Application Note
Titanium Dioxide - Sulfate Process

Chemical Industry: TiO_2

Titanium dioxide (TiO_2) is a common additive for paints, inks, cosmetics and plastics. The product has a high refractive index which provides whiteness and opacity making it ideal for covering over surfaces. This paper reviews several processes for TiO_2 production and looks at the important role that pH measurement serves to control the end product quality.

The Sulfate & Chloride Processes

There are two processes used to leach titanium from ore: the chloride process and the sulfate process. The chloride process uses chlorine gas (Cl_2) and coke (C^+) at elevated temperature to create titanium tetrachloride ($TiCl_4$). Secondary oxidation removes the chlorine gas and creates titanium dioxide (TiO_2). pH measurement is not used in the initial phases of the chloride process; however, it is used later on in downstream surface treatment of TiO_2.

The sulfate process relies on sulfuric acid (H_2SO_4) to leach titanium from ilmenite ore ($FeTiO_3$). The resulting reaction produces titanyl sulfate ($TiOSO_4$). A secondary hydrolysis stage is used to break the titanyl sulfate into hydrated TiO_2 and H_2SO_4. Finally, heat is used to remove the water and create the end product - pure TiO_2. The reactions are shown below:

Digestion: $FeTiO_3 + 2H_2SO_4 \blacktriangleright TiOSO_4 + FeSO_4 + 2H_2O$
Hydrolysis: $TiOSO_4 + H_2O \blacktriangleright TiO_2(OH)_2 + H_2SO_4$
Calcination: $TiO_2(OH)_2 + \text{Heat} \blacktriangleright TiO_2 + H_2O$

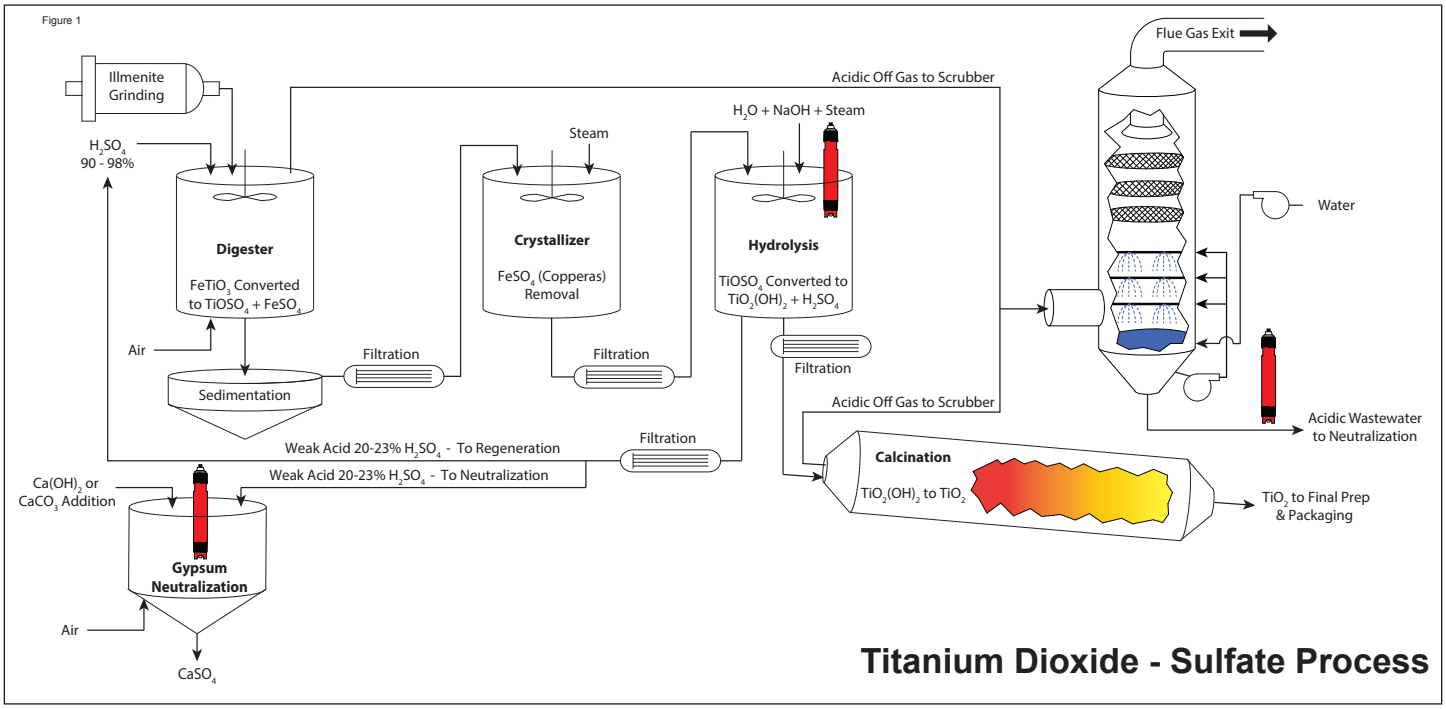
Each stage of the sulfate process uses some form of sedimentation or filtration to remove impurities. The crystallizer stage is important for bulk removal of iron sulfate ($FeSO_4$). $FeSO_4$ is also known as "copperas" or "green vitriol". If not sufficiently removed, $FeSO_4$ will cause an undesirable yellowish tinge to the final TiO_2 product. The $FeSO_4$ by-product is often sold into diverse industries such as water treatment chemicals, cement additives and even food-related additives.

pH at the Hydrolysis Stage

pH control is an important parameter in the next step of the sulfate process - the hydrolysis stage. The incoming mixture of sulfuric acid and titanyl sulfate is often referred to as "black liquor". The liquor is pre-heated to a temperature of ~ 110ºC (230ºF) to initiate the hydrolysis reaction. An alkaline mixture of water and caustic (NaOH) is used to adjust the liquor to 0.5 to 2.5 pH.

Temperature, pH, water addition, and reaction time are the main control parameters. All variables are closely monitored to produce titanium oxide hydrate ($TiO_2(OH)_2$). pH is a critical measurement used to control the particle growth as well as precipitation of impurities. The hydrolysis stage is one of the last steps to control product quality. Downstream filtration and possibly additional acid washing stages prepare the final titanium oxide hydrate for calcination to produce anhydrous titanium dioxide. Waste sulfuric acid is leached off for either purification or gypsum production.

Figure 1



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Gypsum Production - Sulfate Process
Titanogypsum ($CaSO_4$) production can be a unique by-product of the sulfate process. The process is analogous to flue gas desulfurization used for SO_2 reduction in coal-fired power plants. White titanogypsum is highly desirable for use in plasterboard and cement. Red titanogypsum may be created if high levels of iron sulfate and other impurities are present. The red gypsum has a much lesser value but is sometimes sold as soil additive.

Waste acid from the hydrolysis of titanyl sulfate is not strong enough for direct reuse in the process. The mixture includes 20 - 23% sulfuric acid as well as residue water and impurities such as iron sulfate ($FeSO_4$). The addition of either lime or limestone will react with the sulfuric acid to create calcium sulfite ($CaSO_3$). The reaction is shown below.

Lime: $CaO + H_2O + H_2SO_4 \blacktriangleright CaSO_3 + 2H_2O$
Limestone: $CaCO_3 + H_2O + H_2SO_4 \blacktriangleright CaSO_4 + 2H_2O + CO_2$

Additional oxidation using air bubbled through the liquid will create $CaSO_4$.

pH control in gypsum production helps control the final product quality. As noted above, the white titanogypsum is a more valuable end-product. By elevating the pH just above neutral (7.5 pH) iron sulfate will convert to elemental iron Fe^+. As the iron precipitates out of solution it can be removed and white titanogypsum is produced.

pH and TiO_2 Surface Treatment
Titanium dioxide is a photo active chemical. This means that it creates an electrical charge when exposed to light. This reaction is undesirable since it can degrade other products in contact with the TiO_2. The solution is to coat the TiO2 particulates with a protective layer. Common coatings include silica, zirconia and alumina. Often multiple coatings will be added in a multi-stage batch process to create the desired end product.

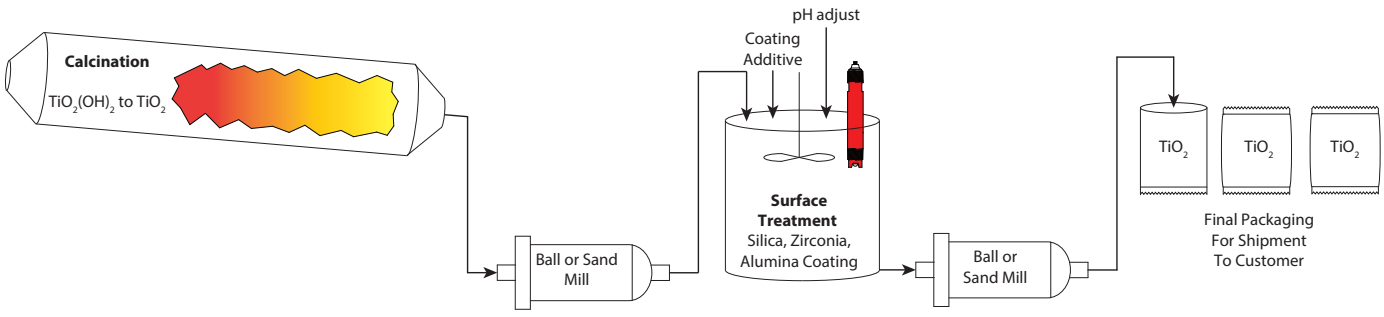
After calcination, uncoated TiO_2 goes through a milling step to eliminate agglomerated particulates. Consistent particle size ensures the proper light scattering effect of the TiO_2. After milling the particulates are combined in a mixing tank with water and the desired surface treatment. For silica coatings the mixture requires > 8.0 pH. Ammonia or caustic is used to elevate the pH to the desired level. A dilute sulfuric acid (H_2SO_4) is slowly added to start the silica deposition process. Silica in the form of sodium silicate (Na_2SiO_3) is slowly added to the mixture. pH, time, temperature, and proper agitation are used to control coating properties such as thickness, durability, and hide.

Alumina is often the final TiO_2 coating. Once the silica deposition process has been completed aluminum sulfate is added at approximately 3.5 pH. The pH level is slowly increased to 7-9 pH to precipitate the hydrated alumina which slowly begins to bond to the silica-coated TiO_2 particles. Once again, pH, time, temperature and proper agitation are all closely monitored to create the desired end product.

After surface treatment the TiO_2 goes through final milling to control the particulate sizing for the desired end-product. The powder will be packaged for shipment to the customer.

pH Measurement Challenges
While pH measurement is critical for TiO_2 production it is also quite difficult. Elevated temperature in the hydrolysis stage can shorten sensor life. Throughout the process fine particulates are well known to coat and plug the porous reference junction used in pH sensors. Once the reference junction is plugged by particulates, the pH sensor is slow to respond to changing pH levels. These applications are often maintenance intensive with frequent cleaning and sensor replacement.

Figure 2



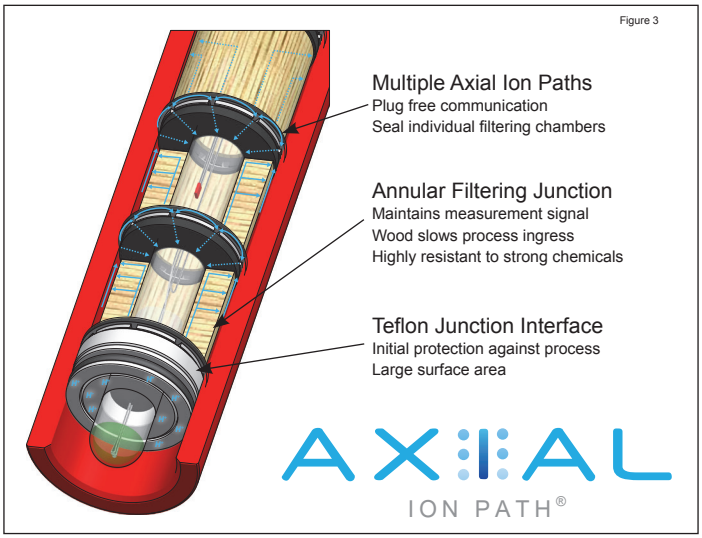
Titanium Dioxide - Surface Treatment

pH Measurement Solutions

Barben Analytical Performance Series pH sensors are uniquely designed to provide long life and less maintenance in titanium dioxide production applications. The patented Axial Ion Path™ reference uses an extremely large Teflon junction at the tip of the sensor (figure 3). The extra surface area of the Teflon junction makes it difficult to coat over thus providing long-term electrolyte contact with the process, less cleaning and less frequent calibration intervals. An added benefit of the large junction is that when cleaning of the sensor is eventually needed, the non-stick Teflon surface is much less labor intensive than tiny, recessed ceramic junctions that are often used in traditional pH sensors. A soft bristle brush is often sufficient to remove build-up.

The internals of the Axial Ion Path™ (AIP) reference also help increase sensor lifespan and reduce maintenance. Internal filtering chambers greatly slow the ion transfer of impurities from the process liquid, reducing contamination of the internal electrolyte. Each chamber is separated with Barben's patented annular AIP seals. The seals ensure electrolyte flow perpendicular to the length of the sensor thus blocking chemical ingress from the process.

Figure 3

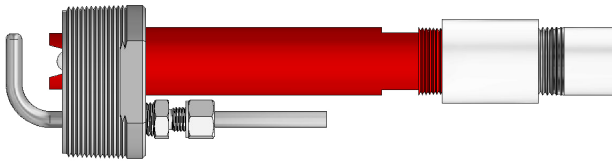


Performance Series pH sensors should be specified with “CR” coating resistant glass electrodes. The coat resistant layer on the glass provides additional protection against buildup in submersible applications. Kynar (PVDF) should be specified as the sensor body material due to its chemical compatibility.

If the pH measurement is taken directly in a tank or vessel then the Barben 546 threaded submersible pH sensor used with a jet spray cleaner accessory (figure 4) can aid in keeping coating from forming on the sensor tip. Either air or water can be used to blast away build-up.

546 Submersible pH Sensor with Jet Cleaner

Figure 4



The pH sensor with jet cleaner (shown sideways above) is a good way to prevent coating and buildup in submersible applications in tanks and clarifiers. The jet cleaner mounts vertically on a 2 inch NPT pipe. Pressurized air or water is connected to the tubing fitting on the jet cleaner. The cleaning can be either manually or automatically actuated from a timer. Consult Barben Analytical for more information.

If feasible in the installation, Barben Analytical highly recommends using a retractable pH sensor for TiO_2 pH measurement. A unique solution is to pair the Barben 551 quick change pH sensor with the Satron PASVE retraction valve. The 551 sensor is mounted in the ball of the PASVE valve. The valve uses a rotary motion to expose the sensor to the process. A similar motion in reverse closes the valve and isolates the sensor for in-line cleaning or removal for calibration or replacement (figure 5).

PASVE valves can be welded directly onto the pipeline or side of the vessel. If a recirculation pipeline is used then the PASVE valve can be installed directly in-line. The valve can be actuated manually, pneumatically or electrically. The Barben 551 pH sensor should be specified with 100mm sensor length, flush tip (FT), and coat-resistant flat glass electrode (CF). Consult Barben Analytical on product options for the PASVE retraction valve.

Satron PASVE Valve with Barben 551 pH Sensor

Figure 5



The weld pad version of the Satron PASVE Valve is shown above. The left image shows the valve with the sensor rotated into the process. The right image shows the valve when the sensor is rotated out of the process. 1/4" cleaning taps on either side of the valve allow for insitu cleaning when the sensor is retracted from the process. The PASVE valve design is well suited to the high particulate applications found in titanium dioxide production applications.

Barben pH sensors easily connect to most modern pH analyzers in use today, Wiring diagrams for commonly available instruments can be found on www.BarbenAnalytical.com or by request from technical support.

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Summary
Barben Performance Series pH sensors offer many benefits for titanium dioxide production including the following:

• Less frequent cleaning and calibration intervals
• High pH / ORP measurement accuracy
• Increased pH / ORP sensor lifespan
• Better end-product quality

Barben sensors can be used at all stages of production thus decreasing spares inventory.

Contact Us

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AMETEK has over 15,000 colleagues at more than 120 manufacturing locations around the world. Supporting those operations are more than 100 sales and service locations across the United States and in 30 other countries around the world.

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