Contemporary methods of production and application of pigments obtained from titanium dioxide

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Abstract. The current article describes the methods of producing titanium dioxide, or titania, which is used in various branches of the industry, including construction as a basis for producing white pigments. The base pigment grades of titania with their qualitative characteristics are listed, the modifying agents, applied in producing pigment grades, are presented, the several technologies of producing titania are mentioned. To obtain titania with different characteristics, various methods of treatment, viz. chemical or heat treatment, are used. To raise the material index of raw materials, used for producing titania and, simultaneously, to lower the obtaining of waste materials, several methods of obtaining titania from titanium slags and waste catalysts are offered. When applying the offered technologies, the range of the usage of titania will be expanded, and the efficiency of using raw materials will be increased.

1. Introduction

Titanium dioxide, or titania, is a polymorphic pigment occurring in the following three crystalline modifications: brookite [1,2], anatase [3,4] and rutile [5,6]. Titania has very high spreading capacity and intensity: with these characteristics about 3 times exceeding those of other white pigments [7]. The higher the dispersion of titanium is, the whiter its colour appears. Titania can form solid solutions with transition metal oxides herewith 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 and, especially, of anatase titania, is its hygroscopicity which results both in the slower solidification of titanium-containing coatings, and the slower water permeability. Titania is chemically inert and extremely resistant to the overwhelming majority of reagents and corrosive media; moreover, it does not react with sulphurous anhydride, hydrogen sulphide; and it is insoluble in water as well as in fatty, organic and weak mineral acids, is very poorly soluble in alkalis; and is completely soluble only in concentrated sulphuric acid with prolonged boiling. The solubility of TiO_2 in sulphuric acid decreases with the increase of the calcination temperature.

2. The composition and application of titania

The properties of titania are significantly influenced by not only the raw material's composition, the treatment conditions, but also the surface modifying and various substances introduced into the raw

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stock. The physical and chemical properties of pigment grades of titania obtained by means of the sulphate method are given in table 1.

Table 1. Qualitative characteristics of pigment grades of titania.

Characteristics	P-1	PO-2	PO-7	PO-8	PO-9	A-1	AO-1	AO-2
Mass fraction of titania (%)	98	93	95	94	93	98	94	94
Mass fraction of rutile titania, no less than (%)	95	95	05	95	95	-	-	-
Mass fraction of volatiles, no more than (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Mass fraction of water-soluble salts, no more than (%)	0.4	0.3	0.2	0.1	0.1	0.4	0.3	0.5
Whiteness, no less then (conventional unit)	92	92	94	-	94	95	95	97
Aqueous extract's pH	6…8	6…8	6…8	6…8	6…8	6…8	6…8	6…8
Bleaching power, no less than (conventional unit)	1500	1700	1800	1800	1800	1170	1200	1300
Spreading capacity, no more than (g/m^2)	30	40	35	35	35	40	40	40
Dispersibility (μm)	-	15	13	12	12	-	15	10

Russian industry applies the sulphate method in producing titania with ilmenite concentrate taken as the main raw material. The technological process includes four main stages: the obtaining of titanium sulphate solutions; the obtaining of hydrolysis products; the thermal treatment of hydrolysis products; the surface treatment of titania. Titanium sulphate solutions, in their turn, are obtained in several substages: the decomposition of titanium-containing raw material; the leaching of the obtained melt; the reduction of Fe^{3+} in Fe^{2+}; the desludging of the solution; the extraction of iron vitriol; the concentration of the solution.

The properties of titania applied in further production of pigments largely depends on the properties of its base grades P-1 and A-1, which are, in their turn, applied for producing other pigment grades by modifying, i.e. surface treatment. The properties of the base grades of titania are also significantly affected by the surface condition to where they are applied, the existence of an electrical bilayer containing potential-determining ions of sulphates and phosphates in the first sublayer and counterions of potassium or sodium and hydrogen in the second sublayer. It is found that the stability of the electrical bilayer is influenced in a greater degree by the change in the medium's pH and in a lesser degree – by the change in the layer's thickness. Based on the results of studies on aggregative stability, the optimal conditions for hydraulic separation and dispergation of rutile titania during surface treatment of titania were specified.

Pigment's surfaces are treated by neutralizing the suspension of titania with various reagents. As a result of the modification, the chemical activity of titania decreases and the weathering resistance of it increases, while the pigment acquires either hydrophobic or hydrophilic properties depending on the application purpose of the resulting titania. The composition and ratio of modifying additives introduced during the surface treatment, depending on the purpose of titania, are given in table 2.

The properties of titania also depend on stabilizing additives introduced into wet grinding. Thus, the introduction of sodium hexametophosphate with mass content of 0.10 to 0.15%, and triethanolamine with mass content of 0.3% of that of TiO2, also caustic sodium in amount sufficient to

equal the medium pH to 10...10.5, increases titania's bleaching capacity to 1760…1780 conventional units and its dispersibility to 15 conventional units.

Table 2. Composition and ratio of additives introduced during the modification of titania, % to TiO_2.

Modifying reagent	AO-1	AO-3	AO-4	PO-2	PO-3	PO-4
Liquid glass in terms of SiO_2	0.4…0.6	3.5...4.0	2.0	0.8	1.0	-
Aluminium sulphate solution in terms of Al_2O_3	1.0...1.4	2.0...2.5	1.0	0.8	-	1.25
NaAlO2 solution in terms of Al_2O3	1.0...1.4	2.0...2.5	-	2.0	3.0	2.75
Zinc sulphate in terms of ZnO	-	-	-	0.3	-	-
Soda solution in terms of $NaCO_3$	2.8...3.1	≤4.5	≤4.5	-	≤4.5	≤4.5
Alkali solution in terms of NaOH	2.3...2.5	≤7.0	≤6.8	≤7.0	≤7.0	≤7.0

3. Improving the quality and expanding the range of the usage of titania

One of the promising methods of improving the quality and expanding the range of the usage of white pigments is the method of coating the pigments' surfaces with relatively cheap titania-containing raw materials (kaolin, alumina, mica, etc.). The surface of the raw material is pre-activated during 10 to 30 mins by micronization, and then sedimented with various reagents.

The sedimentation of titania on the surface of dispersed materials like muscovite, phlogopite, glass-sphere can be performed, among others, by the following methods:

1. To obtain the raw material, finely crushed mica with fineness of 5 to 100 μm is mixed with sulphuric acid solution in the mass ratio of 1:(5...20), then heat treated at a temperature of 60 to 90°C, then blown by compressed air, and finally, the sediment is washed off water-soluble substances and calcined.

2. To obtain a pigment with an improved gloss value, mica with water solution of NaOH or Na_2CO_3 (K_2CO_3) is heat treated, then dispersed in a solution containing titanium sulphate and sulphuric acid, then again heated, dried and, finally, calcined.

3. To increase the reflection coefficient of a pigment, pre-distended mica is sedimented with titania, with the application of titanium salts solution.

4. The obtain a pearlescent pigment with high corrosion resistance, fluorophosphorus-containing titanium sulphate solution is taken as titanium-containing component, and titanium phosphate solution is taken as a by-component; to increase the equity of the coating layer, finely crushed mica is pre-treated with ammonium fluoride solution.

5. To increase the equity of the titania-containing coating layer on the surface of mica, the mica is pre-treated with oxygen or hydrogen peroxide solution, with titanium sulphate solution applied.

4. Production of titania from titanium slags

One of the most important problems in the production of titania is the high consumption of raw materials and the production of large amounts of unused waste. The production of titanium slag based on ilmenite deposits allows us not only to make multipurpose utilization of titanium raw materials, but also to substantially reduce the formation of waste while producing titania and, therefore, to involve a greater number of low-grade ilmenite deposits [8,9].

Compared to ilmenite concentrate, titanium slag used in the production of titania reduces the material index of raw materials from 8.7 to 5.7, and the material index of sulphuric acid by 40 to 45%, increases the product yield by 10%, reduces the number of equipment units by 25 to 30%, reduces energy costs of steam, electricity, water by 15 to 30%. Since the application of titanium slags as well as of ilmenite concentrates requires the sulpharization of slags in large-volume open-type reactors with applying highly-concentrated sulphuric acid, therefore big volumes of waste, especially hydrolysic acid, is still obtained thus far.

Autoclaves where titanium-containing raw material is decomposed, may use 20 to 40%-concentrated sulphuric acid, which reduces the obtaining of sludge and sulphate salts in 7 to 9 times and the obtaining of acidic flows and titanium gypsum after the neutralization in 3.5 times.

The application of waste products or semiproducts containing titanium and iron is of no less importance in the development of low-waste technologies for the production of titania and other white pigments (e.g. lead and zinc pigments and fillers). Of particular interest are waste titanium-containing chips, excess titanium tetrachloride, waste solutions and dusts containing zinc, lead and other metals obtained at non-ferrous metallurgy enterprises.

5. Production of titania from titanium-containing waste catalysts

Various types of catalysts, including titanium-containing catalysts, are widely applied in the production of organic synthesis and refining [10-16]. Catalysts containing 92%-concentrated titania on alumina carriers can accelerate the reactions of the narrowing and widening of heterocycle, also esters' formation, hydrocarbons dehydration, chlorobenzene hydrolysis, etc. The broadest application is gained by the so-called Ziegler-Natta catalysts – complex catalysts consisting of titanium chlorides and various compounds of transition elements.

The produced catalysts are shaped as tablets or granules, and also as fine-dispersed powders mixed with liquid phase, viz. ion-exchange resin. The catalysts' chemical activity depends on their chemical composition, and also on the chemical composition of carriers and cocatalysts. The catalysts' activity decreases during the process, which requires either the catalysts' regeneration or their elimination from the reaction mixture.

Metatitanic acid (MTA) [17,18] containing in terms of dry product no less than 70.0% of titania, about 5.0% of sodium chloride and also organic matter with no more than 20.0% of moisture content, is the most efficient waste product of ion-exchange resins applied while producing titania.

During the cleansing of ion-exchange resin, MTA is mixed with water in the ratio of 1:(1 ... 12) in the reactor, then continuously stirred for 0.5 to 1.0 hour and then the obtained suspension is circulated by the pump through the trap equipped with the metal grid having 100 to 200 μm cell size. The separated resin grains are fed to the hopper, whereas the separated MTA suspension is fed into the stirrer to stir for 3 to 4 hours. In 10 to 15 min before the end of the stirring, a 0.25% solution of flocculant having the amount of 0.25 to 0.5 kg per 1 ton of TiO_2 is fed to the suspension from the measuring tank in order to separate sodium chloride. Later, the stirrer is stopped and the MTA suspension is left to stay for 3 to 4 hours in the vessel, and then the clarified part is poured into the separate container, and the condensed part with TiO2 having concentration of at least 400 to 500 g/l is fed to the filter press for filtering.

After the sediment is filtered and washed off water-soluble substances with the help of chemically treated water or condensate pumped from the vessel, the obtained paste is fed into the combined dryer where it is dried (calcined) and crushed to the necessary sizes. Depending on the processing conditions, the resulting titania must match one of the grades given in table 2.

Waste catalysts containing 92% of titania applied in organic synthesis and on a carrier of active γ-alumina can also be applied to produce titania. While applying such type of catalysts, various solid-phase products, e.g. coke breeze, sulfur-containing substances, etc. [19,20,21,22] are obtained on its surface. In this regard, in order to eliminate these products, the catalyst is either heat treated at a minimum temperature of no more than 600°C or chemically treated with an oxidizing agent applied. After the impurities are eliminated from the catalyst's surface, the cheapest way to eliminate the aluminium oxide is to treat the waste with orthophosphoric acid to obtain monosubstituted aluminium phosphate, which under such production conditions is water-soluble and easily separable from titania on the filter press.

6. Production of titania from titanium-quartz concentrate

The chemical process of enriching titanium-quartz concentrate by leaching silica with sodium hydroxide is developed and tested in autoclaves in semi-industrial conditions.

The concentrate applied for the enrichment must contain 47 to 52% of titania, 41 to 45% of silicon dioxide; 2 to 2.5% of iron oxide (III); 2 to 3% of alumina, 0.5 to 1.0% of sodium oxide; 0.06% of sulphur; and 0.18% of phosphorus oxide (V).

The product obtained during the treatment is separated into titanium concentrate and silicon-containing sediment.

Steam-cured titanium concentrate must contain 88 to 89% of titania, 5 to 6% of silicon dioxide, 2 to 3% of iron oxide alumina, 0.5 to 1.0% of calcium and magnesium oxides; 0.2 to 2.0% of sodium oxide; 0.07% of silver and 0.21% of phosphorus oxide. This type of titanium concentrate is economically efficient not only in the production of welding electrodes coatings, but also in the production of various-purpose titania.

Steam-pured concentrate can also be produced by pre-treatment with sulphuric acid while heating, then separating off water-soluble compounds of sodium, iron, aluminum and magnesium off its surface on the filter press, then drying and crushing the precipitate in the combined dryer in order to obtain the specified grain sizes. Titania obtained under such conditions matches one of the base grades and can be processed into pigment marks after being modified.

Considerable volumes of rutile titania are applied in the production of welding electrode coatings, with 20 to 25% of its mass contents in the coating material. The coating mixture is prepared by dissolving a silicate block in the autoclave, followed by the addition of various kinds of raw materials, including rutile titania, to liquid glass.

Mixture of rutile titania and liquid glass can be obtained and subsequently used in the production of welding electrodes [23]. To obtain such mixture, a 0.4 m3-volume bead mill, a 1.5 m3-volume autoclave, and also vessels for storing raw materials and finished products are used.

To obtain welding electrode coatings, rutile titania-quartz concentrate crushed in the ball crusher to the grain size of 6 to 8 μm and alkali solution with the concentration of Na2O equal 95 to 100 g/cm3, are taken in the ratio of 1:(2.5...5.0). The silicon oxide interacts with the alkali in the autoclave at a temperature of 95 to 105°C and a pressure of 2 to 3 atm for 2.5 to 3.5 hours. The mixture of rutile titania and liquid glass after obtaining is poured from the autoclave into the intermediate vessel from where it is fed to the vacuum filter for separating off the sludge and the finished product each fed into the separate vessels where welding electrodes are produced.

Both the sludge with alkali-siliceous compounds obtained after filtration, and the sludge obtained after crystallization and centrifugation are converted to sodium metasilicate, are subsequently applied in the cooking of liquid glass.

7. Conclusions

The above-presented investigations allowed us to make the following conclusions:

1. Titania is widely used in producing various types of white pigments because of its advantageous characteristics as spreading capacity and insolubility.
2. To sediment titania on the surface of dispersed materials, several methods are offered.
3. Titania can be obtained from titanium slag, which significantly increases the efficiency of the usage of waste materials.
4. Titania can be obtained from waste catalysts, which also significantly increases the efficiency of the usage of waste materials.
5. Titania obtained from titanium-quartz concentrate is applied as welding electrode coatings.

The implementation of advanced technologies for the processing of raw materials and industrial waste makes it possible to solve the problem of providing all industries with high-quality pigments.

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