obvious from table 1, chloride grades of titania are slightly superior in bleaching power, hiding power and dispersibility than sulphate grades of titania. Given this, modified chloride grades of titania have wider application in the manufacture of high-quality paints, plastics, chemical fibres, paper, etc. The comparative quality and the application data of certain chloride and sulphate grades of titania and materials produced on their basis are given in table 2.

As is obvious from table 2, chloride grades of titania are not inferior in quality to sulphate grades of titania. Chloride grades such as R-TC-5 and PTC-9, Runa-676, Tronox CR-801, Cabot RF-30 and others are of especially high quality. Recently, foreign companies producing titania by the chloride method have developed new high-quality grades of titania for various purposes.

The given data proves that chlorination can obtain high-quality grades of titania not inferior in quality to the titania obtained by sulphatization. Chloride grades of titania are more widely applied in various fields of the economy. That is why the offered technology for obtaining titania by chlorination in our country with its enormous reserves of raw materials suitable in quality for the synthesis of such pigment, is of great importance.
Table 2. Comparative data on the physicochemical properties of titania.

| Area of application | Grade    | Whiteness (Conv. unit) | Bleaching power (Conv. unit) | Oil absorption (g/100 g of pigment) | Treatment material and method          | Material properties       |
|---------------------|----------|------------------------|------------------------------|-------------------------------------|---------------------------------------|---------------------------|
| Emulsion paints     | RunaRE-372 - 1850 | 24.0 | Al, Si, chloride method | Strength, opacity                   |
|                     | RN-44    | 97.2 | 1840 | 40.0 | Al, Si, chloride method | Strength, opacity                   |
| Automotive enamel coatings | Runa-676 | - | 1850 | 18.0 | Al, chloride method | Strength, opacity                   |
|                     | R-CR-3   | 97.1 | 1800 | 18.0 | Organic compounds, sulphate method | Strength, opacity                   |
| White gloss paints  | R-TC-5   | 97.0 | 1800 | 15.0 | Al, Si, chloride method | Gloss                                 |
|                     | R-830    | 96.0 | 1760 | 18…20 | Al, Si, Zn, sulphate method | Strength, weatherability             |
| High-quality coatings | PTC-6   | 97.5 | 1800 | 15.0 | Al, Si, organic compounds, chloride method | High durability, opacity             |
|                     | R-HD-3   | 96.2 | 1850 | 17.0 | Al, Zn, sulphate method |                                         |
| Electro-deposited enamels | Runa RO-676 | - | 1850 | 18.0 | Al, chloride method | Strength, opacity                   |
|                     | RN-59    | 96.6 | 1760 | 21.4 | Al, sulphate method | Durability                            |
| Latex paints        | RF-31    | 97.1 | 1800 | 19.0 | Al, Si, chloride method | Dispersability                        |
|                     | R-XL     | 97.0 | 1600 | 30.0 | Organic compounds, sulphate method |                                         |
| Plastic materials, rubber, paper | RF-2    | 97.5 | 1650 | 21.0 | Al, Si, chloride method | High dispersability                   |
|                     | RC-K-2   | 97.0 | 1750 | 18.0 | Organic compounds, sulphate method |                                         |
| Universal pigments  | RH-172   | 1850 | 19.0 | Al, chloride method | Dispersability                        |
|                     | RH-56    | 96.4 | 1800 | 20…22 | Al, Si, sulphate method |                                         |
4. Raw materials used in chlorination of titania
Rutile concentrates [21] and titanium slags with the high titanium content [22] are the main raw materials
for the production of titania by means of chlorination. Chlorination of titaniferous raw materials is
performed at a temperature of 700 ... 1000 °C in the presence of reducing agents (usually coke), with
the following reactions proceeding:

\[ 2 \text{TiO}_2 + 2\text{C} + 2\text{Cl}_2 = \text{TiCl}_4 + 2\text{CO} ; \]

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During chlorination, there are obtained from the feedstock impurities not only TiCl₄, but also
chlorides. Purification of titanium tetrachloride from solid impurities is performed by filtration, and
from soluble impurities – by stage rectification. Because of the strong corrosive action of TiCl₄ and
chlorine, the instrumentation of the chlorination process is difficult. The required technological
equipment includes TiCl₄ evaporators, TiCl₄ and oxygen-vapour superheaters, burners, reaction devices
and catchers.

By now, plasma torches have become the most important sources of heating. To obtain plasma, there
are used voltaic arc heating or induction heating. The use of plasma torches excludes oxygen
superheaters as a means of usage, which significantly simplifies the process instrumentation. In addition,
when using plasma torches, the temperature conditions of the process and, therefore, the properties of
the produced pigment can be varied over a wide range.

5. Preparation of titanium raw materials for chlorination and special features of chlorination
To obtain titania and other products by chlorination, various titaniferous raw materials, e.g. high-
titanium-content ilmenite concentrates, rutile or titanium slags are required. Chlorination of titanium
raw materials can be cost-effective only when high-titanium-content and low-iron-content raw materials
or iron chloride are applied. In this regard, in order to yield titanium-enriched product, the most
beneficial is to apply cast-iron and titanium slags re-melted from titaniferous raw materials or to utilize
natural or hydrometallurgically chlorinated “artificial” rutile.

Depending on the chemical composition of titaniferous raw materials, the process of its chlorination
is performed at a temperature of 800...1000°C in mine-type devices, e.g. closed-tank-shaped
chlorinators. Chlorination consists of the following stages: grinding of the charge components, mixing
of the charge with the binding additive, briquetting, coking and chlorination of the applied mixture, with
the following processes performed:

1. Dissolution of chlorine on bubbles’ surfaces in the melt;
2. Diffusion of chlorine from bubbles’ surfaces through the boundary diffusion layer of the
   surrounding slurry.
3. Permutoidal diffusion of chlorine in the slurry through neighbouring bubbles with simultaneous
   chlorine absorption as a result of the irreversible reaction.

All the above-mentioned processes run quickly.

Titanium slag and petroleum coke, pre-ground to a particle size of 100 μm, are fed with the screw
feeder onto the melt surface in the chlorinator. The charge feedstock is automatically adjusted to the
concentration and the amount of the supplied chlorine. Titanium tetrachloride obtained by chlorination
is cleaned of solid impurities by settling or filtration, according to the process conditions and the raw
materials’ quality. In order to clean the obtained tetrachloride of aluminium and vanadium compounds,
it is subject to copper reduction with the further separation and treatment of vanadium oxide.

6. Physicochemical basis of the oxidation process for titanium tetrachloride
The oxidation process of titanium tetrachloride can be described by the following equation:

\[ \text{TiCl}_4 (g) + \text{O}_2 (g) = \text{TiO}_2 (s) + 2\text{Cl}_2 (g) . \]
Depending on the conditions, during oxidation, there are obtained either rutile or anatase, with their Gibbs function described by the following equations, respectively:

$$\Delta G(s) = 47747 + 42.262T - 9.1T\lg T - 1.511 \times 10^{-3}T^2$$

and

$$\Delta G(s) = -35175 + 34.68T - 6.6T\lg T + 1.561 \times 10^{-3}T^2.$$ 

The calculated Gibbs function dependence on the temperature change suggests the high probability as well as the practical irreversibility of the above reaction. The thermodynamic probability of the formation of low titanium oxides, viz. Ti$_3$O$_5$, Ti$_5$O$_9$, increases with decreasing oxygen content in the system, which is particularly typical for Ti$_5$O$_9$. The introduction of additives, viz. AlCl$_3$, TiCl$_3$, SiCl$_4$, H$_2$O, into the reaction mixture enables the obtaining of finely dispersed high-quality rutile titania. These additives enable the formation of crystallization nuclei, thus reducing the process temperature.

The interaction between titanium tetrachloride and oxygen begins at a temperature of 500°C without the obtaining of titanium oxychloride. At a temperature of 650°C, the reaction accelerates with the formation of white aerosol of titania and chlorine, which amount increases with increasing temperature. Almost complete oxidation of titanium tetrachloride is performed at a temperature of 1000...1100°C.

The oxidation process of titanium tetrachloride consists of the following stages:
1. Gas-phase oxidation with the formation of crystalline-free particles of titania.
2. Formation of crystallization nuclei.
3. Growth of the crystallization nuclei at the solid-gas phase boundary during the oxidation process.
4. Growth of the formed crystalline titania particles due to sintering and recrystallization.

At temperatures of 700...900 °C, the dispersibility of the obtained titania is low, i.e. about 40...70%. With the temperature rising to 1000...1100°C, the ratio of particles smaller than 1 μm increases to 90...95%. The stepwise oxidation of titanium tetrachloride with crystallization nuclei formed from much smaller disperse particles of titania obtains higher-dispersed resulting product.

Particles of titania, treated at high temperatures in the reaction device for a certain time, can aggregate, i.e. sinter into large conglomerates, while moving, which reduces the dispersibility of titania. Various methods are proposed to decelerate crystal growth: rapid cooling of the product by means of mixed gaseous chlorine or inert gases; application of titania impurities, etc.

Additives of aluminum and silicon compounds not only increase the surface area and pore volume with respect to unmodified titania, but also significantly decelerate the shrinkage of surface area while heating, and, thus, prevent the further particle aggregation. Therefore, the calcination process of the product both in vacuum and in hydrogen, as well as the growth of titania particles and phase transformation are accelerated. At a temperature of 700...800°C, the anatase titania is obtained, and at a temperature of 1000...1200°C, the mixture of anatase and rutile titania is formed, the amount of rutile increasing with increasing temperature. The Gibbs function of anatase-rutile transformation is \( \Delta G_t = -10900-4.03T \) and remains negative in the whole temperature range, i.e. the transformation of anatase to rutile is thermodynamically possible at any temperature.

The anatase-rutile transformation rate depends on the conditions for its obtaining, i.e. the composition of the raw material and the process temperature. The transformation of spectroscopically pure anatase to rutile begins at a temperature of 600±10°C and, according to the Arrhenius law, the activation energy of this reaction is 80±10 cal/mol, which is equivalent to the activation energy of the formation of rutile crystallization nuclei.

The influence of certain additives on the anatase-rutile transformation rate, grain size of rutile, and the relative electrical conductivity of rutile are given in Table 3.
Table 3. The influence of additives introduced during the synthesis on the quality of titania.

| Component name | The amount of rutile at a temperature of 900°C (µm) | Grain size at 900°C (µm) | Relative electrical conductivity |
|----------------|-----------------------------------------------|------------------------|-------------------------------|
| None           | 82                                            | 0.5                    | 1.0                           |
| Na₂O           | 14                                            | 0.5                    | 1.70                          |
| Cu             | 100                                           | 2.0                    | -                             |
| CoO            | 100                                           | 1.5                    | 0.33                          |
| NiO            | 100                                           | 1.5                    | 0.33                          |
| MnO            | 100                                           | 1.8                    | -                             |
| Fe₂O₃          | 100                                           | 1.8                    | 0.5                           |
| Cr₂O₃          | 96                                            | 0.3                    | 3.50                          |
| MoO₃           | 80                                            | 5.0                    | 0.50                          |
| WO₃            | 15                                            | 0.3                    | 4000.0                        |

Anatase-rutile transformation is accelerated by the addition of copper, zinc, manganese, cobalt or iron, and decelerated by the addition of compounds of sodium, lead and molybdenum. The additives of ions Al³⁺, Zn²⁺, PO₄³⁻, SO₂⁻, Cl⁻ stabilize the anatase structure, with the stabilization degree decreasing in the following order: Cl⁻ < SO₂⁻ < PO₄³⁻.

The introduction of aluminium, silicon and zirconium additives during the oxidation process of titanium tetrachloride influences the physicochemical properties of the obtained titania. The introduction of 1.0...2.5% of aluminium compound in terms of aluminium oxide and 0.5 ... 6.0% of zirconium compound in terms of zirconium oxide enables the obtaining of rutile titania, with aluminium compounds being more powerful rutile promotors, whereas the introduction of 0.7% or more of silicon compounds into the reaction zone in terms of SiO₂ enables the obtaining of anatase titania.

It has also been confirmed that the pigment properties of titania are improved when chlorides of the above-mentioned elements are taken in an amount of 1...2% with respect to titanium tetrachloride and having a weight ratio of aluminium, silicon, zirconium chlorides equal to (0.5...5.0):(0.2...1.5):(0.3...3.0).

The micronization of titania in a steam-jet mill in the presence of 20...30% ammonia solution taken in an amount of 0.2...2.0% increases the pigment whiteness to 97.0 conventional units and pigment reflectance factor to 96%.

7. Submethods of chlorination of titania from titanium tetrachloride

There are used several submethods of chlorination, depending on the ways additional heat is introduced into the reaction zone:

1. Thermal submethods, viz. oxidation of titanium tetrachloride with the preheating of the fed components to the specified temperature; oxidation of titanium tetrachloride in oxygen with the addition of combustible gases.

2. Plasma-chemical submethods: oxidation of titanium tetrachloride using arc plasma; oxidation of titanium tetrachloride using high-frequency induction oxygen plasma.

7.1. Thermal submethods for chlorination of titania

The oxidation of titanium tetrachloride with the preheating of the fed components is widely applied in industry in small-diameter reaction chambers with the heating of the reagents to a temperature of 400...1100°C. To reduce heat loss and accelerate the process, titanium tetrachloride and oxygen, beforehand preheated to a temperature of 900...1000°C, are fed into a lined vertical chamber from two
opposite sides. Sometimes titanium tetrachloride and oxygen are heated while mixing with the products of carbon or carbon monoxide combustion. This method yields high-quality titania. The disadvantages of this submethod are difficulties in finding materials stable at high temperatures in titanium tetrachloride and oxygen. One of the submethods, which eliminates this drawback, is the oxidation process of titanium tetrachloride in a "fluidized bed".

The oxidation of titanium tetrachloride in oxygen with the additional introduction of a combustible gas is widely applied in industry, especially when the combustible gas is introduced as a part of gas-vapour mixture. Since the temperature of the mixture fed into the reactor is equal to 250...300°C and is much lower than the process temperature, the oxidation reaction begins at a certain distance from the nozzle, which significantly reduces the formation of titania sediments as well as the clogging of the burner holes. The decrease of the process temperature significantly simplifies the process instrumentation.

The disadvantage of this process is the obtaining of diluted gaseous chlorine necessary to be subjected to the further regeneration, as well as difficulties of working with poisonous gaseous carbon monoxide. Another serious drawback is the precipitation fouling of the reactor walls, which impedes the whole process.

In this regard, the interaction of titanium tetrachloride with oxygen involves great difficulties. The heating of the fed reagents to high temperatures significantly complicates the process instrumentation, and the concentration of the obtained chlorine decreases with introducing combustible gas into the reaction zone.

7.2. Plasma-chemical submethods for chlorination of titania

As for plasma-chemical submethods for producing titania, with the arc-plasma submethod, inert gases are heated in two arc plasma torches, with oxygen and titanium tetrachloride subsequently introduced into each plasma jet separately, and next fed to the common reactor for the further mixing and oxidation. One reagent is superheated to high temperatures, while the other is introduced into the reactor without heating, for example, liquid-state titanium tetrachloride.

The arc-plasma submethod maintains a very high temperature in the reaction zone; therefore, the formation of crystallization nuclei of the new rutile phase occurs without the presence of special reagents. The residence time of the reagents in the reaction zone does not exceed 1 second. Arc plasma or induction plasma generators are used as a heat source for the heating of one of the reagents.

The electrodes of arc plasma generators are manufactured from materials serving as modifying additives during the erosion process. The main disadvantage of the arc plasma submethod is the dilution of the gaseous chlorine with the inert cooling agent, as well as the sharp decrease in operation life of the plasma torches and the increase in the working cost with increasing oxygen content in the orifice gas.

With the high-frequency induction plasma submethod, in comparison with the arc plasma submethod, there are a number of advantages: this method enables the heating of not only inert gases, but also oxygen, hydrogen and even halogens, as well as the long service life and the absence of wearable parts of the device.

Unlike arc plasma torches used in the arc-plasma submethod, a 1 MW high-frequency plasma torch heater does not have electrodes, its body is cooled by water, sharply reducing the corrosion of the heater parts and the heater contamination with the obtained titania compounds. The heater is connected to the standard high-frequency pipe-welding generator (with the power 1.2 MW and the frequency 200...500 kHz). Since the plasma heating process is most effective at 10000...12000 K, and the oxidation of titanium tetrachloride requires either or both reagents heated to 1900 K, the heating of the reagents, e.g. oxygen and titanium tetrachloride, is feasible in order to maintain the specified temperatures in the reaction zone.

The main advantages of the oxidation process of titanium tetrachloride in the presence of monatomic oxygen obtained in high-frequency induction discharge are as follows:
1. Significant size diminution of technological devices.
2. Possible usage of water-cooled metal units.
3. Long continuous non-replacement working time of the high-frequency device.
4. Absence of wearable parts, which enables the obtaining of pure oxygen.

In this regard, the high-frequency induction oxygen plasma submethod is of the greatest interest for the production of titania, since it obtains high-quality titania and higher-concentrated gaseous chlorine, which enables the use of it in a closed cycle with chlorination of titaniferous raw materials. High-frequency induction plasma torches provide high technical and economic performance of this method.

8. Conclusions
The above-presented investigations allowed us to make the following conclusions:
1. The most applicable raw material for production of titania is titanium tetrachloride.
2. There are applied 2 main methods of obtaining titania from titanium tetrachloride – chlorination and sulphatization,
3. Titaina grades obtained by chlorination are superior to those obtained by sulphatization in bleaching power, hiding power, and dispersability, however, having almost equal cost.
4. Depending on the heat introduction into the reaction zone, there are applied thermal or plasmachemical methods for production of titania.
5. The high-frequency induction oxygen plasma submethod is the most efficient among other submethods for production of titania due to its technological and economical advantages.

It follows that the production of titania by means of high-frequency induction oxygen plasma enables high technological and economical efficiency.

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