

**PROCESS AND FURNACE FOR THE PRODUCTION OF  $\text{TiO}_2$   
PIGMENT ACCORDING TO THE SULFATE PROCESS**

The invention relates to a process for the production of  $\text{TiO}_2$  pigment from titanium dioxide hydrate with very low sulfur content and a furnace for calcining titanium dioxide hydrate.

According to the art (Ullmanns Encyclopaedia of Technical Chemistry, 4th Edition, Vol. 18 (1979), pages 574-576), the titanium dioxide hydrate accumulating in the hydrolysis of titanyl sulfate is separated by filtration from the mother liquor, an approximately 25% metal sulfate-containing sulfuric acid. The content of coloring metal ions such as Fe, V, Cr ions is lowered to a minimum by a reducing treatment in diluted acid. After this treatment, characterized as bleaching, the titanium dioxide hydrate still contains approximately 80 kg  $\text{SO}_4^{2-}$  ions per t  $\text{TiO}_2$  which cannot be removed by washing with water. After addition of so-called doping chemicals, different amounts of alkali hydroxide, phosphoric acid and optionally rutile nuclei for controlling the pigment quality, the titanium dioxide hydrate is calcined in a directly heated rotary kiln. Flue gas with a temperature of 1100 to 1400°C and solids are moving counter-currently through the rotary kiln. In the first section of the rotary kiln, the titanium dioxide hydrate is dried. After heating it to approximately 500°C, sulfuric acid, split off by further temperature increase, is partially decomposed in the hot flue gas to  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The formation of pigment particles into the modifications anatase or rutile finally occurs at 800 to 1100°C.

The rotary kilns are very large apparatuses with respect to through-put capacity, especially because in the first section, requiring approximately 50% of the furnace length, in which the drying of the titanium dioxide hydrate filter cake occurs, the introduction of heat into the product is very ineffective (Dumont, Belanger, Ind. Engn. Chem., Process Des. Dev. 17 (1978), 107-114). The filter cake falling out of the rotary kiln in the region at the feed end must be mashed and returned for filtration. The flue gas emerging from the

rotary kiln with approximately 400°C contains TiO<sub>2</sub> dust which is partially converted to pigment, besides SO<sub>2</sub> and sulfuric acid vapor which forms mist as the gas cools. This requires large-scale facilities for dust collecting and reclaiming TiO<sub>2</sub> dust as well as for removing the H<sub>2</sub>SO<sub>4</sub> mist and the SO<sub>2</sub> (EP-A 0 320 682). The utilization of the heat energy of the flue gas is technically complicated, especially as a result of the sulfuric acid vapor content (EP-A 476 172, EP-A 0 097 259).

The customary process for the production of titanium dioxide by calcining sulfate-containing titanium dioxide hydrate in rotary kilns is characterized by several disadvantages.

Consequently, the conventional process for production of TiO<sub>2</sub> pigments from titanium dioxide hydrate is characterized by two considerable disadvantages:

- As a result of the coupled execution of the filter cake drying and the solid calcination in one apparatus, the rotary kiln, it is not possible to carry out both of these processes each under optimal conditions.
- As a result of the high content of sulfate ions in the filter cake, an exhaust containing TiO<sub>2</sub> dust, sulfuric acid and SO<sub>2</sub> results whose heat content can only be used in a difficult manner and requires extensive procedures for recovery of the TiO<sub>2</sub> dust and for the removal of the sulfur compounds.

It is known that the performance of the calcining furnace can be increased and the specific energy consumption can be decreased by pre-drying the charged material before a calcination (DE-A 37 25 513, US-A 4 224 288, Kirk-Othmer, Encyclopaedia of Chem. Techn., 3rd Vol. 14 (1981), pages 360-364). However, the described technology cannot be applied to conventional TiO<sub>2</sub> calcination because the sulfuric acid vapor released in the calcining furnace would be condensed in the pre-drier. An internal sulfuric acid circulation with continually increasing amounts of acid would result thereby. A certain increase in the capacity of the facilities can be obtained according to EP-A 0 406 605 in that a portion of the

titanium dioxide hydrate filter cake to be calcined is pre-dried with separately produced  $\text{H}_2\text{SO}_4$ -free flue gas and the dried titanium dioxide hydrate is mixed with the residual filter cake before charging in the calcining rotary kiln.

5 Narrow limits are set thereby for the pre-drying by the required crumbly consistency of the mixture. The exhausts from the rotary kiln also require the above described extensive treatment.

An object of the present invention is to provide a process and a plant for the production of  $\text{TiO}_2$  pigments with high feed rate and low costs which avoid the disadvantages of the art.

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This problem is solved in accordance with the invention in that a titanium dioxide hydrate filter cake mixed with doping chemicals which contains less than 3 kg  $\text{SO}_4^{2-}$  ions per t  $\text{TiO}_2$  after a treatment with alkali hydroxide and washing out of the alkali metal sulfate is used as a starting material for the  $\text{TiO}_2$  pigment production by calcining titanium dioxide hydrate, this filter cake is dried in a suitable apparatus at

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20 100 to 300°C and subsequently calcined in a rotary kiln at temperatures up to a maximum of 1100°C, preferably 750 to 1100°C, and the exhausts are withdrawn directly into the atmosphere after separation of the  $\text{TiO}_2$ -containing dust.

The subject matter of the invention is a process for the production of  $\text{TiO}_2$  pigments by dissolving titanium raw materials with sulfuric acid, producing a metal sulfate-containing titanyl sulfate solution, hydrolysing the titanyl sulfate, separating the titanium dioxide hydrate from the metal sulfate-containing sulfuric acid by filtration, optional

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30 bleaching the titanium dioxide hydrate by reducing treatment in acidic solution, mixing the titanium dioxide hydrate with doping chemicals, and calcining the titanium dioxide hydrate to  $\text{TiO}_2$  pigment, characterized in that titanium dioxide hydrate is used as a starting material for the  $\text{TiO}_2$  calcining

35 which has less than 3 kg sulfate ions per t  $\text{TiO}_2$  after a treatment with alkali hydroxide and washing out the alkali metal sulfate, the filter cake containing the titanium dioxide

hydrate and doping chemicals is dried in a solid drier at 100 to 300°C and the dried solid is subsequently calcined in a calcining furnace at temperatures up to 1100°C (solid temperature) to TiO<sub>2</sub> pigments and the exhaust is de-dusted.

5 Preferably, the SO<sub>4</sub><sup>2-</sup> content of the titanium dioxide hydrate mixed with adjustment chemicals should obtain the highest value of  $(x + 0.2)$  kg/t TiO<sub>2</sub> with  $x = 2.087 m + 1.2 n$ , wherein m signifies the Na<sup>+</sup> content and n signifies the K<sup>+</sup> content in kg/t TiO<sub>2</sub> in the titanium dioxide hydrate mixed  
10 with doping chemicals. Particularly preferred is a sulfate content which is smaller than x kg/t TiO<sub>2</sub>.

According to the inventive process, the drying of the titanium dioxide hydrate filter cake mixed with doping chemicals preferably occurs with direct contact between  
15 combustion gases and filter cake, wherein the dust-containing exhausts of the calcining furnace and in particular additional flue gas created with a separate burner are used as combustion gases. A further preferred embodiment of the process according to the invention is to de-dust the SO<sub>2</sub>-poor,  
20 preferably SO<sub>2</sub>-free, flue gas emitted from the dryer with 100 to 300°C in a dry manner by filtration or electrostatic gas cleaning and to lead the dust together with the dried filter cake taken from the solid drier to the calcining furnace.

The dried titanium dioxide hydrate can be advantageously  
25 compacted before the introduction into the calcining furnace.

Preferably, a fluidized bed drier with or without a stirrer, a spray drier or a flash drier is used as a solid drier which is provided with a feed for dust-containing exhausts from the calcining furnace and a feed for flue gases  
30 which are created with a separate burner. Alternatively, the dust from the filter can be advantageously mixed with the titanium dioxide hydrate filter cake mix with doping chemicals before feeding into the drier.

Advantageously, the calcining exhausts and the flue gases  
35 can be introduced together into the drier.

The subject matter of the invention is also a calcining furnace for executing the calcination according to the process

of the invention. The calcining furnace is a rotary kiln whose ratio of length to diameter is in the range of 5 to 10. With conventional  $\text{TiO}_2$  furnaces, this ratio is approximately 20. In addition to the ring-shaped weirs on the ends of the rotary kiln, additional ones are preferably installed in a distributed manner over the length of the furnace; 1 to 5 additional weirs are particularly preferred. In order to guarantee the optimal adjustment of the operation parameters with respect to pigment quality, capacity and fuel demand, the rotary kiln according to the invention is preferably equipped with a device for altering the speed of rotation that is variable especially in the range of 0.2 to 1  $\text{min}^{-1}$ .

For the separation of dust from the calcining and drying exhaust, dust filters or electrostatic precipitators are preferred whose dust outlet is directly connected with the solid inlet organ of the rotary kiln.

The execution of the process according to the invention in a plant according to the invention is exemplified by means of Fig. 1. Sulfate-poor or sulfate-free titanium dioxide hydrate filter cake provided with adjustment chemicals (4) is introduced into a solid dryer (1). The dust-containing exhaust (5) from the calcining furnace (2) are introduced into this as heating gases. Additionally, flue gases (6) created in a separate burner are introduced. The amount and temperature of the flue gases (6) are adjusted such that a temperature between 100 and 300°C is in the drier (1) and the solid (10) taken out of the drier (1) is consistently and free-flowing.

The flue gases (7) containing dust which emerge with the temperature of 100 to 300°C, preferably 100 to 180°C are dedusted in an apparatus for dry dust separation (3) preferably a dust filter or an electrostatic precipitator, and are withdrawn into the atmosphere as exhaust (8). The dust (9) containing  $\text{TiO}_2$  separated in the dust separator (3) is introduced together with the solid (10) taken from the drier (1) into the calcining furnace (2) at the opposite end for the introduction of heating gas (11).

A rotary kiln (Fig. 2) which preferably has a ratio of length to diameter of about 6 is used as a calcining furnace (2) for example. Aside from ring-shaped weirs at the ends, this rotary kiln possess 4 additionally installed weirs which are distributed over the length of the furnace. The  $\text{TiO}_2$ -containing solid is heated by counter-current flowing flue gases (11) and discharged with a temperature in the range of 750 to 1100°C as  $\text{TiO}_2$  pigment (12) into a cooling aggregate.

A preferred embodiment relating an apparatus of the rotary kiln according to the invention is represented in figure 2. The rotary kiln (20) is characterized in that its length for a given throughput capacity is less than 50 % of those conventional rotary kilns for  $\text{TiO}_2$  calcining. In addition to the ring shaped weirs on the upper solid feed end of the pipe (21) and on the lower product discharge end (22) four weirs are installed in a distributed manner over the length of the furnace. Heating occurs by means of the burner (25) installed in the combustion chamber (24). The possible introduction of secondary air into the combustion chamber is not shown. The product discharge occurs below (26) at the burner side end. The dried solid containing titanium dioxide hydrate falls into the rotary kiln through the inlet pipe (27). Alternatively, the feeding of the solid can occur by means of a conveying screw or belt. The dust-containing calcining exhausts are led from the gas outlet housing (28) over the line (29) to the solid drier (1). Optionally, dust removed in the gas outlet housing (28) can be drawn off over the outlet (30) and led back to the solid feed (27).

The invention offers several advantages.

- Through the use of an extremely sulfate-poor or sulfate-free filter cake instead of the conventional titanium dioxide hydrate filter cake with approximately 80 kg  $\text{SO}_4^{2-}$   $\text{TiO}_2$ , the necessity for complicated equipment for removal of  $\text{H}_2\text{SO}_4$  mist and  $\text{SO}_2$  of the exhaust of the  $\text{TiO}_2$  calcining is omitted.
- By de-coupling the filter cake drying and  $\text{TiO}_2$  calcining steps, both processes can be carried out independently

from each other in optimized equipment.

- The  $\text{TiO}_2$  calcining can be carried out in a rotary kiln optimized for this process which guarantees a tighter residence time spectrum by additional weirs and, therewith, a more uniform product quality.
- As a result of the additional weirs, the speed of rotation of the rotary kiln can be relatively high without considerably shortening the product residence time. As a result, the product surface is more frequently renewed and the temperature difference between heating gas and product can be decreased. This also leads to a uniform product quality.
- Changes in the furnace speed of rotation and the heating gas rate are of considerably less influence on the product residence time than with conventional rotary cylindrical calcining furnaces with simultaneous filter cake drying in the furnace.
- The heat content of the gases escaping from the calcining furnace can be directly used to a temperature of  $100^\circ\text{C}$  in the filter cake drying, whereas the exhaust from conventional calcining furnaces must be at least  $350^\circ\text{C}$  so that the temperature does not fall below the dew point of  $\text{H}_2\text{SO}_4$  temperature and a sufficient temperature difference between the gas and filter cake must be maintained for the cake drying in the rotary kiln.
- Whereas filter cake drying and  $\text{TiO}_2$  calcining influence each other and prevent an optimal furnace control with the  $\text{TiO}_2$  calcining according to the art, the manner of operation of the calcining furnace with the process according to the invention can be optimally coordinated for the required pigment quality.
- As a result of the fact that the filter cake drying has a higher energy requirement than that corresponding to the useful heat content of the calcining exhaust, the constant optimal quality of the dried filter cake can be ensured by means of flue gas from an additional burner.

- The sulfuric acid-free exhaust from drying and calcining do not cause corrosion of the apparatuses such that the separated  $\text{TiO}_2$  containing dust can be introduced directly into the calcining furnace without additional cleaning procedures (bleaching).
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- The process according to the invention is not only substantially simpler with respect to the apparatus as conventional processes but also permits considerable energy cost savings by optimization of the process.



What is claimed is:

1. Process for the production of  $\text{TiO}_2$  pigments by dissolving titanium raw materials with sulfuric acid, producing a metal sulfate-containing titanyl sulfate solution, hydrolysing the titanyl sulfate, separation of the titanium dioxide hydrate from the metal sulfate-containing sulfuric acid by filtration, optional bleaching the titanium dioxide hydrate by reducing treatment in acidic solution, mixing the titanium dioxide hydrate with doping chemicals, and calcining the titanium dioxide hydrate to  $\text{TiO}_2$  pigment, characterized in that titanium dioxide hydrate is used as a starting material for the  $\text{TiO}_2$  calcining which has less than 3 kg sulfate ions per t  $\text{TiO}_2$  after a treatment with alkali hydroxide and washing out the alkali metal sulfate, the filter cake containing the titanium dioxide hydrate and doping chemicals is dried in a solid drier at 100 to 300°C and the dried solid is subsequently calcined in a calcining furnace at temperatures up to 1100°C (solid temperature) to  $\text{TiO}_2$  pigments and the exhaust is dedusted.
2. Process according to claim 1, characterized in that the maximal sulfate-content of the titanium dioxide hydrate filter cake mixed with doping chemicals obtains the highest value of  $(x + 0.2)$  kg/t  $\text{TiO}_2$  with  $x = 2.087 m + 1.2 n$ , wherein  $m$  signifies the  $\text{Na}^+$  content and  $n$  the  $\text{K}^+$  in kg/t  $\text{TiO}_2$ .
3. Process according to claim 1, characterized in that the maximal sulfate-content of the titanium dioxide hydrate filter cake mixed with adjustment chemicals is smaller than  $x$  kg/t  $\text{TiO}_2$ , wherein  $x$  has the same meaning as in claim 2.
4. Process according to claim 1, characterized in that the gas containing dust escaping from the calcining furnace

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is introduced into the solid dryer and that the hot, dust-containing gases escaping at 100 to 300°C from the solid dryer are de-dusted and withdrawn into the atmosphere.

- 5     5.     Process according to claim 1, characterized in that in addition to the dust-containing exhausts from the calcining furnace, flue gases are introduced into the solid dryer for the filter cake drying step.
- 10     6.     Process according to claim 1, characterized in that the  $\text{TiO}_2$ -containing dust separated in the exhaust de-dusting are fed into the calcining furnace together with the dried filter cake taken from the solid drier.
- 15     7.     Calcining furnace for the production of  $\text{TiO}_2$  pigments from dried sulfate-poor or sulfate-free titanium dioxide hydrate in the form of a rotary kiln with a length:diameter ratio in the range of 5 to 10.
- 20     8.     Calcining furnace according to claim 7, characterized in that the rotary kiln contains weirs installed in a distributed manner over the length of the furnace in addition to ring-shaped weirs at the ends of the kiln.
- 25     9.     Calcining furnace according to claim 7, characterized in that 1 to 5 additional ring-shaped weirs are installed in the rotary kiln.
10.     Calcining furnace according to claim 7, characterized in that the rotating cylindrical furnace is equipped with a device for changing the speed of rotation.

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