

Effects of processing parameters on hydrolysis of TiOSO_4

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The influence of both TiOSO_4 concentrations in the starting solution and a way of conducting hydrolysis on the degree of titanyl sulphate conversion to hydrated titanium dioxide were studied. Titanyl sulphate solution, an intermediate product in the commercial preparation of titanium dioxide pigments by sulphate method, was used. The continuous method of conducting hydrolysis was applied using one or two reactors connected in series. It was found that the degree of hydrolysis markedly depends on the studied parameters. It was also found that TiOSO_4 hydrolysis using the continuous method should be conducted : i) at a possibly low concentration of free sulfuric acid in the solution and; ii) in two or more reactors connected in series.

Keywords: hydrate titanium dioxide, hydrolysis, titanyl sulfate, continuous method.

INTRODUCTION

Between 1980 and 2005 the worldwide production of titanium dioxide increased by 21.6%. It was triggered by the dynamic development of new possibilities of the product's application. TiO_2 pigment is mainly used in paint and varnish industries, but additionally it is widely applied in paper, artificial fibre, plastic, rubber and food industry, where it has contact with products to be later consumed by people. Titanium dioxide found its latest application in electronics where it is used as a ceramic material with dielectric properties as well as in various chemical processes in which it is used as a great photocatalyst. Titanium dioxide has also managed to dominate pharmaceutical, cosmetic and energy industries¹⁻⁸. Its latest applications are connected with using TiO_2 pigments in sunscreens, in photocatalytic self-cleaning, antibacterial, super-hydrophilic coatings eliminating smells, hardening surfaces or used as semiconductors in solar cells. Titanium dioxide is even used in photocatalytic disinfection and to destroy cancerous cells⁹⁻¹¹.

Hydrolysis is one of the decisive stages determining the final product's properties in the industrial production of titanium dioxide pigment by sulphate method. In this reaction hydrated titanium dioxide precipitates from an acidified solution of titanyl sulphate at the boiling point. It is a complex physiochemical process. The mechanism of hydrothermal hydrolysis has not, as yet, been fully explained and it is still the focus of attention of many scholars. The following pattern has been generally accepted: titanium dioxide particles grow to achieve colloidal size followed by precipitation of a deposit with agglomerate size varying between 10 and 200 μm ¹²⁻¹⁶. The analysis of the precipitate obtained as a result of titanyl sulphate hydrolysis (after washing with water and filtration) demonstrated that apart from TiO_2 (33 – 34 wt.%) it contained water and some sulfuric acid (approximately 8% in comparison with TiO_2)^{12, 14}.

In industrial practice two methods of conducting hydrolysis of titanyl sulphate are used. The first, the so-called Blumenfeld, method consists in producing nuclei in all the volume of hydrolysed solution by means of diluting it and bringing it to the boiling point¹⁷. In the second method nuclei are obtained separately and they are added to a solution in order to accelerate hydrolysis. It is the so-called Mecklenburg method¹⁸. Naturally, both

methods have been numerously modified. The modifications mainly aimed at changing parameters of hydrolysis or at introducing into a system various additions which, in turn, would make it possible to obtain titanium dioxide with various physiochemical properties¹⁹⁻²³.

Hydrolysis can be affected by the following factors: the concentrations of titanyl sulphate and sulfuric acid in a solution, the content of additions, the viscosity of a solution, the temperature, time and method of mixing and the addition of nuclei^{12, 14, 24-26}.

Nuclei are one of the most important factors affecting both hydrolysis and physiochemical properties of products. Nuclei are the source of structural information at a molecular level or at the stage when micelles are created. These are molecules which consist of sulphate polytitanic acids, which in a solution of titanium compounds (IV) disaggregate into separate micromolecules¹⁴.

Sikhar Sathyamoorthy et al.²⁷ investigated the mechanism of particle formation during anatase precipitation from a concentrated solution of titanyl sulphate containing nuclei in an industrial installation (506 g of $\text{TiOSO}_4/\text{dm}^3$ and 464 g of $\text{H}_2\text{SO}_4/\text{dm}^3$). They used an industrial solution of nuclei obtained as a result of hydrolysis of titanium tetrachloride in a solution of sodium hydroxide. They demonstrated that the solution contained particles of three sizes, i.e. crystallites, original agglomerates and aggregates. They found that the application of nuclei in industrial installations makes it possible to control the size of crystallites. Nuclei with a large specific surface area induce the formation of a larger number of crystallites through secondary nucleation. Crystallites do not exist freely in a suspension, but they are to be found in the form of original agglomerates. Crystallites are interconnected with crystallite bridges and form dense structures resistant to changes in surface charge. The size of original agglomerates depends on the number of crystallites found in their structure, whose average size varies between 4 and 8 nm. Original agglomerates collide with one another and as a result of physical attraction aggregates with sizes between 1 and 2 μm are formed. These aggregates are final particles of anatase, which precipitate during hydrolysis. The process of particle formation strongly depends on the amount of added nuclei. It was found that nucleation and aggregation are important stages in controlling the size of particles. A high rate of precipitation can be reached by

means of adding nuclei, which stimulate nucleation. Simultaneously, by controlling supersaturation decrease as a result of nucleation it is possible to optimise the processes of aggregation and agglomeration. The size of aggregates affects the effectiveness of separating solid and liquid phases at the stage of filtration^{14, 27}.

Many patents present methods of obtaining nuclei and ways of conducting hydrothermal hydrolysis of titanyl sulphate in the presence of nuclei^{28 - 30}. According to patent 30 two solutions of titanyl sulphate with the same concentration of TiO₂ (230 - 260 g TiO₂/dm³) but with a different coefficient of acidity (1.75 - 1.85 and 2.1 - 2.4) are mixed in an appropriate voluminal ratio (3 : 100 - 12 : 100) and heated to 88 - 98°C. Hydrolysis is conducted using the so-called auto-nucleation method.

Several studies^{14, 25, 26, 31, 32} contain findings regarding the influence of TiOSO₄ concentration on the rate of TiO₂·nH₂O formation from concentrated solutions. In a study conducted by Dobrowolski¹⁴ it was found that an increase of TiOSO₄ concentration lead to a decrease of hydrolysis degree due to a declining rate of hydrated titanium dioxide formation. It is generally considered that the mechanism of TiO₂ formation from titanyl sulphate solutions depends on the concentration of TiOSO₄^{25, 32}. Studies^{26, 32} present the influence of sulfuric acid on TiOSO₄ hydrolysis. An addition of sulfuric acid inhibited the process of hydrolysis.

Yasir et al.³³ investigated the influence of solution concentration, temperature, the time of the process at the boiling point and the calcination temperature of hydrolysis' product on the specific surface area of anatase obtained in reactions. An increase of temperature, hydrolysis time, and calcination temperature lead to a significant decrease of TiO₂ specific surface area.

The influence of Fe(II) and Fe(III) on hydrolysis of titanyl sulphate has been previously reported^{14, 24, 34}. It was found³⁵ that the rate of stirring (200 - 1200 r.p.m.) did not have any significant influence on the kinetics of TiO₂ precipitation during hydrolysis. Similarly, it did not affect the size of either original agglomerates (60 - 80 nm) or crystallites (4 - 8 nm). However, it did have an influence on the average size of aggregates (0.7 - 1.6 μm). The faster the speed of stirring the smaller aggregates were formed from particles of hydrated titanium dioxide.

Nowadays, almost all around the world, when titanium dioxide pigments are produced using a sulphate method, hydrolysis of titanyl sulphate is conducted in the presence of TiO₂·nH₂O nuclei. In the batch method TiO₂ nuclei are first obtained in a separated reaction system and then introduced into a hydrolysed solution^{14, 28 - 30}. A part of the final suspension of hydrated titanium dioxide in sulfuric acid can also be used in a new manufactured unit¹⁴. It seems that conducting TiOSO₄ hydrolysis by means of a continuous method using the phenomenon of auto-nucleation would seem to be a more favourable solution.

EXPERIMENTAL

An industrial acidified aqueous titanyl sulphate solution was used in the present study (480 g/dm³). The hydrolysis of TiOSO₄ solution was conducted in a continuous way. Single glass reactor (designated volume 0.5 dm³)

or two reactors connected in series (designated volume 0.5 dm³ and 1.0 dm³) were used. Each reactor was equipped with an agitator (rotation 960 r.p.m.), reflux condenser and an apparatus for feeding and receiving reagents. The temperature of the dosed substrates was 20°C. The hydrolysis was conducted at approximately 108°C. The initial concentration of TiOSO₄ and H₂SO₄ in the reaction mixture varied from 200 to 380 g of TiOSO₄/dm³ (98 - 186 g H₂SO₄/dm³). Depending on the rate of dosing and receiving reagents the process was conducted 3 - 8h.

Throughout all the course of the process samples of suspension were collected after defined periods of time. The precipitates were separated from the liquid phase (post-hydrolytic sulfuric acid) by centrifuging (20 min, 8000 r.p.m), washed with distilled water to remove free sulfuric acid, dried at ambient temperature (so-called air-dry state), and crushed.

The conversion degree of titanyl sulfate (α) into hydrated titanium dioxide was calculated from the equation:

$$\alpha = \frac{C_0 - C}{C_0} \cdot 100\% \quad (1)$$

where C₀ - initial concentration of Ti calculated as TiOSO₄ in the solution, g/dm³, C - concentration of Ti as TiOSO₄ in the solution after time τ , g/dm³.

Titanium was determined in the liquid phase using a spectrometric method³⁶. The X-ray diffraction analysis was used to determine the crystallite size in the hydrated titanium dioxide samples (X'Pert PRO Philips diffractometer with CuK _{α} radiation)³⁷. The crystallites average size (d_{crys}) variation was determined on the basis of Scherrer's equation:

$$d_{\text{crys}} = \frac{\lambda \cdot K}{\beta \cdot \cos \theta} \quad (2)$$

where λ is the wavelength of Cu K _{α} radiation, K is the particle shape factor, β is the full width at half maximum of the intensity peak.

The variation of crystallites average size of anatase phase was calculated from the (101) reflection of anatase. The width of the peak at half maximum was calculated taking into account the so-called instrumental broadening. This parameter was determined on the basis of the sample of coarse crystalline silicon. The particles average size of TiO₂ was determined using of a scanning electron microscope (DSM 962, Zeiss)³⁸.

A continuous method of hydrolysis in single reactor

A continuous method of hydrolysis required the reactor to be initially filled with a reaction mixture of highly reacted TiOSO₄ amounting to approximately 94%. The procedure of preparing such a mixture was as follows: an appropriate amount of concentrated titanyl sulphate solution was introduced into a dropper, while at the same time an appropriate amount of water was introduced into the glass-reactor, depending on the initial TiOSO₄ concentration in the solution. The water and titanium liquor were heated up to the temperature of 96°C. When they reached the desired temperature, the liquor was being dropped in for 20 min, while at the same time the temperature was increased to 102°C. After the dropping-in was over the reaction mixture was heated for 20 min to the so-called first boiling point, i.e. to about 108°C. (depending on the

concentrations of TiOSO_4 and free H_2SO_4). The solution was kept at this temperature for 90 min. After that a continuous dosing of a concentrated solution of TiOSO_4 commenced. These streams came from feeding tanks equipped with their own heating and stirring systems. The reagents were dosed and received at a varying rate (16.7 cm^3/min , 8.3 cm^3/min , 4.2 cm^3/min and 2.8 cm^3/min). The residence time of the reagents in the hydroliser amounted to 30 min, 60 min, 120 min and 180 min respectively. The initial concentration of TiOSO_4 in the investigated solution amounted to 200 g/dm^3 , 236 g/dm^3 , 300 g/dm^3 and 380 g/dm^3 , respectively.

A continuous method of hydrolysis in two reactors

When TiOSO_4 hydrolysis was conducted using a two-stage continuous method, reactors were filled with a reaction mixture containing titanyl sulphate converted to various degrees (I lower, II higher degree). Until the moment when reaction mixtures reached 102°C the procedure was exactly the same as in the previously described case. The procedure of preparing a starting reaction mixture in hydroliser II began 20 min earlier. The reaction mixture in hydroliser I and II was kept at the temperature of 102°C for another 10 or 20 min. After that fresh substrates (concentrated acid solution of TiOSO_4 and water) were fed into reactor I at the rate of either 16.6 or 8.3 cm^3/min . The residence time of the reaction mixture in hydroliser I amounted to 30 or 60 min. The reaction mixture in hydroliser II was additionally heated up to its boiling point (108°C) for 20 min. After that the reaction mixture from the first reactor was pumped into the second reactor at the rate of 16.6 or 8.3 cm^3/min and then the product of hydrolysis from reactor II was received (TiO_2 suspension in sulfuric acid). The reaction mixture stayed in reactor II twice as long as in reactor I and this time amounted to 60 or 120 min. The initial concentration of TiOSO_4 in the solution amounted to 236 g/dm^3 .

RESULTS AND DISCUSSION

A continuous method of hydrolysis in single reactor

In the first experiment the initial concentration of TiOSO_4 in the solution was equal to 380 g/dm^3 (H_2SO_4 186 g/dm^3), and the residence time of the mixture in the reactor for 60, 120 and 180 minutes respectively (the rate of dosing the reagents: 8.3 cm^3/min , 4.2 cm^3/min and 2.8 cm^3/min). Substrates were being dosed continuously to the initial reaction mixture, in which the hydrolysis degree of titanyl sulphate amounted to 94% (Figure 1). It was found that in each experiment that was carried out, shortly after the substrates started being continuously dosed (for 90 min., Fig. 1), the conversion degree of TiOSO_4 significantly decreased to around 20–60% after continuous hydrolysis time of 90 min. (time 180 min. in Fig. 1). The slower was the rate of dosing the substrates and the slower was the rate of receiving the reaction products, the smoother was the decrease of the degree of TiOSO_4 hydrolysis. However, it had no influence on the final conversion degree. In all the experiments, after the reactor's full capacity had been exchanged two or three times and re-

gardless of the degree of dosing reagents, the conversion degree oscillated between 25 and 27% and it did not change to the end of the process.

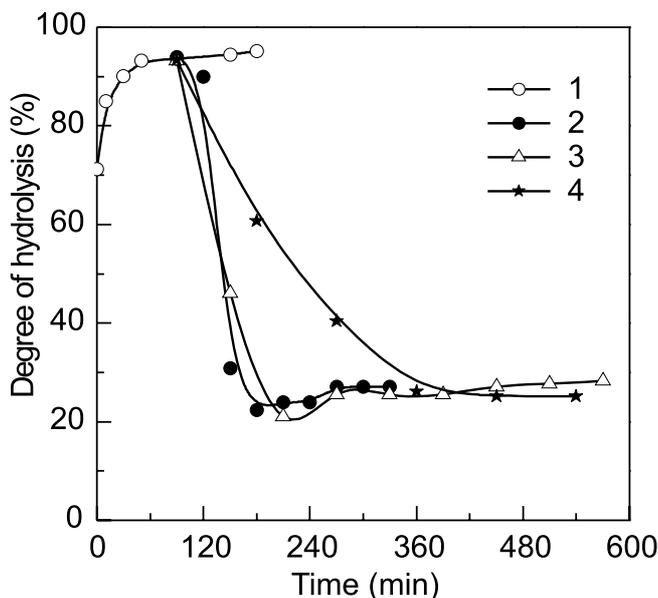


Figure 1. The influence of residence time on the degree of titanyl sulphate hydrolysis (the initial concentration of TiOSO_4 – 380 g/dm^3), 1 – reference test (batch hydrolysis), 2 – 60 min, 3 – 120 min, 4 – 180 min

It was found that the average size of the obtained products' crystallites ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) varied between 11 and 19 nm and it depended on the residence time the reaction mixture in the reactor. The longer the time the larger crystallites of hydrated titanium dioxide tended to be. A similar dependence was observed in reference to the size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles. The diameter of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles increased from 0.6 to 1.3 μm . The shape of all the grains of the obtained products in this series of experiments was irregular. However, they did have smooth edges.

Because the obtained final degree of hydrolysis was low, it was decided that another series of experiments should be carried out at a lower initial concentration of TiOSO_4 amounting to 300 g/dm^3 and at a lower content of free sulfuric acid (147 g/dm^3). The residence time of the reaction mixture in the reactor amounted to 30 min., 60 min., 120 min. and 180 min. and the rate of dosing reagents was 16.7 cm^3/min , 8.3 cm^3/min , 4.2 cm^3/min and 2.8 cm^3/min , respectively.

It was found that the character of the recorded relations (Figure 2) was analogous to that obtained in the first series of experiments. From the moment when the substrates started being dosed in a continuous manner, the degree of TiOSO_4 hydrolysis always decreased, and sometimes the decrease was quite sudden. However, the decrease was never as low as in the first case. A degree of conversion after the reactor's volume had been changed 2 or 3 times was higher and varied between 50 and 60%.

The average size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ crystallites in the separate experiments varied between 14 and 20 nm and depended on the residence time the reaction mixture in the reactor. The longer the time the larger crystallites of the obtained product tended to be. Similarly, the size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ grains depended in the same way on the above

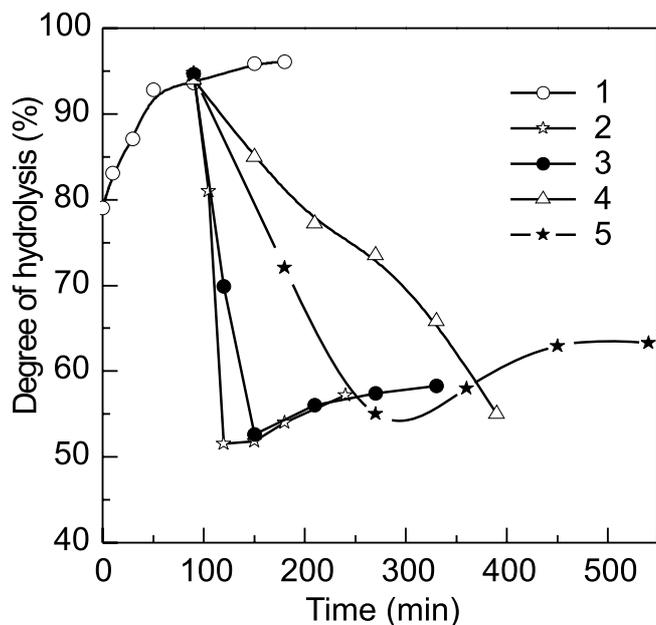


Figure 2. The influence of residence time on the degree of titanyl sulphate hydrolysis (the initial concentration of TiOSO_4 – 300 g/dm^3), 1 – reference test (batch hydrolysis), 2 – 30 min, 3 – 60 min, 4 – 120 min, 5 – 180 min

mentioned parameter of the process and it varied between 0.7 and $6 \mu\text{m}$ (Figure 3) – so the increase was eight-fold. The average size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles obtained in TiOSO_4 hydrolysis using the batch method oscillated around $1 \mu\text{m}$.

Because the degree of TiOSO_4 hydrolysis was still low, it was decided to carry out an experiment in which the initial concentration of TiOSO_4 in the solution was drastically lowered down to 200 g/dm^3 ($98 \text{ g H}_2\text{SO}_4/\text{dm}^3$). The residence time of the reaction mixture in the reactor amounted only 60 min. The reaction mixture was kept in the reactor for only 60 min. As in the previous experiments, the substrates were continuously dosed into the so-called starting reaction mixture whose degree of conversion amounted to 98% due to a low, initial TiOSO_4 content in the solution. The obtained results are presented in Figure 4.

The lowering of TiOSO_4 and sulfuric acid concentrations led to an increase of the reaction's yield. After the reactor's volume had been changed twice the degree of conversion stabilised at the level of approximately 77% and it was higher by around 20% from that obtained in the experiment in which the initial concentration of TiOSO_4 amounted to 300 g/dm^3 . However, it was still lower by approximately 20% from that obtained in hydrolysis conducted using the periodic method. In that experiment no sudden decrease of hydrolysis degree was

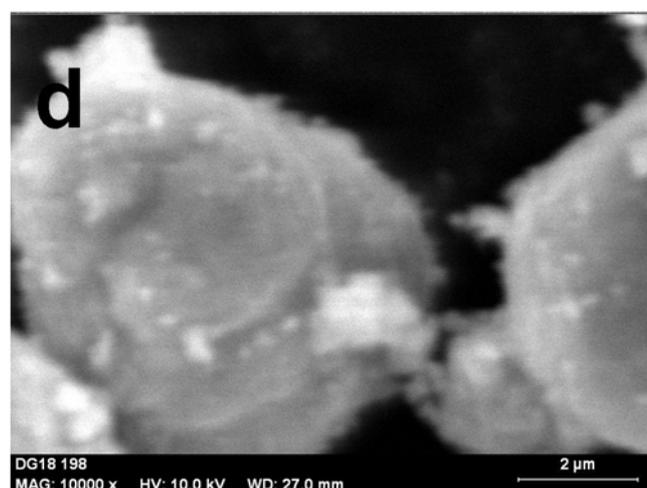
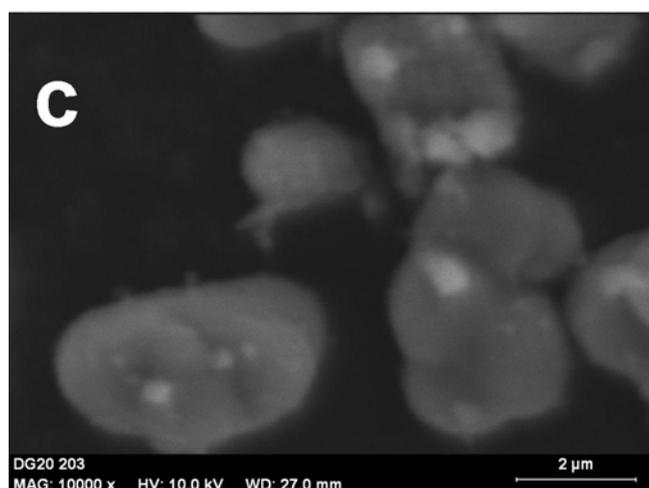
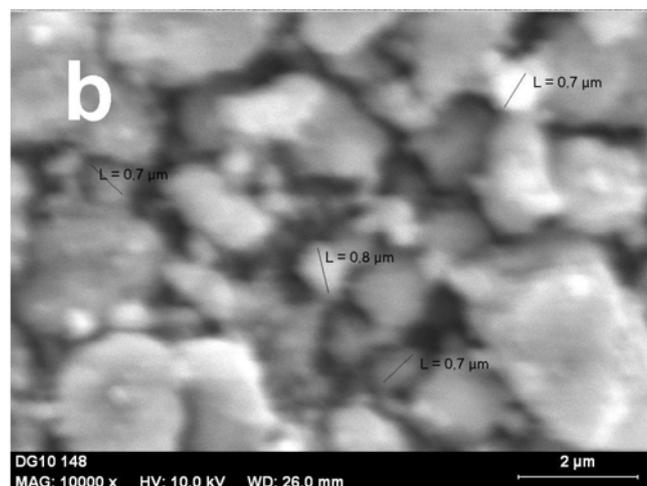
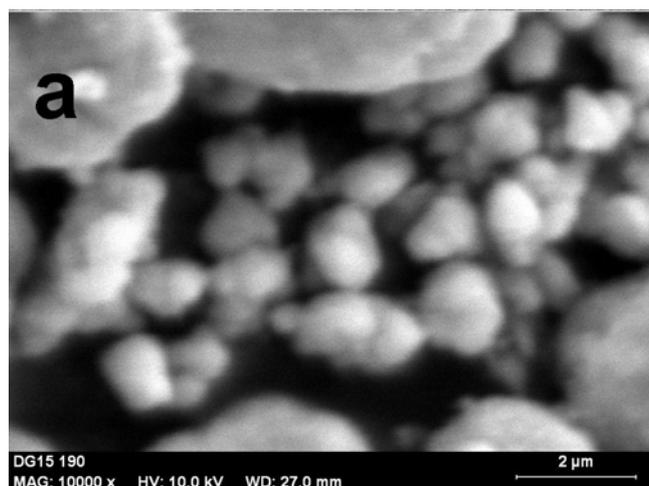


Figure 3. SEM images (magnification of $\times 10000$) of titanium dioxide obtained in the hydrolysis of titanyl sulphate using a) batch method and continuous method when the residence time the reaction mixture in the reactor was: b) 30 min, c) 60 min, d) 180 min. (the initial concentration of TiOSO_4 – 300 g/dm^3)

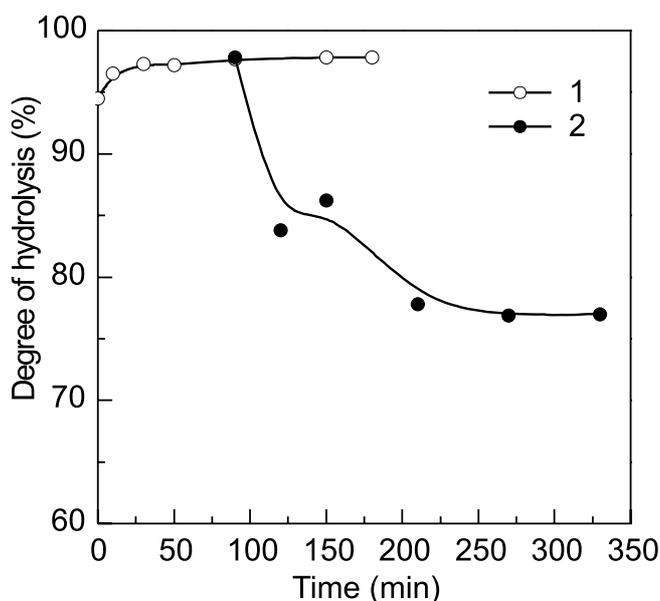


Figure 4. The influence of residence time on the degree of titanyl sulphate hydrolysis (the initial concentration of TiOSO_4 – 200g/dm^3), 1 – reference test (batch hydrolysis), 2 – 60 min

observed along with continuously dosed substrates, which took place in previous experiments (higher initial TiOSO_4 concentration in a solution).

The average size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ crystallites obtained in these experiments varied around 12 nm. It was found that in this case the morphology of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ grains from the continuous process was almost identical with that from the batch process (diameter approx. $2.5\ \mu\text{m}$).

Since the lowering of the initial concentration of titanyl sulphate in the solution down to $200\ \text{g of TiOSO}_4/\text{dm}^3$ did not bring satisfactory results, it was decided that the process should be slightly modified. The pH of the reaction mixture was decreased in order to lower the concentration of free sulfuric acid which is the reaction's product and which inhibits the course of the reaction. Additionally, a water solution of sodium hydroxide, instead of water, was being dosed to the reaction system in an amount necessary to neutralise 8% of free sulfuric acid which was formed as a result of the reaction. The initial TiOSO_4 concentration in the solution amounted to 200 and $380\ \text{g/dm}^3$ (98 and $186\ \text{g of H}_2\text{SO}_4/\text{dm}^3$). The residence time of the reagents in the hydroliser amounted to 60 min. The lowering of free sulfuric acid's concentration in the reaction mixture led to an increase of TiOSO_4 conversion degree from 77% to approx. 98% in the first case and from 27% to 68% in the second one.

In the above described experiments, in hydrolysis conducted using the continuous method the conversion degree of TiOSO_4 varied between 27 and 98% and the lower the initial concentrations of TiOSO_4 and H_2SO_4 in the reaction mixture the higher the conversion degree actually was. However, it was significantly lower than the conversion degree obtained in a batch reactor except for the experiment in which the content of free H_2SO_4 in the reaction mixture was lowered and the initial concentration of TiOSO_4 in the solution was $200\ \text{g/dm}^3$. A low reaction yield was caused by too high concentration of free sulfuric acid in the reaction mixture which inhibited the process of hydrolysis. Sulfuric acid was a product of

hydrolysis and it was also already to be found in the initial industrial solution of titanyl sulphate (the sulphate method of obtaining titanium dioxide).

Additionally, in the continuous process of TiOSO_4 hydrolysis conducted in single reactor two stages of the reaction should proceed simultaneously: 1st – formation of stable active centres of TiO_2 and 2nd – coagulation and precipitation of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$. The former was inhibited because of too high concentration of free sulfuric acid in the reaction mixture and because the equilibrium constant for the reaction was shifted towards the substrates. This acid can also dissolve a part of small crystallites or thermodynamically unstable surfaces.

A continuous method of hydrolysis in two reactors

A hydrolysis of an acidified solution of TiOSO_4 was conducted in two stages. It was assumed that the stage of the reaction connected with the formation of colloidal titanium dioxide will take place in the first reactor (at 102°C), whereas in the second reactor hydrated titanium dioxide will precipitate (at the boiling point). Substrates were being dosed to the first hydroliser and the suspension of hydrated titanium dioxide in sulfuric acid was collected from the second hydroliser. The residence time of the reaction mixture in the first reactor was twice as short as in the second one and it amounted to 30, 60 and 60, 120 min respectively. The initial concentration of titanyl sulphate was identical in both cases and it was equal to $236\ \text{g/dm}^3$. The temperature of the concentrated solution of titanyl sulphate being dosed and that of water was 20°C . It was assumed that the beginning of hydrolysis was the moment of stabilising the boiling point in the second reactor.

In the experiment in which the dosing rate of the substrates was higher a relatively sudden decrease of conversion degree was observed from the moment of dosing reagents in a continuous way to the initially filled reactor. The degree of TiOSO_4 hydrolysis fell from 93% to approx. 80% and it oscillated around this value to the end of the process which lasted 3 h (Figure 5).

By contrast, in the experiment in which the dosing rate of the substrates was lowered twice, the course of hydrolysis was quite different. When the substrates were being dosed continuously no drop in hydrolysis' degree was recorded. Throughout all the process (300 min.) the degree of TiOSO_4 conversion oscillated about 94.5% and only slightly (by 3%) deviated from that obtained when hydrolysis was conducted in one reactor using the batch method (Figure 5). It should be added that the degree of TiOSO_4 hydrolysis after the first stage of the reaction (i.e. after 1st reactor) was significantly lower and it amounted to 69%.

It was found that while conducting hydrolysis of acidified solution of TiOSO_4 in two reactors it is necessary to lengthen the residence time of the reaction mixture in both hydrolisers, i.e. to lengthen the time necessary for both stages of the reaction to proceed correctly.

It was found that the average size of the grains of hydrated titanium dioxide obtained in both experiments was approx. $6.5\ \mu\text{m}$. These grains were larger from the grains of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ precipitated in the experiments conducted in a continuous way in single hydroliser. The particles had spherical shapes and smooth edges (Figure 6). The size

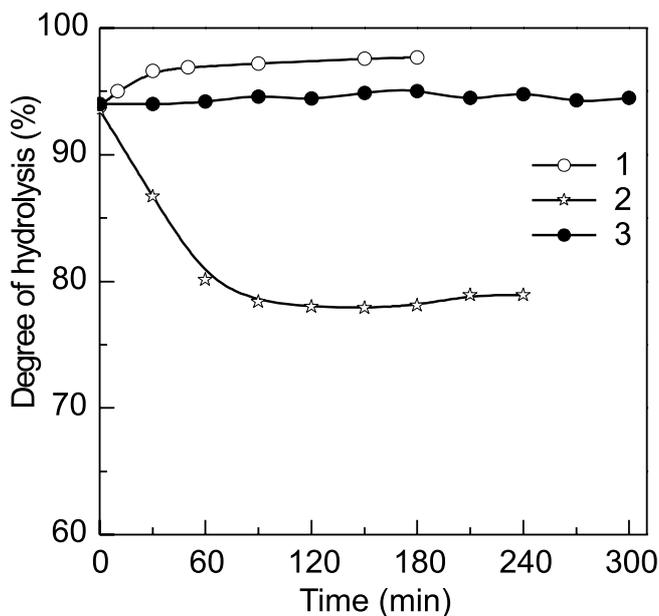


Figure 5. The influence of residence time the reaction mixture in 1st reactor on the degree of titanyl sulphate hydrolysis (the initial concentration of TiOSO_4 – 236 g/dm^3), 2 – 30 min, 3 – 60 min

and shape of the particles did not seem to depend on the dosing rate of the substrates. The average size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ crystallites varied between 14 and 16 nm and it did not depend on the parameter which was changed in the process of hydrolysis.

CONCLUSIONS

On the basis of the conducted experiments on the process of hydrolysis of an acidified solution of titanyl sulphate using the continuous method it was found that:

- the lower the initial concentrations of TiOSO_4 and H_2SO_4 in the solution the higher degree of conversion was obtained,
- the final degree of hydrolysis, depending on the parameters of the process, varied between 25 and 98%,
- a stable course of hydrolysis (a stable value of a degree of hydrolysis) was achieved after 2 – 3 cycles of complete change of the reactor's volume,
- in hydrolysis conducted in single reactor, the final degree of hydrolysis practically did not depend on the

dosing rate of the reagents (at constant concentrations of TiOSO_4 and H_2SO_4 in the reaction mixture),

– when hydrolysis was conducted in two reactors in series a two-fold decrease of the dosing rate of the substrates led to an increase of the degree of hydrolysis by 15%,

– the longer the residence time of the reaction mixture in the reactor, the larger were both the grains and crystallites of hydrated titanium dioxide. This effect was not observed when hydrolysis was conducted in two reactors.

– separating the process into two stages was a step in the right direction in order to achieve a high degree of hydrolysis of an acidified solution of TiOSO_4 using the continuous method.

A lowering of the content of free sulfuric acid in the reaction mixture can be a good method of increasing the degree of titanyl sulphate's hydrolysis in a continuous process. It can be achieved by conducting the process of hydrolysis at a lower initial concentration of sulfuric acid in the reaction mixture through its partial neutralisation, e.g. with sodium hydroxide. Consequently, the products of the reaction will include not only the so-called post-hydrolytic sulfuric acid containing sulphates of metals found in an industrial solution of titanyl sulphate, but additionally sodium sulphate or sulphate of other alkaline elements or ammonium.

Another method which can be used to achieve a high yield of the reaction is to conduct hydrolysis in two or more reactors in series. This would make it possible to conduct individual stages of hydrolysis separately in different reactors. A correct course of the first stage, i.e. the formation of stable active centres of TiO_2 strongly depends on the concentration of free sulfuric acid in the reaction mixture. Consequently, a fresh solution of titanyl sulphate should be dosed into a reaction mixture with a not very high degree of TiOSO_4 hydrolysis. The more concentrated an acidified solution of titanyl sulphate is to be hydrolysed, the lower the degree of TiOSO_4 hydrolysis should be. A higher degree of TiOSO_4 conversion will be achieved in further reactors, in which an intensive coagulation and precipitation of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ will be occurring.

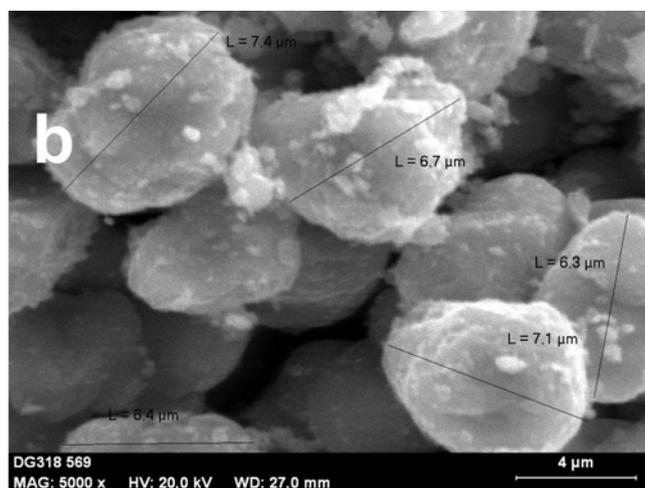
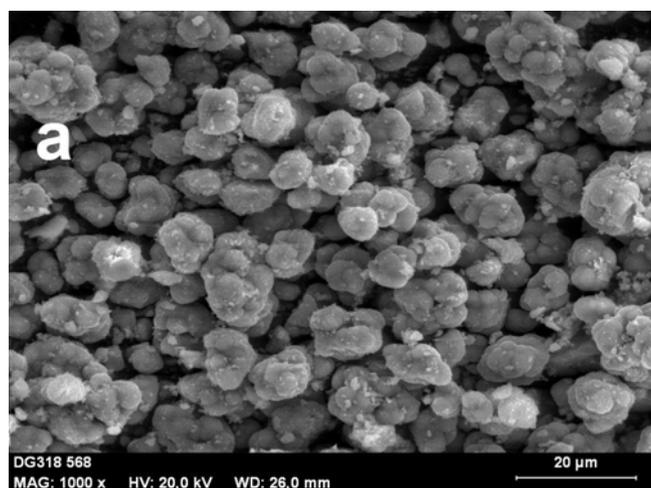


Figure 6. SEM images of titanium dioxide obtained in the hydrolysis of titanyl sulphate using the continuous method in two reactors: a) (magnification of $\times 1000$), b) (magnification of $\times 5000$) (the initial concentration of TiOSO_4 – 236 g/dm^3)

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