PROCESS FOR PRODUCING TITANIUM DIOXIDE SLURRIES FROM MICRONIZER TAILS

The present invention generally relates to slurries of titanium dioxide. More specifically, the present invention relates to concentrated slurries of titanium dioxide and methods for producing concentrated slurries of titanium dioxide.

Titanium dioxide ("TiO_2") has many known uses in industry. For example, TiO_2 is used as a pigment for many paints. It is also used in other applications such as paper making, plastics applications and coating compositions.

Methods for producing TiO_2 are also known in the art. TiO_2 is generally produced by hydrolyzing an aqueous solution of titanium sulfate and calcining the hydrolyzate at from 750 – 1000 °C, or oxidizing titanium tetrachloride ("$TiCl_4$") at elevated temperatures followed by cooling at temperatures below about 600 °C. The TiO_2 thus prepared is dry or wet ground and then dry milled. One method of dry milling is accomplished by utilizing a micronizer (also sometimes referred to as a fluid energy mill). Utilizing a micronizer typically involves introducing dry TiO_2 pigment and a fluid, typically steam, into the micronizer. The output of the micronizer typically contains from 20 percent of TiO_2 to 50 percent of TiO_2 , with substantially all of the remaining output composition comprising steam.

In most pigment manufacturing operations the TiO_2 in the output from the micronizer is separated from the steam, cooled and packaged as a dry particulate. This finished TiO_2 pigment can then later be formed into an aqueous slurry for the production of paints, coatings, and the like. In one process for preparing such aqueous slurries of TiO_2, the finished TiO_2 pigment is added to a water-dispersant package in a batch mixer having a high shear agitator. The slurry is then stirred until the degree of dispersion required is achieved in the slurry. Typically the dried TiO_2 pigment is shipped to a customer and the slurry preparation is performed by the customer. However, it is becoming more and more common for the producer of the TiO_2 pigment to produce and sell the pigment in a slurry form, and higher solids (that is, more concentrated) slurries containing from 60 to 80 percent solids and

higher, more particularly comprising at least 60 weight percent of titanium dioxide, preferably at least 65 and more preferably at least 76 weight percent of titanium dioxide, are in increasing favor.

To separate the TiO_2 in the micronizer output from the steam in the micronizer output, the output of the micronizer is typically introduced into a cyclonic gas-solids separator (or cyclone), wherein solid TiO_2 product falls to the bottom of the cyclone and is removed in the underflow while the steam typically exits from the top in the overflow. The solid TiO_2 product is then sent to a silo for packaging and shipping or to be used to produce a slurry as described above. The steam that exits from the cyclone is sometimes referred to as micronizer tailings. These micronizer tailings can be processed to produce TiO_2 slurries using known methods such as the one taught in U.S. Patent No. 4,427,451 issued to Baloga.

The present invention relates in a first aspect to an improved method of producing titanium dioxide slurries. According to the present invention in this first aspect, the output from a micronizer (that is, substantially steam and TiO2) is passed through a condenser to condense the steam and form an aqueous slurry of titanium dioxide, which can in most cases then be further concentrated as desired or which can be sold or used without further concentration, instead of passing the micronizer output to apparatus for separating the TiO2 from the steam, as is currently practiced in the art.

The resultant slurry from the condenser (hereinafter also referred to as the "condensate slurry") is in a further refinement preferably sent to an agitated storage tank together with dispersant and anti-settling compounds to aid in preventing settling of the titanium dioxide solids out of the slurry, with the amounts of dispersant and anti-settling compounds added being based on the weight of titanium dioxide fed to the micronizer. To help facilitate condensation of the steam/pigment mixture sent to the condenser, a portion of the condensed slurry is in yet a further refinement pumped from the slurry storage tank to a heat exchanger. The output from the heat exchanger is then fed to the condenser to facilitate the condensing of the steam in the condenser. A secondary benefit of this re-circulation of condensate is to keep the condenser from fouling due to deposits of titanium dioxide on the internal plates or tubes of the condenser and thereby lose cooling efficiency. The temperature and volume (flow) of cooled condensate to the condenser are set to match the amount of

steam and its temperature so as to ensure that substantially all of the steam and contained pigment are collected from the condenser.

To start the operation without a supply of condensate, sufficient deionized water is fed to the condenser until the level of condensate in the storage tank is adequate to allow for the re-circulation loop described above to be put into operation. At that point the use of deionized water is discontinued. While this results in some initial dilution of the condensate, the amount added is small and would not be expected to significantly impact the overall operation.

The present invention relates in a second aspect to a process of making a concentrated titanium dioxide slurry containing at least 60, preferably at least 65 and more preferably at least 76 weight percent of titanium dioxide in an aqueous medium, wherein a condensate slurry prepared as described above is further concentrated as to the titanium dioxide component of the condensate slurry. Various apparatus and methods are known which can be used for accomplishing the further concentration of the condensate slurry, for example, by membrane filtration as shown by United States Patents No. 4,952,317 and 5,014,564 to Culkin and by United States Patent No. 5,622,628 to Trendell et al. The present invention relates in its final aspect to the concentrated slurries produced by such methods.

The present invention is illustrated by way of example only in the accompanying drawing, in which like references indicate similar elements. Fig. 1 thus illustrates one preferred way to carry out the present invention, though other ways of practicing the invention are within the capabilities of those skilled in the art and so Fig. 1 is not intended to be limiting of the invention's scope as defined in the claims below.

Referring now to Figure 1, the apparatus 100 comprises a micronizer 102, a condenser 104, and a storage tank 106. Titanium dioxide 108 and steam 110 are introduced into the micronizer 102. Micronizers useful in the present invention and how they work are known in the art. Generally, steam is added to the TiO_2 to provide energy sufficient to maintain particle-to-particle separation and good grinding efficiency. The output of the micronizer is a mixture of TiO_2 and steam, having a TiO_2 content of from 25 percent to 50 percent by weight. The temperature of the micronizer output is sufficiently high to prevent the mixture from condensing, typically being at least 149 degrees Celsius (300°F) and preferably being at

least 204 degrees Celsius (400 °F). Typically, the temperature of the micronizer output mixture is no more than 315 degrees Celsius (600 °F) and preferably no more than 260 degrees Celsius (500 °F).

The micronizer output (that is, the TiO_2/steam mixture) is fed to condenser 104 by any appropriate means known in the art as indicated in Figure 1 by the arrow 112. Inside the condenser 104, the TiO_2/steam mixture is combined with an aqueous TiO_2 slurry, with the aqueous TiO_2 slurry being introduced into the condenser 104 by any appropriate means known in the art. Preferably, the TiO_2 slurry will be introduced (that is, recycled) into the condenser 104 from the storage tank 106 via a recycle line 114 as shown in Figure 1. The condenser 104 may have a vent 120 as is known in the art. Additionally, the condenser may utilized cooling water 122 as is known in the art to maintain a desired temperature in the condenser 104.

The percentage by weight of TiO_2 in the TiO_2/steam mixture and the percentage by weight of TiO_2 present in the added slurry are preferably approximately the same. The temperature of the slurry added to the condenser 104 is lower than the temperature of the micronizer output added to the condenser 104. The volume and temperature of the added slurry are sufficient to condense substantially all of the TiO_2/steam mixture. It will be appreciated that the volume and temperature of the added slurry that is needed to be sufficient to condense substantially all of the TiO_2/steam mixture will vary depending on the volume and temperature of TiO_2/steam mixture to be condensed. However a sufficient volume and temperature can be determined without undue experimentation.

The condensed TiO_2/steam mixture is combined with the added slurry in the condenser 104 to produce a resulting condensate slurry. The resulting slurry will generally have a TiO_2 content of at least 25 percent by weight and preferably at least 30 percent by weight. In one preferred embodiment of the present invention, the resulting slurry contains at least 40 percent by weight of TiO_2. The resulting slurry can then be transported to the storage tank 106 by any appropriate means known in the art as indicated in Figure 1 by the arrow 116.

In a preferred embodiment, some of the slurry stored in the storage tank 106 is recycled to the condenser 104 as described above. The slurry in the storage tank 106 that is

not recycled can be transported by any appropriate means known in the art as indicated in Figure 1 by arrow 118 to be used, for example, as a precursor slurry to a final slurry production process wherein the precursor slurry is made suitable for a customer's intended use. A slurry intended for use in the manufacture of latex paints would, for example, be made by further concentrating the precursor slurry through any known means to at least 60 weight percent of titanium dioxide, for example, by membrane filtration using apparatus and process as shown by United States Patents No. 4,952,317 and 5,014,564 to Culkin and by United States Patent No. 5,622,628 to Trendell et al. Other applications may seek still higher concentrations on the order of at least 65 percent to 76 percent and greater; those skilled in the art will however be well able to make final slurry products in a variety of concentrations and for a variety of applications, starting from the slurries enabled by the present invention.

The temperature and volume of the recycled slurry can be controlled by any means known in the art so that it meets the temperature and volume requirements described above. For example, the temperature of the slurry in the storage tank 106 may be higher than the desired temperature of the slurry to be recycled to the condenser 104. Accordingly, when the slurry to be recycled leaves the storage tank 106 it may be cooled via any appropriate method known in the art before it is added to the condenser 104. Additionally, the volume of slurry that is recycled from the storage tank 106 can be controlled by any means known in the art such that the recycled slurry will have a TiO_2 content that is approximately the same as the TiO_2 content of the micronizer output that is fed to the condenser 106.

The present invention is further illustrated in its various aspects in the examples which follow:

Example 1

A micronizer with an internal diameter of 10 cm (4 inches) and flat parallel plates mounted horizontally was assembled so that both steam and pigment fed to the micronizer exited from the top side of the unit. Piping connected to the top of the micronizer thereafter conducted the steam-pigment mixture to a condensing unit. To aid in condensing the steam-pigment mixture a small amount of water was added to a holding tank into which the steam-pigment mixture was collected. A pump connected to the holding tank circulated a portion of the water/steam-pigment mixture to a heat exchanger and from the exchanger into the top of

the condenser. Once the holding tank was approximately one-third to one-half full, dilute condensate was bled from the hot side of the heat exchanger to a separate product holding tank.

Using the above-described process, sufficient dilute condensate slurry at about 40% solids was generated to provide a suitable feed to a VSEP® concentration unit manufactured by NEW LOGIC RESEARCH INC., 1295 Sixty Seventh Street, Emeryville, CA 94608 and described more fully below. The titanium dioxide fed to the micronizer in this first example was in-process TRONOX™ CR-813 titanium dioxide, an interior architectural paint grade produced by Kerr-McGee Chemical LLC. The feed was obtained from routine commercial production after the surface treatment had been applied, followed by washing and drying, but prior to the final micronization step.

For generating the condensate slurry in this Example, 56.8 kg/hr (125 lbs/hour) of superheated steam along with approximately 40.9 kg/hr (90 lbs/hour) of titanium dioxide were metered into the micronizer system, for a weight/weight ratio of about 1.4:1 steam to pigment. Solids levels in the slurry discharging to the product holding tank were monitored at fixed time intervals until a solids level of about 40% by weight was obtained.

Prior to concentrating a sample of the 40% solids condensate slurry in the VSEP apparatus, a calculated amount on a weight/weight basis of a commercial blend of dispersants was added to a known quantity of condensate slurry. The slurry was pre-screened through a 200 mesh sieve to remove any oversize material prior to being fed to the VSEP unit. A VSEP Series L/P unit operated in Single Membrane mode with a 0.1μ pore size Teflon membrane was used. The slurry was re-circulated through the VSEP unit until the solids level ranged between 65 and 66%.

Comparative Example

The second example was carried out to serve as a control and to demonstrate the advantage of the present invention over existing art. Using an identically-sized micronizer to that used in Example 1, a quantity of dry micronized pigment was generated. The micronizer arrangement for this second example was such that it allowed for the micronized pigment to be separated from the superheated steam without any increase in the moisture content of the finished pigment, in keeping with the existing art methods. Separation of the pigment from

the steam was for this Comparative Example achieved through the use of a series of cyclones providing approximately 85-90% recovery of the pigment fed to the micronizer. Steam and pigment flow-rates along with steam temperature were identical to those used in Example 1. The pigment used was the same starting pigment also described in Example1.

Next, using a torque sensing-capable DISPERMAT™ Model M AE3C available from Byk-Gardner, U.S.A., finished slurry was made from the above micronized pigment. The technique involved adding 775 grams of the pigment sample being tested to 370 grams of water along with a quantity of the same propriety dispersant package as used in Example 1, so that after wetting/dispersion the resulting solids level was in the 65 to 66% solids range.

Standard latex paint formulations, designed for interior architectural applications, were made from both the respective high solids slurries of Example 1 and this Comparative Example. The paint formulations were standard latex paint formulations, designed for interior architectural applications. The formulations were formed by incorporating the pigment slurry samples in portions of a freshly prepared polyvinyl acetate latex emulsion. In each formulation, the amount of pigment incorporated into the emulsion was sufficient to provide a 60% pigment volume concentration (in the dry paint film).

The resulting paint formulations were applied to black glass plates and white cards. The Y reflectance values of the dried paint films were measured with a HunterLab Color Difference Meter as known to those skilled in the art. These readings, in combination with measured film weights, were used to calculate the scatter value, expressed as hiding power in square meters per kilogram (square feet per pound) of pigment.

Next, a fixed amount of a black tint base was added to each portion of the white latex paint formulation described above (from the slurries of Example 1 and this Comparative Example) to obtain a grey paint to allow tint strength calculations to be made. Drawdowns of these tinted formulations were then made alongside corresponding controls on standard LENETA™ charts. Using all of these drawdowns, both dryhide and tint strength calculations were carried out. The results are shown in Table 1 below.

Table 1

Optical Properties of Paint Formulations

Test Method	Paint made from Example 1's Slurry	Paint made from Comparative Example's Slurry
Dryhide, in sq.meters/kg of TiO_2 (Ft^2/lb)	44.9 (219)	43.7 (213)
Tint Strength	99.9	109.9

Pigment slurries made by means of the present invention are thus shown to be quite satisfactory in relation to slurries made by the more complex conventional methods known in the art.

What is claimed is:

1. A process for producing a titanium dioxide slurry, comprising the steps of:

feeding the output of a micronizer comprising a titanium dioxide and steam mixture to a condenser; and

adding a first titanium dioxide slurry to the condenser, wherein the volume and temperature of the added titanium dioxide slurry are sufficient to condense substantially all of the micronizer output, and wherein the added titanium dioxide slurry combines with the condensed micronizer output to produce a resulting titanium dioxide slurry.

2. The process of Claim 1, wherein the titanium dioxide content of the titanium dioxide and steam mixture is approximately the same as the titanium dioxide content of the first titanium dioxide slurry.

3. The process of Claim 1, wherein the titanium dioxide and steam mixture contains from 25 percent to 50 percent by weight of titanium dioxide.

4. The process of Claim 1, wherein the resulting titanium dioxide slurry has a titanium dioxide content of at least 20 percent by weight.

5. The process of Claim 1, wherein the resulting titanium dioxide slurry has a titanium dioxide content of at least 30 percent by weight.

6. The process of Claim 1, wherein the resulting titanium dioxide slurry has a titanium dioxide content of at least 40 percent by weight.

7. The process of Claim 1, wherein the temperature of the micronizer output is sufficient to prevent the titanium dioxide and steam mixture from condensing before the mixture is combined with the first titanium dioxide slurry.

8. The process of Claim 1, additionally comprising the step of further concentrating the resulting titanium dioxide slurry to at least 60 weight percent of titanium dioxide.

9. The process of Claim 8, wherein the resulting titanium dioxide slurry from the process of Claim 1 is further concentrated to at least 65 weight percent of titanium dioxide.

10. The process of Claim 9, wherein the resulting slurry is concentrated to at least 76 weight percent.

11. A process for producing a titanium dioxide slurry, comprising the steps of:

feeding the output of a micronizer comprising a titanium dioxide and steam mixture to a condenser;

adding a first titanium dioxide slurry to the condenser, wherein the volume and temperature of the added titanium dioxide slurry are sufficient to condense substantially all of the micronizer output, and wherein the added titanium dioxide slurry combines with the condensed micronizer output to produce a resulting titanium dioxide slurry;

transporting the resulting titanium dioxide slurry to a storage tank; and

recycling some of the resulting titanium dioxide slurry to the condenser to be used as the first titanium dioxide slurry in the adding step.