

**PURE TITANIUM DIOXIDE HYDRATE AND A PROCESS
FOR THE PRODUCTION THEREOF**

The invention relates to a process for the production of titanium dioxide hydrate with low sulfate content from a hydrolysate which was obtained by hydrolysis of titanyl sulfate as well as particularly pure titanium dioxide hydrate.

It is well known to produce a titanium dioxide hydrate hydrolysate, which still contains chemically bound sulfate ions after the removal of metal sulfate-containing diluted sulfuric acid, from titanyl sulfate solutions in metal sulfate-containing sulfuric acid, which solutions are obtained by digestion of titanium raw materials with concentrated sulfuric acid. This hydrolysate still contains 5 to 10% by weight SO_4^{2-} ions with respect to TiO_2 after intensive washing with water or diluted acid and an optional reducing (so-called bleaching) treatment (Ullmanns Encyclopaedia of Technical Chemistry, 4th Edition, Vol. 18 (1979), pages 574-576).

This sulfate ion content is a great disadvantage for most of the uses of the hydrolysate. In the production of TiO_2 or TiO_2 -containing mixed oxides by calcination of the hydrolysate, the sulfate ions are split off as sulfuric acid or SO_3 which are partially decomposed to SO_2 , O_2 and H_2O at high temperatures.

This requires large-scale gas purification measures. In the production of catalysts, their activity is frequently influenced in a negative manner by the sulfate ions. Therefore, many attempts to produce sulfate-free titanium dioxide hydrate have been made.

According to US-A 3 518 053, a sulfate-poor hydrate is created by treating a bleached hydrolysate with ammonia, ammonium hydroxide or carbonate and washing out the ammonium sulfate. The hydrate obtained in this manner still contains 0.5 to 2.0% sulfate. Even when so much of the ammonium compounds are added according to US-A 3 658 539 such that the pH value of the suspension is increased to 8.0, the S-content of the washed hydrate is still at 0.3% by weight corresponding to 0.9% by weight SO_4^{2-} .

DE-A 43 21 555 describes a process for the production of

mixed oxide powders for denitrating catalysts in which the sulfur ion-containing titanium dioxide hydrate suspension is partially neutralized with lye to a pH value between 4.0 and 6.0, filtered and the filter cake is washed intensively. The starting material is a preferably bleached titanium dioxide hydrate suspension with 20 to 40% by weight solids. In this manner, a hydrate can be produced with approximately 2.5% SO_4^{2-} and 20 ppm Na_2O content.

A further reduction of the sulfate content with simultaneously low Na_2O content is possible according to US-A 5,527,469. Accordingly, the sulfate-containing hydrate suspension is mixed with 0.1 to 2 parts by weight alkali metal hydroxide or carbonate and stirred at 60 to 120°C for 30 to 60 minutes.

After washing out the alkali metal compounds, the pH value of the hydrate suspension must be lowered with organic acids to below 6, preferably below 4.5, in order to remove chemically bound alkali metal ions from the hydrate. Residual organic acids are decomposed by calcining. The titanium dioxide hydrates created with this very extensive process contained between 110 and 480 ppm S corresponding to 330 and 1440 ppm SO_4^{2-} as well as up to 293 ppm Na^+ .

Consequently, according to the art, it has not been previously possible to produce titanium dioxide hydrate with very low sulfate and alkali and/or ammonium content despite numerous attempts.

An object of the present invention is to provide a simple process for the production of titanium dioxide hydrate with low sulfate content from a optionally bleached hydrolysate which was produced by hydrolysis of titanyl sulfate solutions that contain other metal sulfates and optionally free sulfuric acid.

Additionally, an object of the invention is to provide a pure titanium dioxide hydrate that contains less than 250 ppm SO_4^{2-} ions and less than 50 ppm ammonium or alkali metal ions with respect to TiO_2 .

The objects according to the invention could be

surprisingly achieved by neutralization of a 2 to 18% by weight titanium dioxide hydrate suspension.

Subject matter of the invention is process for the production of pure titanium dioxide hydrate with less than 100 ppm SO_4^{2-} ions and less than 25 ppm ammonium or alkali metal ions from titanium dioxide hydrate produced by titanyl sulfate hydrolysis, characterized in that an aqueous suspension is produced with the sulfate-containing titanium dioxide hydrate with 2 to 18% by weight, preferably 5 to 15% by weight, solid calculated as TiO_2 , the sulfate content of the suspension calculated as H_2SO_4 is determined, 95 to 101.1 mol-% of the stoichiometric amount of ammonia or alkali metal hydroxide required for neutralization of the calculated H_2SO_4 amount is added under stirring, the suspension is filtered after a stirring time of 5 to 60 minutes, preferably 10 to 30 minutes, and washed with water of low salt content, preferably deionized water, and a diffusion wash with deionized water at a pressure of 3 to 5 bar is then performed.

The sulfate-containing hydrate is conventionally obtained in that titanium crude materials such as ilmenite or titanium slag are decomposed with concentrated sulfuric acid. The metal sulfates obtained thereby are dissolved in water or dilute sulfuric acid. After the separation of undissolved solids and the adjustment of a suitable Ti^{3+} concentration, the titanyl sulfate is hydrolysed at 90 to 110°C in the presence of hydrolysis nuclei under formation of sulfate-containing titanium dioxide hydrate and sulfuric acid. After separation of the metal sulfate-containing sulfuric acid by filtration and washing of the filter cake, the filter cake can be freed from coloring heavy metal ions such as Fe^{3+} , Cr^{3+} , V^{3+} if required by a reducing treatment in dilute acid ("bleaching") or by dissolving in sulfuric acid and renewed hydrolysis in the presence of Ti^{3+} ions.

This titanium dioxide hydrate filter cake which contains 5 to 10% by weight SO_4^{2-} ions with respect to TiO_2 that is obtained according to the art by hydrolysis of titanyl sulfate represents the starting material for the production of the

pure titanium dioxide hydrate according to the invention and the products produced therefrom by drying or calcining.

According to the invention, an aqueous suspension with 2 to 18% by weight solids calculated as TiO_2 , preferably with 5 to 15% by weight solids, is produced from the obtained titanium dioxide hydrate filter cake. The SO_4^{2-} ion content, calculated as H_2SO_4 , of this suspension is determined and 95 to 100.1 mol-%, preferably 99.5 to 100.1 mol-%, most preferably 99.8 to 100.05 mol-% of the stoichiometric amount of ammonium or alkali metal hydroxide required for neutralization of the calculated H_2SO_4 amount are added under stirring at 20 to 100°C, preferably 30 to 80°C. After the suspension mixed with hydroxide has been stirred for 5 to 60 minutes, preferably 10 to 30 minutes, it is filtered and washed with hot water at 30 to 100°C, preferably 50 to 95°C. The wash occurs with low-salt, preferably deionized water. According to the invention, filtration and washing with vacuum filters or preferably pressure filters is carried out at pressures up to a maximum of 3 bar. If the conductivity of the filtrate is clearly lowered, preferably to approximately 300 mS/cm, then the removal of the residual sulfates is carried out on a pressure filter by diffusion washing with salt-free water at 30 to 100°C and a pressure of 3 to 5 bar. Preferably, this is washed until the conductivity of the wash filtrate is below 100 $\mu\text{S}/\text{cm}$. If a membrane filter press is used as the preferred filter aggregate, then the mother liquor is pressed out with a pressure of 3 to 5 bar before the beginning of the diffusion wash. Advantageously, a partial removal of water from the filter cake can occur with increased compacting pressure after the completed diffusion wash.

The filter cake obtained by applying the process according to the invention generally contains less than 1% by weight sulfate ions and less than 100 ppm ammonia and alkali metal ions, each with respect to TiO_2 . When using the preferred ammonium or alkali metal hydroxide amounts, one obtains the pure titanium dioxide hydrate according to the invention which contains less than 250 ppm SO_4^{2-} ions and less

than 50 ppm ammonium and alkali metal ions, especially less than 100 ppm SO_4^{2-} ions and less than 25 ppm ammonium or alkali metal ions, each with respect to TiO_2 . This titanium dioxide hydrate is distinguished by a particularly large reaction capability, a high absorption capacity for anions and cations and, depending on the degree of removal of water, a high catalytic activity.

Subject matter of the invention is also a method for the production of titanium dioxide and/or titanium dioxide hydrate of the composition $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ with $1 \geq n \geq 0$ which contains less than 250 ppm, preferably less than 100 ppm, sulfate ions and less than 50 ppm, preferably less than 25 ppm, ammonium and alkali metal ions, each with respect to TiO_2 that is obtainable by drying and/or calcining the titanium dioxide hydrate according to claim 5 at temperatures in a range of 50 to 750°C.

These products are not producible from convention sulfate-containing titanium dioxide hydrate because the thermal cleavage of the sulfate ions first occurs at higher temperatures.

The invention is illustrated by the examples without limiting the scope of the invention to them.

Examples

Technical, sulfate-containing titanium dioxide hydrate was produced by hydrolysis of a sulfuric acid, metal sulfate-containing titanyl sulfate solution. The washed filter cake was "bleached" by a reducing treatment. The washed filter cake of the "bleached" titanium dioxide hydrate was mashed with water. The suspension obtained in this manner contained 25.24% by weight titanium dioxide hydrate calculated as TiO_2 and 2.14% by weight sulfate ions calculated as H_2SO_4 .

The suspension served as the starting material for all examples.

Comparative Example 1

6240 kg of this suspension were mixed with 213 kg 50% by

weight NaOH under intensive stirring. The NaOH amount was sufficient for the neutralization of 97.7 mol % of the H_2SO_4 contained in the suspension such that a residual content of 1950 ppm H_2SO_4 is to be expected after washing out the Na_2SO_4 .
5 30 minutes after the NaOH addition, the suspension was pumped into a membrane filter press. After completed filtration, the mother liquor was pressed off with 4 bar membrane pressure and washed for 180 minutes with deionized water. The conductivity of the filtrate fell off thereby to 122 μS . The filter cake
10 was suspended in deionized water and a sample was analyzed. The sample contained 3184 ppm H_2SO_4 and 266 ppm Na_2O with respect to TiO_2 .

Comparative Example 2

This was carried out analogously to comparative example
15 1 except the mother liquor was not pressed off after completed filtration but was washed for 30 minutes with deionized water through the slurry channel. Pressing and washing for 75 minutes through the wash canals of the filter press was only carried out after this, whereby the conductivity of the
20 filtrate fell off to 97 μS . The filter cake suspended and homogenized after this contained 2730 ppm H_2SO_4 and 28 ppm Na_2O .

Example 1

4340 kg of the sulfate-containing suspension was mixed
25 with 6653 l deionized water of a temperature of 80°C. The suspension which contained 9.96% by weight titanium dioxide hydrate calculated as TiO_2 was mixed under intensive stirring with 213 kg 50% NaOH that is sufficient for neutralization of 97.7 mol-% of the contained H_2SO_4 . After 30 minutes, the
30 suspension was pumped into a membrane filter press and filtered during approximately 20 minutes, whereby the pressure increased to 2.5 bar. Subsequently, this was washed for 15 minutes with deionized water through the slurry canal at a water pressure of 2.5 bar. Thereby, the conductivity of the
35 wash filtrate fell to 290 mS/cm. After the filter cake had

been pressed off with 5 bar membrane pressure, this was washed with deionized water through the wash canals of the membrane filter press at a water pressure of 5 bar until the conductivity of the wash filtrate was 81 $\mu\text{S}/\text{cm}$. The filter cake was removed and suspended in deionized water. The homogenized titanium dioxide hydrate suspension contained 2030 ppm SO_4^{2-} and 5 ppm Na^+ each with respect to TiO_2 .

Example 2

4340 kg of the sulfate-containing suspension was mixed with 4550 l deionized water (TiO_2 content of the suspension: 12.3 % by weight). 335 l of an aqueous ammonia solution with 10% by weight NH_3 sufficient for neutralization of 99.5 mol-% of the contained H_2SO_4 was added to the intensively stirred suspension. After a 20 minute stirring time, the suspension was filtered analogously to example 1 and washed. The diffusion wash was completed as the conductivity of the wash filtrate was 72 $\mu\text{S}/\text{cm}$. The suspended and homogenized titanium dioxide hydrate filter cake contained 217 ppm SO_4^{2-} with respect to TiO_2 . Ammonium ions could not be detected.

Example 3

4340 kg of the sulfate-containing suspension were mixed with 6500 l deionized water and mixed under intensive stirring at 80°C with 705 l 10% by weight NaOH sufficient for neutralization of 99.95 mol-% of the contained H_2SO_4 . The filtration and filter cake wash were carried out analogously to example 1. The diffusion wash was completed when the wash filtrate conductivity was 64 $\mu\text{S}/\text{cm}$. The homogenized titanium dioxide hydrate suspension contained less than 50 ppm SO_4^{2-} and 16 ppm Na^+ each with respect to TiO_2 .

Example 4

The sulfate-containing suspension was mixed analogously to example 3 and mixed with 706 l 10 % by weight NaOH corresponding to 100.1 mol-% of the amount required for the neutralization of the contained H_2SO_4 . Filtration and cake

washing were carried out analogously to example 1 until the conductivity of the wash filtrate was 83 $\mu\text{S}/\text{cm}$. In the homogenized titanium dioxide hydrate suspension, no sulfate could be detected such that $< 50 \text{ ppm } \text{SO}_4^{2-}$ with respect to TiO_2 were present. The Na^+ content was 86 ppm with respect to TiO_2 .

What is claimed is:

1. Process for the production of pure titanium dioxide hydrate with less than 100 ppm SO_4^{2-} ions and less than 25 ppm ammonium or alkali metal ions from titanium dioxide hydrate produced by titanyl sulfate hydrolysis, characterized in that an aqueous suspension is produced with the sulfate-containing titanium dioxide hydrate with 2 to 18% by weight, preferably 5 to 15% by weight, solid calculated as TiO_2 , the sulfate content of the suspension calculated as H_2SO_4 is determined, 95 to 101.1 mol-% of the stoichiometric amount of ammonia or alkali metal hydroxide required for neutralization of the calculated H_2SO_4 amount is added under stirring, the suspension is filtered after a stirring time of 5 to 60 minutes, preferably 10 to 30 minutes, and washed with water of low salt content, preferably deionized water, and a diffusion wash with deionized water at a pressure of 3 to 5 bar is then performed.
2. Process according to claim 1, characterized in that 99.5 to 100.1 mol-%, preferably 99.8 to 100.05 mol-% of the stoichiometric amount of ammonium or alkali metal hydroxide required for the neutralization of the calculated H_2SO_4 amount is added to the suspension of the sulfate-containing titanium dioxide hydrate in water.
3. Process according to claim 1 and 2, characterized in that the filter cake is washed with water at a maximum pressure of 3 bar for so long until the conductivity of the filtrate is lowered to below 300 mS/cm.
4. Process according to one or more of the claims 1 to 3, characterized in that the diffusion wash is carried out at 3 to 5 bar for so long until the conductivity of the filtrate is lowered to below 100 $\mu\text{S/cm}$.
5. Titanium dioxide hydrate obtainable according to claim

1 that contains less than 250 ppm sulfate ions and less than 50 ppm ammonium or alkali metal ions each with respect to TiO_2 .

5 6. Titanium dioxide hydrate according to claim 5, characterized in that it contains less than 100 ppm sulfate ions and less than 25 ppm ammonium or alkali metal ions each with respect to TiO_2 .

10 7. Titanium dioxide and/or titanium dioxide hydrate of the composition $\text{TiO}_2 \times n\text{H}_2\text{O}$ with $1 \geq n \geq 0$ which contains less than 250 ppm, preferably less than 100 ppm, sulfate ions and less than 50 ppm, preferably less than 25 ppm, ammonium and alkali metal ions each with respect to TiO_2 obtainable by drying and/or calcining the titanium dioxide hydrate according to claim 5 at temperatures in
15 the range of 50 to 750°C.