1 INTRODUCTION

The presence of heavy minerals in South Africa has been known for several decades. During the 1950's ilmenite was mined at Umgababa as feedstock for a sulphate pigment plant located at Durban in KwaZulu-Natal (Lee and Poggi, 1978). In the late 1970's Richards Bay Minerals was founded on the east coast of South Africa. Heavy minerals are extracted from the dunes there and upgraded to produce rutile, zircon and ilmenite as the major products. The ilmenite is smelted in several electric arc furnaces to produce high titania slag and a metallic iron product. In 1997 Richards Bay Minerals had an annual production capacity of 1 million tons of titania slag (Anonymous, 1997). On the west coast of South Africa Namakwa Sands was founded in the early 1990's to extract heavy minerals from deposits situated near Vredendal. Again rutile, zircon and ilmenite are the main products. The products are transported to Saldanha where the ilmenite is smelted in DC arc electric furnaces to produce high titania slag and a metallic iron product. An increase in smelting capacity from 97 000 to 230 000 tons per annum was announced in 1998 (Anonymous, 1998). Iscor has also completed a feasibility study on the recovery of heavy minerals near Richards Bay, with approval of the project been given in the first half of 2000. This project also includes the smelting of ilmenite at a complex that will be erected at Empangeni. The capacity of this project will be 250 000 tons of high titania slag per annum.

The expansion of the titanium industry in South Africa over the last three decades shows the increasing importance of the industry to the local economy. South Africa has over this period evolved into one of the major titanium feedstock producers in the world. It is therefore important that the technical body of knowledge on the relevant metallurgical processes be expanded. This should enable the industry to optimise the processes and thereby obtain the maximum benefit for all.

This study will concentrate on aspects relevant to the smelting of ilmenite. In particular the focus will be on the following two aspects:
1. Characterisation of cooled high titania slags produced during the smelting of ilmenite. This will include the following:
    *   The mineralogy of the slags.
    *   The chemistry of the slags.
    *   Relationships between the chemistry of the slags and the tapping temperatures of the slags.
2. The decrepitation behaviour of high titania slags after tapping.

A brief review of the titanium industry relevant to this study is given as background.

1.1 FEEDSTOCKS TO THE TITANIUM DIOXIDE PIGMENT INDUSTRY

The titanium dioxide pigment industry consumes over 90 per cent of the titanium mineral production worldwide (Stanaway, 1994; Fisher, 1997). The remaining uses for titanium minerals are as a flux for electric welding rods and for certain metallurgical and electronic applications. The most common titanium minerals that are mined are rutile and ilmenite. Rutile can be used directly in the pigment production processes to produce titanium dioxide pigment. Ilmenite is preferably treated to selectively remove the iron content in order to provide a product with a lower iron content. The removal of the iron content results in a

product with a high titanium content, resulting in less waste being produced in the processes producing the titanium dioxide pigments. The two main processes used for the upgrading of ilmenite are briefly discussed below.

1.1.1 SMELTING OF ILMENITE TO PRODUCE TITANIA SLAG

Ilmenite can be smelted at high temperatures (approximately 1650 to 1700 °C) with a suitable carbonaceous reductant in electric furnaces to produce high titania slag as the major product. In the process liquid iron is produced as a by-product. The iron product can subsequently be modified by secondary treatment (de-sulphurisation, carburisation, alloy additions) to optimise the value of the product (Lee and Poggi, 1978). The TiO_2 content (total Ti expressed as TiO_2) of the slag after reduction can range between 75 and 86 per cent. Not all the iron can be reduced, as some FeO in the slag is required to act as a fluxing agent. The final quality of the titania slag is dependent on both the quality of the ilmenite and the reductant. According to Grau and Poggi (1978) the reduction process can broadly be described by the following reactions:

$$Fe_2O_3 + C = 2FeO + CO \ ...(A)$$

$$FeO + C = Fe + CO \ ...(B)$$

$$2TiO_2 + C = Ti_2O_3 + CO \ ...(C)$$
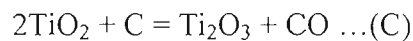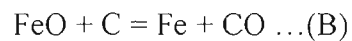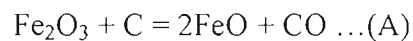
In the smelting process contact between the molten slag and the furnace refractories is prevented by the presence of a solid freeze lining. This freeze lining is required to prevent attack on the refractories by the corrosive molten slag (Grau and Poggi, 1978). Due to the high electrical conductivity of the slags (Desrosiers et. al., 1980) the electrodes are above the slag level in an "open arc" position. The high titania slag is tapped into ladles, water-cooled and crushed to produce the final products. Titania slag is used for both the sulphate and chloride process routes for the production of pigments. The criteria used for determining to which process route the slag should be allocated is determined mainly by the chemical quality and size distribution of the slag products. This will be discussed in more detail later.

Several producers worldwide use various smelting technologies to produce high titania slags. The producers are Richards Bay Minerals (RBM) and Namakwa Sands in South Africa, QIT in Canada and Tinfos in Norway. RBM and QIT use 6-in-line alternating current furnaces, while Namakwa Sands use two circular furnaces with direct current configurations.

1.1.2 SYNTHETIC RUTILE

The second type of process involves the partial or complete solid-state reduction of iron, followed by a leaching process to remove the iron content. An example of this type of process is the Becher process (Battle et. al., 1993). At present the leached iron is considered to be a waste product, although recent progress has been made in recovering this iron as a valuable product (McLoughlin et. al., 1998). A synthetic rutile product is produced containing approximately 90 to 96 per cent TiO_2. Current synthetic rutile production is

dominated by the Becher process (Grey, 1992). Other commercial processes for synthetic rutile production include the following (Battle et. al., 1993; Grey, 1992):

- The Benelite process involves a partial reduction of the iron in altered ilmenite to the ferrous state, followed by acid leaching of the iron and other impurities using hydrochloric acid.
- The Ishihara process utilises waste sulphuric acid from a sulphate-route pigment plant in Japan to leach ilmenite after partial reduction of the iron.

In Figure 1 the flowsheet of the improved Becher process are shown. This process is essentially a pyrometallurgical operation followed by a number of wet chemical process steps. It consists of the following three main process steps as described by Formanek et. al. (1997):

- Ilmenite, coal, char and sulphur are reacted in a rotary kiln at approximately 1200 °C in such a way that the iron oxide content of the ilmenite is reduced to metallic iron. This is different to the other synthetic rutile processes where the iron content of the ilmenite is only partially reduced. The sulphur is added to assist with the removal of manganese. Manganese sulfide is produced and then separated from the final product by a subsequent leaching step (Battle et. al., 1993). The reduced ilmenite is separated from the gangue materials by screening and magnetic separation. Coarse char recovered from the process is recycled to the kiln.

Figure 1: Flowsheet of the improved Becher process (from Formanek et. al., 1997)
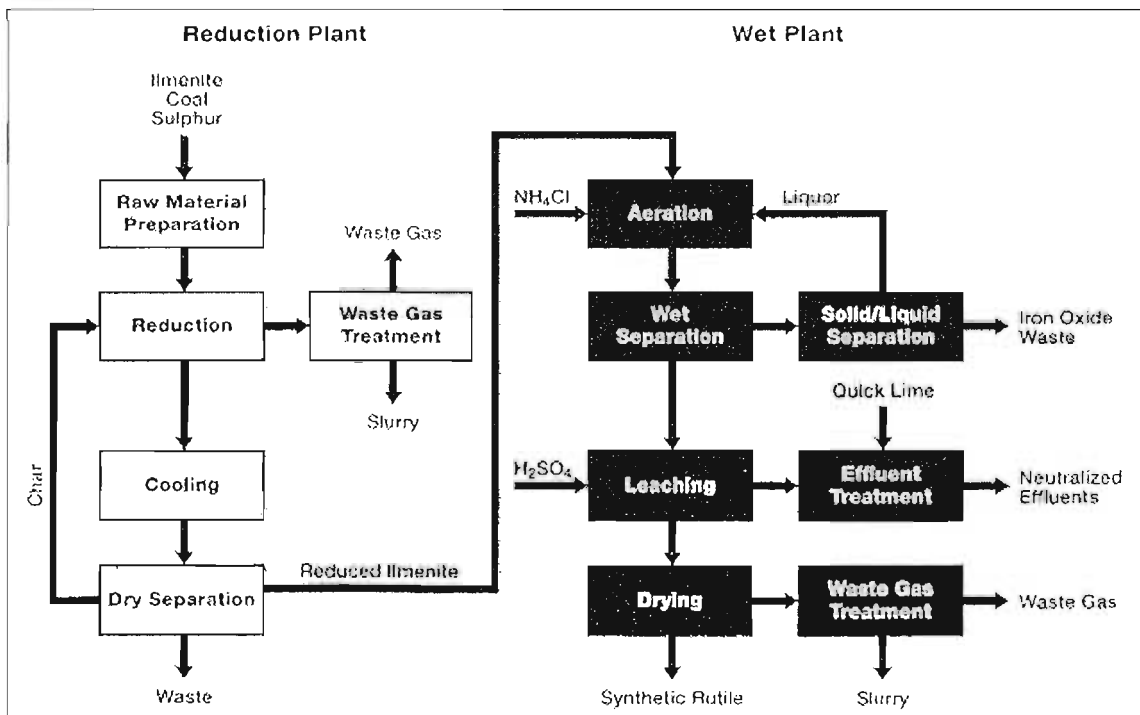
- The reduced ilmenite is aerated and stirred inside tanks in a 1.0 to 1.5 per cent ammonium chloride solution so that the iron is "rusted" from the ilmenite. The aeration process is carried out in batches. The mixture of synthetic rutile and iron oxide from the aeration step is separated in a multi-stage hydrocycloning system. At this stage the aerated product contains approximately 90 per cent TiO_2.

- The aerated product is separated from the iron oxide and leached with 10 per cent sulphuric acid to obtain a high quality synthetic rutile product. The leached product is separated from the acidic liquor in a spiral classifier. The remaining acid is removed from the synthetic rutile by counter-current washing on a belt filter. The synthetic rutile can then be dried in a flash or fluidised bed dryer. The final product contains 93.2 per cent TiO_2, with the main impurity being iron (2.4 per cent total iron). The product is porous, with a grain size similar to the original ilmenite.

The synthetic rutile product is generally sold to the chloride processing route for the production of pigments.

1.2 THE TITANIUM DIOXIDE PIGMENT INDUSTRY

Two processes are used to produce titanium dioxide pigments, these being the sulphate and chloride process routes respectively. All the high titania slag produced in the world via smelting processes is used as feedstock in one of these two processes.

1.2.1 PIGMENT MANUFACTURING PROCESSES

1.2.1.1 Sulphate processing route

The sulphate process for the production of titanium dioxide pigments was first used in Norway in 1915 (Fisher, 1997). This process is a batch process, using a number of unit operations. A flowsheet of a typical sulphate process is shown in Figure 2.

The main process steps are as follows (Fisher, 1997; Stanaway, 1994):
a) The titaniferous feed is reacted with sulphuric acid to produce titanyl sulphate. For ilmenite as feed the reaction can be written as follows:

$$FeTiO_3 + 2H_2SO_4 = TiOSO_4 + FeSO_4 + 2H_2O \ ...(D)$$
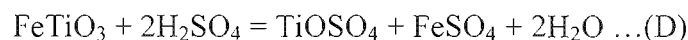
The highly exothermic reaction also emits hydrogen sulphide and sulphur dioxide as pollutants from various side reactions. Iron sulphate is removed from the solution as solid copperas ($FeSO_4.7H_2O$).
b) After the iron removal, titanyl sulphate is hydrolysed to titanium dioxide hydrate.
c) The precipitate is then chemically purified, filtered and calcined at 800 to 1100 °C to produce titanium dioxide (Habashi, 1997).

Subsequent process steps are required after this for the TiO_2 product to function as a pigment. These process steps are shown in Figure 3. These processes include milling of the particles to the required size specification and the addition of chemicals to the surface of the pigment particles to obtain the required optical and physical properties. These post-treatment processes can be similar for pigments produced by both the sulphate and chloride processes.

There is one operation in South Africa that uses this technology, this being the Huntsman Tioxide plant situated at Umbogintwini in the KwaZulu-Natal province. This plant supplies

titanium dioxide to the South African market and also exports approximately 30 per cent of its production (Tioxide Southern Africa, 1997).

Figure 2 : Flowsheet for a typical sulphate processing route (from Fisher, 1997)
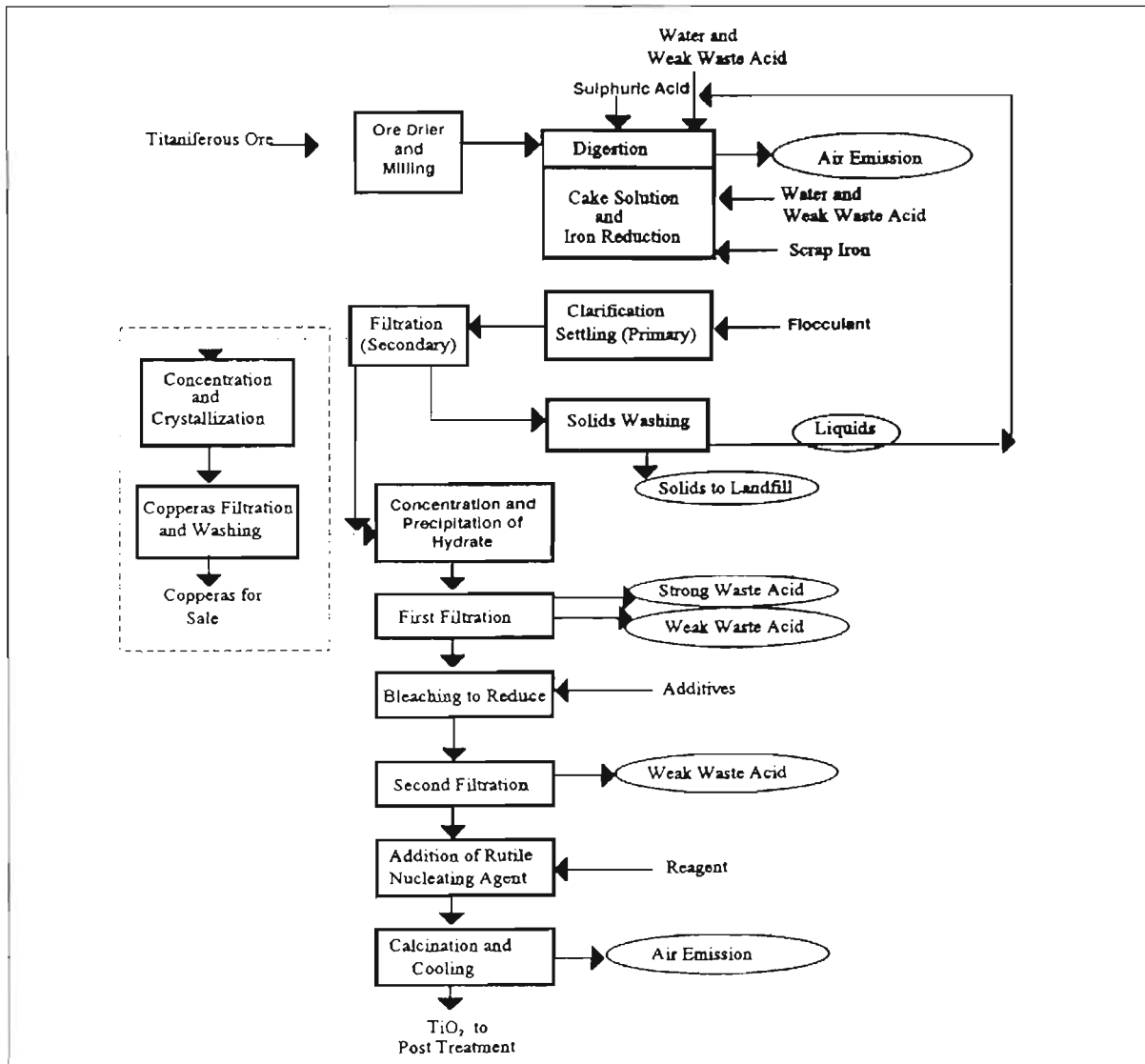

1.2.1.2 Chloride processing route

The chloride process was commercialised in the United States in 1958 (Fisher, 1997). The process is continuous and is carried out in a fluidised bed reactor. A flowsheet of a typical chloride process is shown in Figure 4. The main process steps are as follows (Fisher, 1997; Stanaway, 1994):

a) Chlorination of titanium feedstock using chlorine gas and coke to form various chloride species. The chlorination reaction is exothermic and is carried out at approximately 900 °C in a reducing atmosphere. The basic reactions can be written as follows:

$$2C + O_2 = CO \ ...(E)$$

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$$TiO_2 + 2Cl_2 + 2CO = TiCl_4 + 2CO_2 \ ...(F)$$
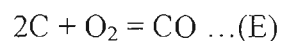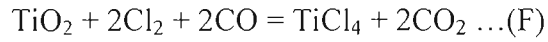
b) The volatile chloride species are separated by fractional distillation into low, medium and high boiling chlorides.

Figure 3 : A typical post-treatment process for titanium dioxide pigments (from Fisher, 1997)
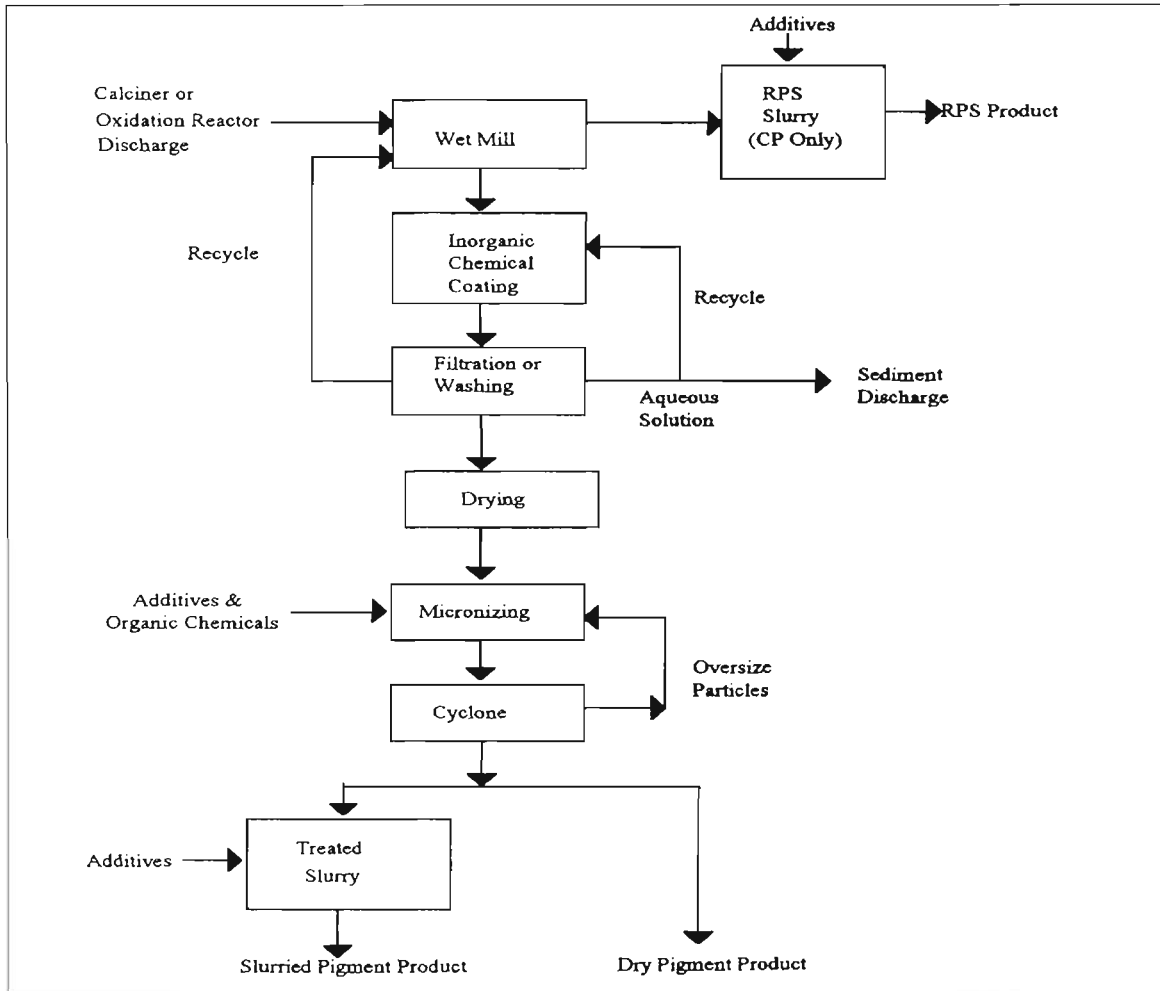

c) Titanium tetrachloride is then reacted with oxygen according to the following reaction:

$$TiCl_4 + O_2 = TiO_2 + 2Cl_2 \ ...(G)$$

The chlorine is recycled to the chlorinator, while the titanium dioxide can be processed further if required according to the flowsheet presented in Figure 3.

Because of commercial and environmental reasons the chloride processing route is preferred over the sulphate processing route. Approximately 57 per cent of all titanium dioxide pigments are produced by the chloride processing route. It is estimated that this will increase to approximately 69 per cent by the year 2010 (Fisher, 1997).

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Figure 4 : Flowsheet for a typical chloride processing route (from Fisher, 1997)
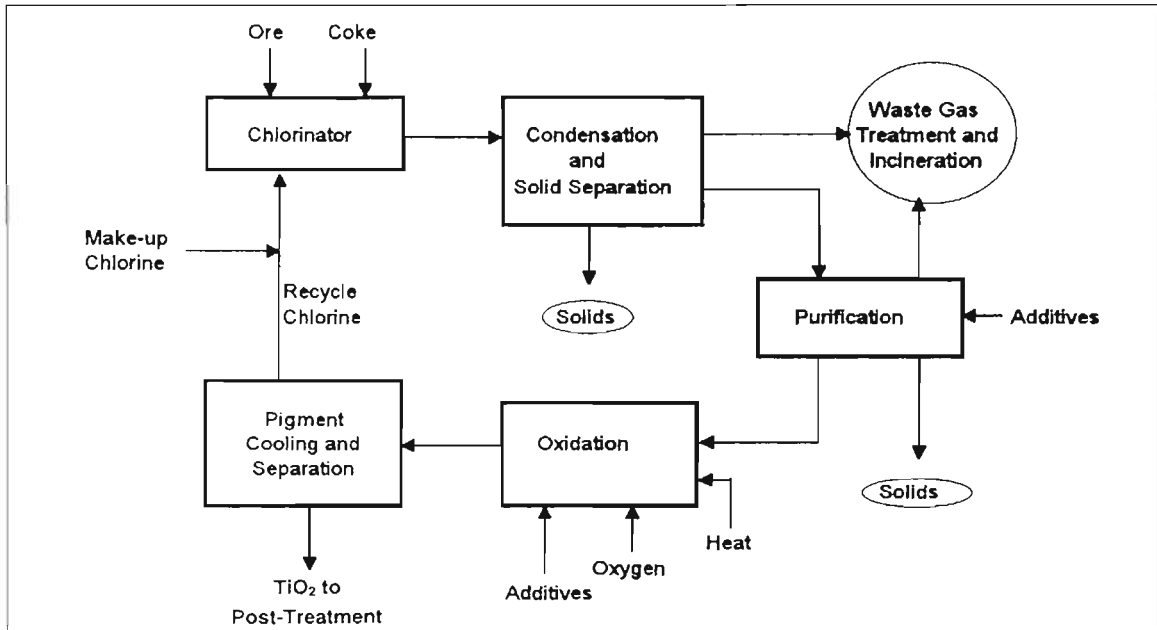
1.2.2 PIGMENT MARKETS

Titanium dioxide pigments are used across a wide range of applications. The major uses for titanium dioxide pigments are listed in Table 1 (Fisher, 1997). By far the largest use is as surface coating. In western countries titanium dioxide is now the most widely used white pigment in paints, having replaced zinc oxide, lithopone and white lead. Plastics represent the fastest growing market segment of the titanium dioxide pigment, with growth rates ranging between 5 and 18 per cent over the last two decades. Examples of some of the other uses of the titanium dioxide pigments include applications in ceramics, concrete, cosmetics, food, titanates and photovoltaic cells.

Table 1 : Global TiO₂ pigment consumption by industry (Fisher, 1997)

Use	Percentage of total world consumption
Surface coatings	59.8
Plastics	15.2
Paper	12.1
Printing inks	2.5
Fibres	2.7
Other	7.7