

## **7.41 Titanium dioxide production**

### **7.41.1 Coverage**

Titanium dioxide can be produced from 2 chemical processes: the chloride process and the sulphate process. This chapter covers both processes. Titanium dioxide production is mainly a source of sulphur dioxide and dust emissions. Hence this chapter does not cover NO<sub>x</sub> emissions. [1].

### **7.41.2 Emission sources**

In the titanium dioxide (TiO<sub>2</sub>) production, pure TiO<sub>2</sub> powder is produced by dissolution of TiO<sub>2</sub> from its mineral feedstock forming TiOSO<sub>4</sub>. This is hydrolysed and precipitated to separate the titanium species from the main impurities then calcined to give the pure product.

In the sulphate process, sulphuric acid is used to digest TiO<sub>2</sub> containing feedstock, either ilmenite (low concentrated TiO<sub>2</sub> ore) or synthetic slags (higher TiO<sub>2</sub> content). Ilmenite is a natural product while slags come from metal processing industry. The digestion process can be batch or continuous. Batch process is the most used process. EU production is only based on this process.

Highly concentrated acid (80 - 95 %) is necessary to digest ilmenite or slag containing the TiO<sub>2</sub>. During the exothermic batch process temperature is raised from 180°C to 210°C. Flue gases from digestion process contain dust and SO<sub>2</sub> which need to be treated.

The solid cake resulting from the digestion is then dissolved into water to form titanyl sulphate (TiOSO<sub>4</sub>) liquor. This liquor is hydrolysed with steam leading to the precipitation of hydrated TiO<sub>2</sub>, which is then separated by filtration and washed to absorb any metal ions.

The separated hydrated titanium dioxide is calcined in a rotary kiln to convert back into titanium dioxide. Traces of residual sulphuric acid are emitted as SO<sub>2</sub> and scrubbed typically using catalytic systems. Pure titanium dioxide then goes through finishing processes during which the surface properties are modified by addition of surface coatings to suit the particular end use application e.g. paints, plastics inks. The finishing process is typically a wet batch process involving several stages including coating, milling and drying. It is micronised to 0.2 – 0.4 µm, the required size in order to achieve optimum pigment properties [1].

In the chloride process, titanium oxide is extracted from ore using a chlorination process. Ore and coke are fed to a fluidised-bed reactor in which an exothermic reaction with chlorine gas takes place at 1000 °C. During the chlorination, titanium tetrachloride (TiCl<sub>4</sub>) is formed. Flue gases from chlorination contain dust and SO<sub>2</sub> which need to be treated. SO<sub>2</sub> arises mainly due to the presence of sulphur in the coke.

TiCl<sub>4</sub> is condensed and distilled. It is then preheated and oxidised using preheated oxygen to form titanium dioxide between 900°C and 2000°C. The products are finally cooled and TiO<sub>2</sub> powder formed is transferred to the finishing processes, which are identical to the ones used in the sulphate process. [1].

### **7.41.3 BAT, Associated Emission Levels (AEL)**

**SO<sub>2</sub>:**

- **Sulphate process**

In the sulphate process, digestion by sulphuric acid is a main source of SO<sub>2</sub> emissions. Therefore flue gases from digesters need to be scrubbed. BAT to reduce SO<sub>2</sub> emission levels from digestion process is to use a water scrubber if the feedstock is ilmenite or a caustic scrubber if the feedstock is slag.

Calcining process is also a large source of SO<sub>2</sub> emissions since it takes place in a rotary kiln fed with gas or oil. Emission level depends on the sulphur content of the fuel used. Flue gases, which also contain last traces of sulphur from the products are captured and dedusted. BAT to reduce sulphur dioxide emission levels from calcination is to capture SO<sub>2</sub> and to transfer it to a sulphuric acid plant. The captured SO<sub>2</sub> is oxidised in SO<sub>3</sub> on catalysts (sulfadip process). SO<sub>3</sub> is then absorbed to form sulphuric acid. This sulphuric acid is recycled into the process.

The following table gives an overview of BAT associated SO<sub>2</sub> emission levels for titanium dioxide manufactured using the sulphate process. [1].

**Table 1: Associated SO<sub>2</sub> emission levels with BAT to reduce emission in titanium dioxide produced using the sulphate process. [1]**

Emission source	Techniques	Associated emission level with BAT (kg/t TiO <sub>2</sub> pigment)
Digestion process	Water or caustic scrubbing system	<b>SO<sub>2</sub>:1 – 6</b>
Calcining process	SO <sub>2</sub> recovery to form H <sub>2</sub> SO <sub>4</sub>	

- **Chloride process**

In the chloride process, chlorination is the main source of SO<sub>2</sub> emissions. Emission level is influenced by the sulphur content of cokes used. BAT to reduce SO<sub>2</sub> emission levels from chlorination process is first the use of low sulphur content coke as primary measure and then the use of an effective off-gas scrubbing system (NaOH can be used) as secondary measures.

The following table gives an overview of BAT associated SO<sub>2</sub> emission levels for titanium dioxide manufactured using the chloride process. [1].

**Table 2: Associated SO<sub>2</sub> emission levels with BAT to reduce emission in titanium dioxide produced using chloride process. [1] [6]**

Emission source	Techniques	Associated emission level with BAT (kg/t TiO <sub>2</sub> pigment) <sup>1</sup>
Chlorination	Low sulphur content cokes Off-gas scrubbing system	<b>SO<sub>2</sub>:1.3 – 1.7</b>

<sup>1</sup>SO<sub>2</sub> is dependent on the feedstock and low sulphur petroleum coke that was available when the brief was written is no longer available [8]

**Dust:**

In TiO<sub>2</sub> produced using the sulphate process, the main sources of dust emissions are the pre-treatment processes, calcination and the finishing processes.

In TiO<sub>2</sub> produced using the chloride process, the main sources of dust emissions are the feedstock handling and treatment processes and the finishing processes.

Pre-treatment and finishing processes are similar for sulphate and chloride processes, hence BAT are identical for the both processes. However, BAT emission levels are not the same. The dust emission levels are then presented in separated tables (3 and 4).

BAT to reduce emission levels from the pre-treatment processes is to use bag filters during the handling, drying and milling of ores.

Bat to reduce emission levels from the finishing processes is to use bag filters.

BAT to reduce emission levels from the calcining process is to apply an electrostatic precipitator to remove dust. It reduces dust emissions but also avoids interactions between dust particles and catalysts during SO<sub>2</sub> oxidation.

Dust removed from the different processes can be recycled into the process.

The following table gives an overview of BAT associated dust emission levels for Titanium dioxide production.

**Table 3: Associated dust emission levels with BAT to reduce emissions in titanium dioxide produced using the sulphate process. [1][5]**

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Pre-treatment processes	Bag filters	<b>dust: 5 – 20</b> (0.004 – 0.45 kg/t TiO <sub>2</sub> )
Calcining process	ESP or scrubbing system	
Finishing (milling, micronising)	Cyclones / Fabric filters	
	cloth filters	

**Table 4: Associated dust emission levels with BAT to reduce emissions in titanium dioxide produced using the chloride process. [1]**

Emission source	Techniques	Associated emission level with BAT (kg/t TiO <sub>2</sub> )
Pre-treatment processes finishing (milling, micronising)	Bag filters Reverse pulse bag filters	<b>dust:</b> 0.1 – 0.2

#### 7.41.4 Emerging techniques

There is no emerging technique available to reduce SO<sub>2</sub> or dust emission from titanium dioxide manufacturing. [1]

#### 7.41.5 Cost data for emission reduction techniques

The following tables give an overview of the costs for SO<sub>2</sub> abatement techniques in titanium dioxide production.

**Table 5: Gaseous emissions treatment costs of techniques for controlling SO<sub>2</sub> emission in digestion process (sulphate process). [1]**

Digestion	Slag	Ilmenite
SO <sub>2</sub> (kg/t)	1	0.2
<b>Scrubbing system</b>		
Capital +/- (30%) (EUR/t)	85	75
Treatment (EUR/t)	10	5

**Table 6: Gaseous emissions treatment costs of techniques for controlling SO<sub>2</sub> emission in calcination process (sulphate process). [1]**

Calcination	Catalyst standard	Catalyst High	Scrubbing
Catalyst load (m <sup>3</sup> /t per hour of TiO <sub>2</sub> feed)	30 – 50	70 – 90	
SO <sub>2</sub> (kg/t)	8	2	1
Dust (kg/t)	0.4	0.004	0.001
Capital <sup>2</sup> +/- (30%) (EUR/t)	70	140	170
Treatment (EUR/t)	5	10	9

<sup>1</sup>Definition of catalyst load: Volume of catalyst (m<sup>3</sup>) / TiO<sub>2</sub> feed (t/h)

<sup>2</sup>Definition of costs Capital for a new unit (EUR) / Annual production (t)

#### **7.41.6 References used in chapter 7.41**

- [1] Reference document on Best Available Techniques for the manufacture of large volume inorganic chemicals – Solids and others industry. August 2007.
- [2] IER, institut für Energiewirtschaft und Rationnelle Energieanwendung, Universität Stuttgart, 2004.
- [3] Directive 92/112/EEC, ECOJ, 31/12/1992.
- [4] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc", EGTEI, 02/2009.
- [5] Comments from Bente Sleire, SFT, 03/2009.
- [6] Comments from Birgit Brahner, UBA Germany, 03/2009.
- [7] EGTEI-State of progress.doc", for WGSR, March 2009.
- [8] Comments from Greg McNulty, Huntsman Pigments, February 2009.