

UDC 661.882.22-14

DOI: 10.15372/CSD2020201

Development of the Technology to Obtain Finely Dispersed Titanium Dioxide from the Solutions of Titanium Salts

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Abstract

Chemical precipitation deposition of titanium oxyhydrate $\text{TiO}(\text{OH})_2$ from the solutions of titanium salts and the features of thermal decomposition of $\text{TiO}(\text{OH})_2$ are studied for the purpose of improving and developing an efficient technology for obtaining nanodisperse powders of titanium dioxide with the required particle size and chemical composition. The effect of the basic synthesis parameters on the size of the formed agglomerates of titanium oxyhydrate is established. A method of the heterogeneous synthesis of titanium oxyhydrate using calcium hydroxide is proposed. The effect of the porosity of the crystalline precipitant (calcium hydroxide) on the disperse characteristics of the resulting product is studied. It is shown that a decrease in the average size of pores in calcium hydroxide causes a proportional decrease in the average size of the aggregated particles of titanium dioxide. Under the conditions of different methods of drying (convective, radiation and microwave), the kinetic regularities of the dehydration of titanium oxyhydrate are investigated. The effect of the temperature of titanium oxyhydrate dehydration on the size and crystalline structure of titanium dioxide powders is evaluated. To prevent agglomeration of the formed nanoparticles of titanium dioxide, it is proposed to add ammonium carbonate before the final stage of drying. Relying on the results of the studies, a technology of the synthesis of fine titanium dioxide particles with the concentration of the major component ≥ 98 mass % is developed.

Keywords: titanium tetrachloride, chemical precipitation, titanium oxyhydrate, alkaline precipitants, finely dispersed titanium dioxide powders

INTRODUCTION

The number of scientific publications dealing with the studies in the area of synthesis of ultra- and nanodispersed powders of titanium dioxide is increasing substantially [1–7]. TiO_2 powders with highly developed surface are extensively used in the technology of the production of protective coatings [8, 9], polishing and abrasives [10], in the production of varnish-and-paint and construction materials [11, 12], utilization of polypropylene wastes [13], in optics [14], as well as in the production of photocatalysts [15–19], solar batteries [20, 21], adsorbents [22], hydrogen [23] and nanodispersed metal titanium powders [24].

The methods most frequently used to synthesize nanodispersed powders include hydrolysis,

deposition, electrodeposition, thermal decomposition and pyrolysis, gas-phase chemical reactions [25–28]. The rates of formation and growth of the solid phase nuclei may be controlled by changing the process temperature, the ratio between reagents and supersaturation degree.

Chemical deposition, aggregation, agglomeration and oxidation form the basis of the technology of obtaining nanodisperse products, proceed with rather high rate, which causes definite difficulties in managing these processes. In this connection, the development of relatively simple but efficient technology of obtaining nanodisperse titanium dioxide powders with the required granulometric and chemical composition deserves substantial attention.

It is known that the production of TiO_2 , based on concentrating titanium-containing ores (ilmenite, titanomagnetite, leucosene etc.) may be carried out using either sulphate-based procedure or chlorine method. The sulphate procedure is based on processing titanium-containing ore in the solution of sulphuric acid, leading to the formation of TiOSO_4 . Within the chlorine method, the ore enters the reaction with chloric gas, which results in the formation of TiCl_4 .

Rather efficient method from the technological and economical points of view is the synthesis of TiO_2 powders from titanium salts obtained as a result of titanium ore concentrating. The existing methods of synthesis, in spite of the apparent simplicity of their implementation, require permanent improvement for the purpose of obtaining TiO_2 nanoparticles with a high degree of uniformity.

Thereupon, the integrated investigation of the formation of nanometer-sized TiO_2 particles with the help of modern physicochemical methods providing the reliable information on the structure, morphology and composition of the products of chemical synthesis, as well as the development and improvement of technical and technological measures ensuring the required level of control over the functional characteristics of the synthesized product become highly relevant.

The goal of the present work was the experimental investigation of the chemical deposition of titanium oxyhydrate from the solutions of titanium salts, the features of its thermal decomposition, and the development of the technology of obtaining nanodisperse powders of titanium dioxide.

EXPERIMENTAL

The deposition of titanium oxyhydrate $\text{TiO}(\text{OH})_2$ from the aqueous solutions of titanium thiosulphate TiOSO_4 and titanium tetrachloride TiCl_4 was carried out in the continuous and periodic modes with the help of the solutions of alkalis NH_4OH , KOH , NaOH and crystal $\text{Ca}(\text{OH})_2$ powder.

The set-up for the periodic deposition of titanium oxyhydrate was made of a glass reactor equipped with a dropping funnel and a vertical rotor-type mixer WiseStir HT50DX (DAIHAN Scientific, Korea). The necessary amount of the aqueous solution of titanium salt with the required concentration was poured into the glass vessel, and the mixer was switched on. The intensity of mechanical mixing remains constant in all experiments and was evaluated with the help of

Reynolds modified criterion ($\text{Re} = 820$). The necessary amount of alkaline precipitator was introduced through the dropping funnel into the solution of titanium salt. Titanium oxyhydrate precipitate formed during the chemical reaction was subjected to filtering, followed by washing and drying.

To investigate deposition in the continuous mode, we used a laboratory set-up providing a simultaneous introduction of the reacting compounds into solution with the help of peristaltic pumps of LOIP LS-301 grade (JSC LOIP, Russia). The volume flow rate of the solution of titanium salt was 2.1 mL/min for all experiments. The flow rate of alkaline reagents was varied depending on acidity in the reaction zone from 1.7 to 3.8 mL/min.

The humid precipitate after filtration was dried under the conditions of convective, radiation and microwave drying [29]. The activation energy of the drying process was determined using the Arrhenius equation with the help of kinetic curves depicting the dependence of $\text{TiO}(\text{OH})_2$ dehydration degree on time, presented in [29]. To establish the regularities of titanium oxyhydrate dehydration, we used an STA 449 C Jupiter derivatograph (Netzsch, Germany) to study $\text{TiO}(\text{OH})_2$ sample dried through convective dehydration.

Dehydration of titanium oxyhydrate was studied in a tubular electric furnace PT-1.2-40 (Russia) within a temperature range of 300–1000 °C. In the case of heterogeneous synthesis, TiO_2 was obtained as a result of calcination of titanium oxyhydrate formed in the pores of $\text{Ca}(\text{OH})_2$, at a temperature of 600 °C after preliminary drying at 150 °C.

Investigations of the physicochemical properties of synthesis products were carried out using a Lasentec D600L FBRM laser analyzer of particle size (Mettler Toledo, Germany), XRD-7000 X-ray diffractometer (Shimadzu, Japan), NOVA 4200e surface analyzer (Quantacrome, USA), high-resolution scanning electron microscope S-3400N (Hitachi, Japan) with the attachment for X-ray spectral analysis from Bruker (Germany), an instrument for measurements of specific surface and porosity Sorbi-MS (PCMeta, Russia), Zetasizer Nano ZS analyzer of particle and molecule size (Malvern, UK).

The size of pores in calcium hydroxide was determined with the help of the multi-point BET method.

Mathematical processing of the results of the investigation was carried out with the help of Curve and MS Excel software products.

RESULTS AND DISCUSSION

Titanium oxyhydrate obtained through alkaline precipitation is an amorphous product in the form of aggregated hydrated particles with variable composition – $\text{TiO}_y(\text{OH})_x(\text{H}_2\text{O})_n$, which gets structured with the formation of a gel-like mass with time due to the condensation of OH groups.

Effect of synthesis parameters on the average size of the aggregates of $\text{TiO}(\text{OH})_2$ particles

The influence of the concentration and nature of initial reagents, as well as the acidity of the reaction medium, on the size of synthesized particles was evaluated during precipitation.

Effect of reagent concentration. To evaluate the concentration of alkaline reagents on the size of the formed titanium oxyhydrate crystallites, we carried out a series of experiments using KOH, NaOH, NH_4OH solutions within concentration range 0.2–1.5 mol/L.

It was established that a symbate change of the crystallites of the compound under synthesis occurs with the change in the concentration of the alkaline precipitating agent. For instance, with an increase in the concentration of NaOH solution from 0.2 to 1.3 mol/L, the average size of titanium oxyhydrate aggregates increased from 3.9 to 8.7 μm , respectively. A similar dependence is observed also at the stage of chemical deposition with the change in the concentration of titanium salt solution. It was established that a decrease in the concentration of the aqueous solution of TiCl_4 by a factor of 5 (from 0.26 to 0.05 mol/L) causes a decrease in the size of aggregated titanium oxyhydrate particles by a factor of 3 (from 1.2 to 0.4 μm). The dependence of the size of synthesized particles on reagent concentration is due to the fact that the rate at which supersaturation is achieved increases with an increase in the concentration of dissolved substances entering the deposition stage, which promotes the formation of a large number of aggregates of the synthesized particles of titanium oxyhydrate.

Effect of the nature of initial salt. The nature of the anion which is present in the solution under analysis also affects the disposition of crystalline particles to aggregation. A solution of one electrolyte or another in the dispersing system may have a significant effect on the compression of the double electric layer (DEL) of the particles of a solid-phase compound formed as a result of chemical deposition. This influence results in a

decrease in DEL thickness due to the exchange of counter-ions of this layer for electrolyte ions promoting coagulation.

To analyze DEL changes, the value of zeta potential (ζ) was used. Investigation revealed that the size of synthesized $\text{TiO}(\text{OH})_2$ particles decreases in the sequence of anions under analysis: SO_4^{2-} , Cl^- . The minimal ζ value (–21.2 mV) is observed for oxyhydrate titanium crystallites obtained in the medium containing TiOSO_4 . The average size (d_{av}) of agglomerates was 8.6 μm . The zeta potential of $\text{TiO}(\text{OH})_2$ particles obtained from the solution of TiCl_4 was –45.2 mV, and d_{av} was 4.9 μm .

Effect of precipitator nature. The studies of the effect of different alkaline solutions on the size of synthesized $\text{TiO}(\text{OH})_2$ particles revealed that the average size of titanium oxyhydrate crystallites increases in the sequence of alkaline precipitators with cations NH_4^+ , Na^+ , K^+ (Table 1).

One can see that the dissociation constant (K_d) of an alkaline reagent has a symbate effect on the size of aggregated particles of the synthesized titanium oxyhydroxide (see Table 1). It is most probable that an increase in the concentration of hydroxide ions in the medium under analysis leads to an increase in the solution supersaturation degree, which, in turn, promotes an increase in the rate formation of crystal nuclei, followed by their aggregation and the formation of large crystalline agglomerates.

Effect of acidity and duration of solution aging. In the next series of experiments, we evaluated the effect of acidity at which the deposition proceeded and the time of aging of the dispersing medium under the conditions of continuous supply of initial solutions on the size of synthesized $\text{TiO}(\text{OH})_2$ particles. It was revealed that the size of aggregated particles in the precipitate changes in different directions with an increase in the duration of titanium oxyhydrate aging stage in the medium under investigation. However, within 1–1.5 h these oscillations stop, and the average size of crystal agglomerates becomes stable. It

TABLE 1

Effect of the kind of alkaline reagent on the average size d_{av} of $\text{TiO}(\text{OH})_2$ crystallites

Parameter	Kind of cation		
	NH_4^+	Na^+	K^+
Dissociation constant, K_d	$1.76 \cdot 10^{-5}$	5.9	∞
d_{av} , μm	5.8	9.8	20.4

was demonstrated in experiments that aggregated crystalline particles with $d_{av} = 0.2\text{--}0.4\ \mu\text{m}$ are formed in strongly acidic medium (at $\text{pH} < 2$). At the same time, the curves of particle size distribution look less uniform than those for the particles synthesized at $\text{pH} > 5$. It was established that titanium oxyhydrate agglomerates in the neutral and alkaline medium have a much larger size and more uniform granulometric composition. For instance, the average size of aggregated particles of titanium oxyhydrate at $\text{pH} 9$ was $\sim 4\ \mu\text{m}$.

Heterogeneous synthesis of $\text{TiO}(\text{OH})_2$. To evaluate the possibility of governing the size of titanium oxyhydrate crystallites, experiments on the heterogeneous synthesis of $\text{TiO}(\text{OH})_2$ were carried out using crystalline $\text{Ca}(\text{OH})_2$ particles with different porosity as a precipitating agent. It is impossible to carry out laser diffraction analysis of the size of titanium oxyhydrate particles formed on the crystal surface of solid calcium hydroxide, so, in order to analyze the effect of synthesis conditions, we estimated the size of the particles of target product – titanium dioxide, for which $\text{TiO}(\text{OH})_2$ is the precursor. The size of TiO_2 particles was determined with the help of X-ray diffraction and scanning electron microscopy (SEM). It was established that an increase in the molar ratio of $\text{Ca}(\text{OH})_2/\text{TiCl}_4$ from 1 : 1 to 2 : 1 leads to a decrease in the size of the formed TiO_2 crystallites from 39 to 0.4 μm . This kind of dependence may be explained by the fact that $\text{Ca}(\text{OH})_2$ surface during the solid-phase synthesis acts as a porous matrix where $\text{TiO}(\text{OH})_2$ particles are formed. Calcium hydroxide taken in excess prevents substantial aggregation of the synthesized $\text{TiO}(\text{OH})_2$ particles, while calcium oxide obtained as a result of thermal decomposition of $\text{Ca}(\text{OH})_2$ prevents sintering and enlargement of TiO_2 crystallites. During leaching with a diluted solution of hydrochloric acid, CaO is removed from the resulting powder causing no changes of the granulometric characteristics of titanium dioxide.

TABLE 2

Dependence of the average size of TiO_2 crystallites on the size of pores in $\text{Ca}(\text{OH})_2$

$\text{Ca}(\text{OH})_2$ sample	Average size of pores in $\text{Ca}(\text{OH})_2$, nm	Average size of TiO_2 crystallites, nm
1	51	88
2	29	57
3	15	27

The effect of the porosity of different $\text{Ca}(\text{OH})_2$ samples, determined using the multipoint BET procedure, on the size of TiO_2 is presented in Table 2. One can see that the average size of the aggregated particles of synthesized TiO_2 changes in phase with the change in the size of pores in $\text{Ca}(\text{OH})_2$. For example, a decrease in the size of $\text{Ca}(\text{OH})_2$ pores from 51 to 15 nm caused a nearly three-fold decrease in the average size of TiO_2 crystallites (from 88 to 27 nm). Comparing the size of pores in $\text{Ca}(\text{OH})_2$ and the size of TiO_2 crystallites, one may note that titanium dioxide particles are somewhat larger than the pores. This effect is explained by the fact that some $\text{TiO}(\text{OH})_2$ particles are formed in the pores of calcium hydroxide and some on its surface, where the possibility of subsequent particle agglomeration during thermal treatment cannot be excluded. The use of calcium hydroxide as a porous matrix with the definite pore size allows governing the synthesis of titanium oxyhydrate crystallites to obtain the target product in the form of titanium dioxide powder with the required granulometric composition.

Effect of the parameters of drying on the average size of the aggregates of $\text{TiO}(\text{OH})_2$ particles

The stage of drying is one of the essential points in the technology of obtaining fine powders. In the studies of dehydration of titanium oxyhydrate obtained through the interaction of TiCl_4 solution with NH_4OH , we analyzed the following methods of drying: convective, radiation and microwave. It is demonstrated that the slowest method of moisture removal from the fine product was implemented with the convective treatment. The process took place in the diffusion region, and activation energy was 19.1 kJ/mol. The second place in the rate of titanium oxyhydrate dehydration is occupied by radiation method, which is also limited by the diffusion mass transfer of bound moisture from the surface of the solid phase into the gas medium. The activation energy of radiation drying is 22.9 kJ/mol. The most intensive dehydration occurred during microwave drying. In this case, moisture removal proceeded in the kinetic region, and the activation energy was 43.2 kJ/mol.

The mathematical description of drying process was made with a two-parameter equation of the dependence of dehydration degree (r) of titanium oxyhydrate on process time (τ) :

$$r = 1 - \exp(-k\tau^n) \quad (1)$$

TABLE 3

Drying rate constants for different methods of $\text{TiO}(\text{OH})_2$ dehydration

Convective drying		Radiation drying		Microwave drying	
$T, ^\circ\text{C}$	$K \cdot 10^2, \text{min}^{-1}$	$T, ^\circ\text{C}$	$K \cdot 10^2, \text{min}^{-1}$	N, W	$K \cdot 10^2, \text{min}^{-1}$
100	3	100	7	119	8
150	8	150	18	252	33
180	10	180	25	539	130
200	11	200	27	700	176

Note. K is the rate constant of drying, T is drying temperature, N is power.

where k , n are empirical coefficients.

To calculate the rate constant (K) of drying, we used the equation

$$K = nk^{1/n} \quad (2)$$

Results of the calculation of dehydration rate constants for different methods of drying the samples under investigation are listed in Table 3. One can see that an increase in dehydration rate depends not only on temperature T and energy N introduced into the process but also on the method of dehydration. The maximal intensity is demonstrated by the microwave method, which allows a decrease in the time necessary for the dehydration of fine titanium oxyhydrate by an order of magnitude in comparison with convective drying and by a factor of 4 in comparison with radiation method.

Regularities of $\text{TiO}(\text{OH})_2$ dehydration

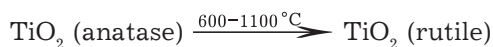
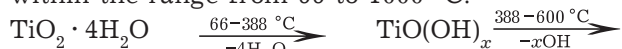
In order to understand the mechanism of dehydration of titanium oxyhydrate and to obtain the target product, the dried precursor ($\text{TiO}(\text{OH})_2$) was subjected to thermal decomposition. Investigation of this stage was carried out with the help of thermogravimetry (TG) and differential scanning calorimetry (DSC). Three thermal effects characterizing the process under investigation are shown in the thermogram (see Fig. 1) within the range of 66–1000 °C. Endo-effect within the range of 66–221 °C is connected with the removal of H_2O molecules and is accompanied by a decrease in the mass of the sample under investigation by 57.5 %.

Within the range of 388–480 °C, dehydration of titanium oxyhydrate occurs with the formation of the anatase modification of TiO_2 as confirmed by the results of X-ray phase analysis (Fig. 2).

A not very large exo-effect connected with the rearrangement of the crystal structure as a result of polymorphous transformations and the

formation of rutile modification of TiO_2 is detected within 750–950 °C.

Thermal analysis of the decomposition of titanium oxyhydrate revealed the stages proceeding within the range from 66 to 1000 °C:



The X-ray phase analysis of the samples of TiO_2 powder obtained at different annealing temperatures showed that thermal treatment involves rearrangement of the crystal structure of the compound under investigation. It is established that the degree of titanium dioxide crystallinity increases substantially with an increase in annealing temperature (see Fig. 2).

To eliminate undesirable agglomeration of titanium dioxide particles during annealing, the stage dehydration of $\text{TiO}(\text{OH})_2$ deposited as a result of heterogeneous synthesis on the surface of $\text{Ca}(\text{OH})_2$ particles was investigated.

During annealing, the mixture composed of the crystal particles of $\text{TiO}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, the formation of new phases CaO and TiO_2 occurs within temperature range 500–600 °C. Titanium dioxide particles formed in the pores of calcium oxide are located at rather long distances from each other and do not form large aggregated structures. A subsequent increase in annealing temperature to 900–1100 °C is undesirable because it leads to the formation of the side product, calcium titanate CaTiO_3 .

To remove CaO particles, the mechanical mixture obtained at a temperature of 600 °C was treated with HCl solution to obtain fine TiO_2 particles.

It was demonstrated by means of SEM that the size of the obtained particles of TiO_2 crystallites varied from 80 to 110 nm (Fig. 3). It was established on the basis of the results of X-ray spectral

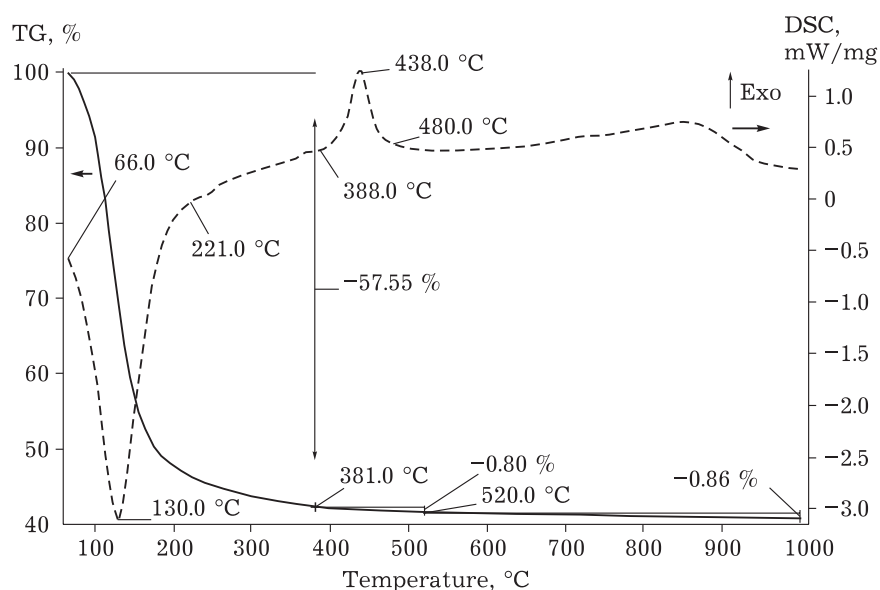


Fig. 1. Thermal analysis of the decomposition of titanium oxyhydrate.

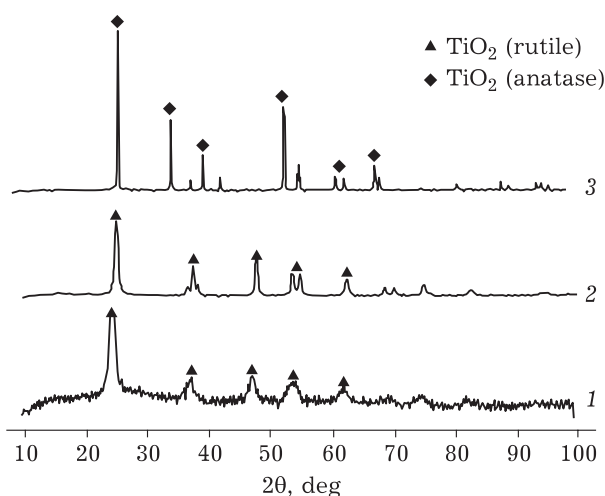


Fig. 2. Diffraction patterns of the products of titanium oxyhydrate decomposition at different temperatures, °C: 300 (1), 600 (2), 1100 (3).

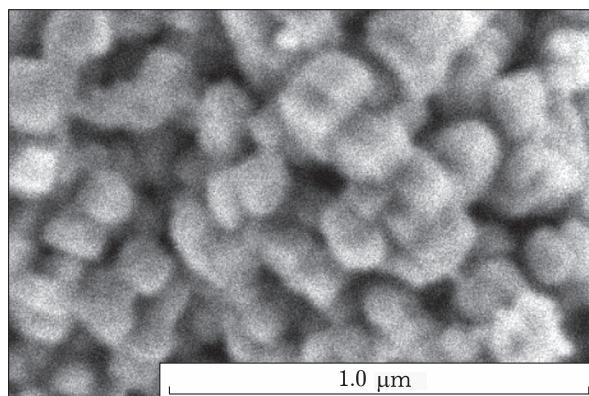


Fig. 3. Microphotograph of TiO_2 particles.

analysis that the fraction of calcium admixture in the obtained powder did not exceed 0.1 mass %.

In order to prevent aggregation of nanodispersed TiO_2 particles, $(\text{NH}_4)_2\text{CO}_3$ decomposing under thermal treatment was introduced into the humid paste at the final stage of drying (after acid removal of CaO). It was established in the experiments that the addition of ammonium carbonate prevents aggregation of TiO_2 particles, increases the porosity of the product and decreases its apparent density. The optimal fraction of $(\text{NH}_4)_2\text{CO}_3$ additive introduced into the paste is 5–7 mass %. This amount of the reagent allowed us to achieve the minimal apparent

density of the powder 0.4 g/cm^3 . Further increase in the amount of the introduced additive does not cause any substantial effect on the characteristics of the target product.

The technology of the synthesis of fine TiO_2 powders

The technology of the synthesis of fine titanium dioxide powders was developed as a result of the investigations carried out within the present work (Fig. 4).

To synthesize $\text{TiO}(\text{OH})_2$, a suspension of calcium hydroxide ($d_{\text{av}} = 3 \mu\text{m}$) and a 2% aqueous solution of titanium tetrachloride at a temperature of $25 \text{ }^\circ\text{C}$ are supplied into the reactor with a

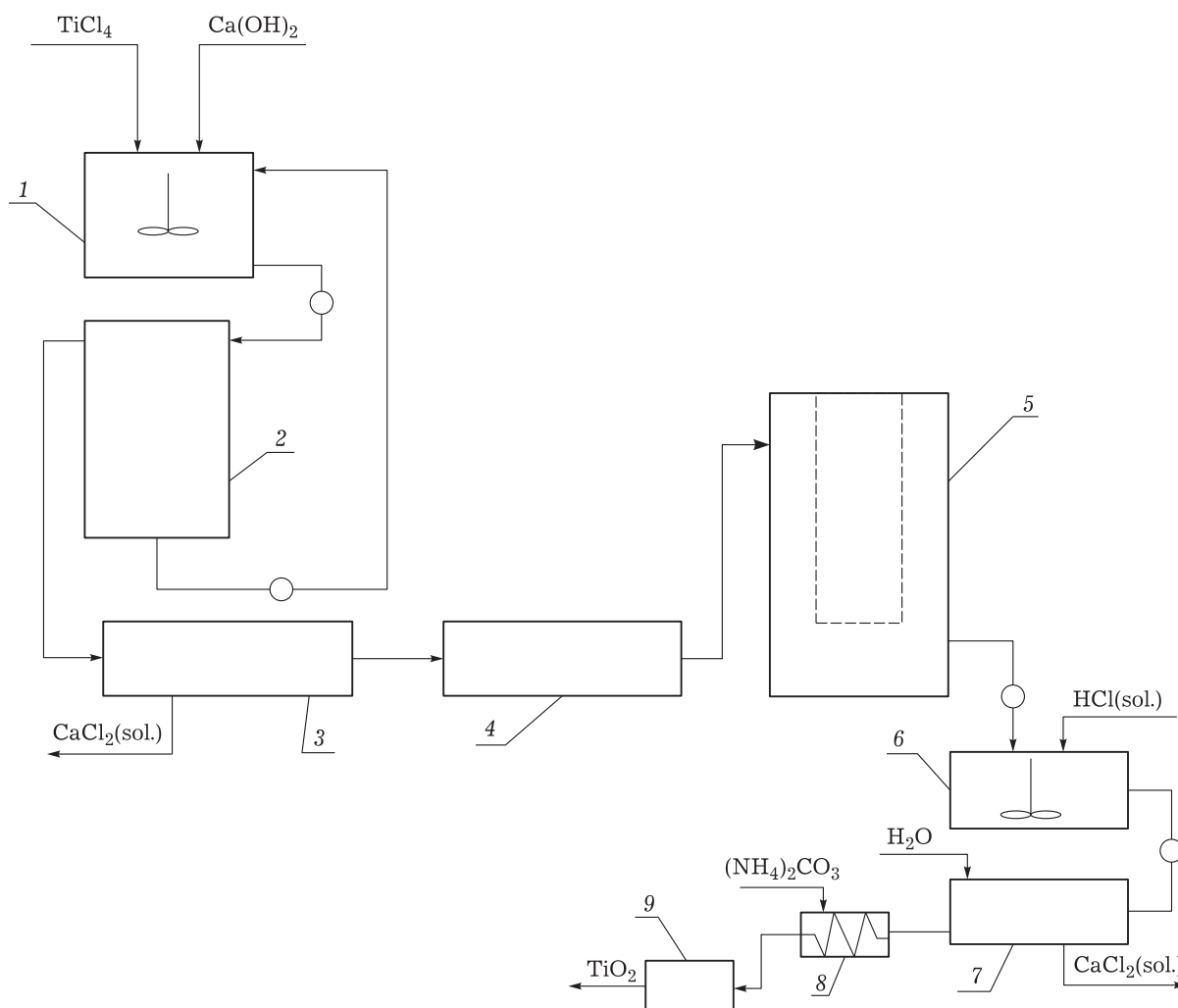


Fig. 4. Technological scheme of the synthesis of titanium dioxide: 1 – reactor, 2 – hydroseparator, 3 – filter press, 4 – microwave dryer, 5 – furnace for calcination, 6 – reactor, 7 – vacuum band filter, 8 – screw feeder, 9 – vacuum dryer.

mixer (1). The molar ratio of the components $\text{Ca(OH)}_2/\text{TiCl}_4$ is 2 : 1. Heterogeneous precipitation lasts for 30 min, after which the suspension enters the stage of hydroseparation (2).

The coarse fraction of the condensed precipitate consisting mainly of Ca(OH)_2 particles is returned back to reactor (1), while the fine fraction enters the stage of filtration (3). The humid precipitate obtained after filtration is dehydrated in the microwave dryer (4) and then annealed for 90 min at a temperature of 600 °C in a muffle furnace (5). A mechanical mixture of TiO_2 and CaO powders discharged from the furnace is directed to the reactor (6) at the stage of leaching with an 8 % solution of HCl . The suspension formed as a result of leaching is filtered through a vacuum band filter (7); simultaneously the paste is washed with water. The ratio of water to the precipitate is equal to

2 : 1. Then the resulting paste is mixed with ammonium carbonate in the amount of 5–7 % of the mass of the dry product and subjected to drying in the vacuum dryer (9) at a temperature of 70–80 °C.

The proposed version of the technology allows obtaining fine TiO_2 powders with the major substance content ≥ 98 %, calcium admixture not more than 0.1 %. The obtained product is characterized by the monodisperse particle size distribution with the average size of TiO_2 crystallites 60–100 nm and specific surface 15–24 m^2/g .

CONCLUSION

The effect of the concentration and nature of reagents, acidity of the reaction medium and process duration on the size of synthesized

titanium oxyhydrate particles deposited from the solutions of titanium salts was revealed as a result of the investigation. It is demonstrated that an increase in the concentration of the solution of titanium salt and the alkaline precipitating agent leads to an increase in the size of the synthesized $\text{TiO}(\text{OH})_2$ aggregates. It is established that the average size of titanium oxyhydrate crystallites increases in the sequence of alkaline precipitating agents with cations NH_4^+ , Na^+ , K^+ and decreases in the sequence of titanium salt anions SO_4^{2-} , Cl^- . It is demonstrated that the precipitates of titanium oxyhydrate composed of smaller particles are formed in a strongly acidic medium (at $\text{pH} < 2$) with the aging stage lasting for 60–70 min.

The possibility to control the size of titanium dioxide particles by using calcium hydroxide at the stage of $\text{TiO}(\text{OH})_2$ synthesis was demonstrated. Calcium hydroxide acts as a porous matrix where the formation of titanium oxyhydrate particles proceeds.

Analysis of titanium oxyhydrate drying using different methods was analyzed. It is revealed that microwave dehydration proceeds in the kinetic region. It is demonstrated that for the convective and radiation methods of drying the rate of water removal is limited by the diffusion transfer of the liquid from the pores of the product into the gas medium.

The effect of the temperature mode of titanium oxyhydrate dehydration on the crystal structure and size of the synthesized titanium dioxide powders is evaluated.

A technology is developed allowing the synthesis of fine TiO_2 powders with the required granulometric composition within the range 60–100 nm and the content of the major substance ≥ 98 mass %.

Acknowledgements

The work was carried out with financial support from the Ministry of Education and Science of the Russian Federation within the project “Development of methods to govern the synthesis of solid-phase compounds in quasi-equilibrium state for obtaining materials with required properties” (State Contract No. 02.740.11.0254).

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