

Report On TiO_2
From Sulphate & Chloride Process
And Importance Of
Surface Treatment In TiO_2 Pigments



Introduction

TiO₂ is produced from ilmenite, rutile or titanium slag. Titanium pigment is extracted by using either sulphuric acid (sulphate process) or chlorine (chloride route). The sulphate process employs simpler technology than the chloride route and can use lower grade, cheaper ores. However, it generally has higher production costs and with acid treatment is more expensive to build than a chloride plant. But the latter may require the construction of a chloralkali unit.

The chloride route produces a purer product with a tighter range of particle size, but anatase pigments can only be produced by the sulphate route. The sulphate route is perceived to be less environmentally friendly but acid recycling or neutralisation, combined with other by-product developments, can make it as clean as the chloride route.

1.0 Sulphate Route

In the sulphate route, there are three main stages. The ore, usually an ilmenite, is dissolved in sulphuric acid to form a mixture of sulphates. Any iron is removed from the solution so the colour of the final product is not spoiled. The titanyl sulphate is then hydrolysed in solution to give insoluble, hydrated titanium dioxide.

The final stage involves heating the solid in a calciner to evaporate the water and decompose the sulphuric acid in the solid. It also turns the solid into seed crystals which can be milled to the size needed. These crystals can be coated with another substance, such as aluminium oxide, to make the titanium dioxide mix more easily with liquids or extend the life the paint manufactured from them.

2.0 Chloride Route

There are two main stages to the chloride process. First, the dry ore is fed into a chlorinator together with coke and chlorine to make titanium chloride. Once the fluid bed has been preheated, the heat of reaction with the chlorine is sufficient to maintain the temperature and recycled liquid titanium chloride may be used to control the temperature.

The next step involves the oxidation of titanium chloride by burning it in oxygen together with another combustible gas (often carbon monoxide). By adding seed crystals, the titanium dioxide is formed as a fine solid in a gas stream and is filtered out of the waste gases. Crystal growth is controlled by adding nucleating agents to the gas stream and the products are cooled by mixing with chlorine gas. The product is then washed and dried before milling and surface treatment.

3.0 Surface Treatment :

3.1 For Plastic Application

General type titanium dioxide for plastic does not usually go through the surface treatment because titanium dioxide coated with inorganic substance such as regular hydrated alumina absorbs the equilibrium water of 1% at a humidity of 60% which at the time of extrusion processing of plastic under high temperature, the water will evaporate, resulting in pores on the surface of plastic. The titanium dioxide not coated with inorganic substance usually requires organic surface treatment (polyhydric alcohols, silane or siloxanes).

3.2 For Other Coating / Paint / Paper Applications

The surface treatment of the base pigment is very important and the surface finishing unit can account for up to one-third the cost of a titanium dioxide plant. The treatment is needed to maximise optical properties, improve durability and reduce yellowing, and improve dispersability.

Most commercial grades of titanium dioxide have inorganic and in some cases organic surface treatments. Inorganic surface modifiers most often are precipitated coatings of alumina and silica, which are meticulously controlled for type, amount, and method of deposition.

4.0 Inorganic Surface Treatments

Inorganic Surface Treatments provide improvements in one or more important performance properties such as dispersability in water and in a range of organic liquids, hiding power efficiency, chalk resistance, and resistance to discoloration by heat.

The most common surface treatments are silica, alumina, zirconia and hydrous titania. A number of other treatments have been used or patented for specialty applications. These treatments include tin oxide, zinc oxide, cerium oxide, phosphate and nitrate. These treatments are most commonly precipitated in layers.

Hydrous titanium dioxide is typically precipitated from aqueous titanium tetrachloride solution or from aqueous titanyl sulfate solution. Hydrous titania is believed to promote the adhesion of subsequent treatment to the base pigment. If present, this treatment is often the first layer applied to the surface.

Zirconia treatment is added to the surface of titanium dioxide pigment to promote durability. Most zirconia-treated pigments on the market are "universal" grades with very good gloss and moderate durability. The presence of both zirconia and tin oxide produces a pigment that can be used in automotive topcoats. The great advantage of zirconia is its ability to promote durability without significantly impacting the optical properties of the titanium dioxide pigment.

Silica treatment can produce a durable pigment or a high dry-hiding pigment. If silica is deposited at acidic or neutral pH, it is deposited as submicroscopic particles joined together in a gel-like structure. This "fluffy" coating provides better spacing and optical efficiency, increases oil absorption, and decreases gloss. These pigments are used in matte, dry-hiding formulations.

Silica treatments can also be deposited as a dense, glassy shell that encapsulates the particle and provides the highest durability available in titanium dioxide pigments.

Dense silica is deposited slowly at basic pH. The dense silica shell does not increase the oil absorption of the titanium dioxide.

Hydrous aluminium oxide treatment is probably the most common treatment on titanium dioxide pigments. It can be deposited from sodium aluminate, which is reacted with acid; or aluminium sulphate, which is reacted with a base. The hydrous alumina particles on the pigment surface reduce the particle-particle attractive forces and improve dispensability. The alumina also acts as a spacer for the particles and improves gloss and opacity of the pigment. When multiple treatment layers are deposited on a pigment, alumina is most often the final layer.

5.0 Organic Surface Treatments

Organic surface treatments can enhance the dispensability of the pigment in selected coatings systems. The organic materials used are most often polyols, amines or amine salts. Silicones and siloxanes are commonly used to produce hydrophobic pigments for plastics applications. Organic treatments are used to improve compatibility with the coating or plastic and to improve dispersion.

Organic coatings also reduce agglomeration during storage of the titanium dioxide. They reduce water absorption on the titanium dioxide surface, which leads to a lower volatile content for plastics processing.





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