

The plasma manufacturing of titania pigment and nano-titania in a pilot plant

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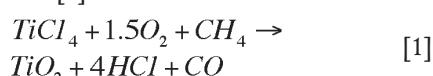
Synopsis

The establishment of a pilot plant for the continuous production of titania pigment and nano-titania is discussed. The plant was designed, constructed and operated on the Necsa site. The TiO_2 production capacity is $7-10 \text{ kg.h}^{-1}$ by the reaction of $TiCl_4$ and O_2 at $>1000^\circ\text{C}$. Liquid $TiCl_4$ is sprayed under pressure into a plasma reactor where it evaporates and reacts with O_2 to form TiO_2 . Process optimization has allowed for continuous production without any clogging or blockages. The primary advantage of the plasma-assisted process is the possibility to recover and recycle the chlorine values in high yield as Cl_2 for use in the manufacture of $TiCl_4$. The HCl formed in most conventional fossil-fuelled processes makes Cl_2 recovery and recycling much more difficult. Particle size distribution analysis of the fine, white product revealed a $d_{50} = 125 \text{ nm}$. The raw product consisted of 60% rutile that could be increased to 80–100% rutile by post-annealing. The specific surface area (SSA) of the pigment was $8-20 \text{ m}^2\cdot\text{g}^{-1}$ (BET). According to the CIE colour index the 'whiteness' ($L^* > 95$) of the plasma-produced pigment was better than that of several commercially available pigments. The particle size could be manipulated by controlling the $TiCl_4$ feed rate, gas flow rates, and the particle quench rate and residence time. Nano-sized TiO_2 powders with a particles size (d_{50}) as small as 50 nm were also successfully produced in this way.

Sands produce about 250 000 tonnes per annum, containing about 85% TiO_2 . Unfortunately, these products are mainly exported from South Africa without further beneficiation or local value-addition. Consequently, the South African government has launched several initiatives over the past few years to establish a bigger local beneficiation industry. These include the Advanced Metals Initiative (AMI) of the Department of Science and Technology (DST) for the manufacture of titanium and zirconium metal, the Titanium Beneficiation Initiative (TBI) of the Department of Trade and Industry (the dti) and several related projects sponsored by the Innovation Fund of South Africa.

Nano-sized and pigment-grade titanium dioxide (TiO_2) are widely used in sunscreens, paints and fillers. The titanium values in titania ores and slags are generally accessed by means of carbo-chlorination, yielding $TiCl_4$. The $TiCl_4$ is purified by distillation and subsequently oxidized to yield a TiO_2 which is suitable as a primary pigment grade. Subsequent surface treatment of these particles, usually with a zirconium compound, resulted in a final pigment.

The conventional oxidation process for the production of pigment-grade TiO_2 is carried out in a methane flame reactor according to Reaction [1]:



The formation of HCl in Reaction [1] is confirmed by thermodynamic equilibrium calculations.⁴ Plasma-assisted oxidation of $TiCl_4$ with O_2 , according to Reaction [2], however, allows the direct recovery of chlorine values from the off-gas in the form of Cl_2 :

Introduction¹⁻³

In this article, the manufacturing of a primary TiO_2 pigment and the manufacturing of nano-titania by a plasma process from $TiCl_4$ on pilot-plant scale is described, as well as a process for the recovery of the liberated chlorine values as Cl_2 gas. The scalability and preliminary techno-economics of establishing such a process in South Africa is also briefly discussed.

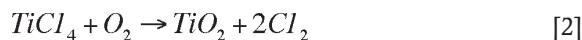
South Africa is blessed with huge resources of titanium-bearing minerals (estimated at about 145 million tonnes) occurring mainly in the form of ilmenite ($FeTiO_3$) and rutile (TiO_2) found in heavy mineral beach sands off the east and west coasts of South Africa. Ilmenite accounts for about 90% of titanium mineral production in South Africa. Richards Bay Minerals (RBM) is the world's largest producer of titania-ferrous slag (>1 million tonnes per annum). Namakwa

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The recovered Cl_2 can be recycled to the front-end of the carbo-chlorination process with the consequent benefits to effective waste management and overall process economics.

Another advantage of the plasma process is that the plasma reactor can be designed to control the particle size of the product by varying the operating conditions. A pilot plant capable of producing 7–10 kg.h⁻¹ TiO_2 from $TiCl_4$ has been accordingly designed and built at Necsa, as will be described below.

Process description

The conversion of $TiCl_4$ to TiO_2 according to Reaction [2] is carried out in a plasma system at temperatures above 1 000°C. Activation energy for the reaction is supplied by a 30 kW (nominal) plasma torch operating on nitrogen as plasma gas. The process is presented schematically in Figure 1. The cylindrical reactor is 0.5 m in diameter and consists of five main sections, totalling 3 m in height (Figure 2). It is constructed on two levels to allow operator access to all sections. The total height of the plant is about 6 metres and the footprint of about 4 meter by 5 metres includes all of the ancillary equipment, the plasma power supply, utilities, off-gas treatment and scrubbers.

The reactor sections have the following functions:

- The plasma torch is mounted at the top of the evaporation chamber. The hot plasma gas evaporates and superheats the $TiCl_4$ droplets
- The $TiCl_4$ vapour then enters the mixing zone where it is diluted with nitrogen shielding gas and mixed with oxygen. Allowance has been made to introduce additional nitrogen for temperature control
- $TiCl_4$ vapour and oxygen react in the upper reaction zone to form TiO_2 vapour and Cl_2
- The lower reaction zone allows the residence time required for vapour condensation and TiO_2 particle coagulation
- Particle growth is controlled by quenching the reaction mixture within milliseconds to below 600°C by means of a cold gas that is introduced through a height-adjustable quench probe.

The particle-laden off-gas mixture is cooled in a heat exchanger and the TiO_2 collected in a cyclone and bag filter arrangement. Chlorine is separated from the off-gas stream by selective adsorption in a suitable zeolite from which it can be recovered by desorption as Cl_2 gas. Any residual is finally removed by scrubbing with 20% KOH solution. The cleaned off-gas (mainly nitrogen) is vented to atmosphere.

The reactor is assembled from several steel sections. A suitable graphite lining is inserted in the evaporating zone and structural ceramics in the reaction zones. Reactor and system parts not lined with graphite or ceramic are constructed from water-cooled stainless steel or aluminium.

Process optimization

Usually, industrial TiO_2 -pigment manufacturing reactors are prone to clogging. Precipitation of solid, fine TiO_2 begins

immediately upon mixing of $TiCl_4$ and O_2 and extensive agglomeration of the particles follows. Modification of the original plasma reactor design decreased the clogging significantly and continuous production rates of 7–10 kg.h⁻¹ can now be maintained easily. The modifications consisted of changing the reactor-lining geometry and inner diameters and the addition of nitrogen in a configuration that creates vortex flows in the direction of the reactor outlet.

Specialized equipment for collecting the product contributes greatly to the efficiency of the pilot plant. The cyclone removes more than 90% of the product and the product can be collected continuously by means of a double

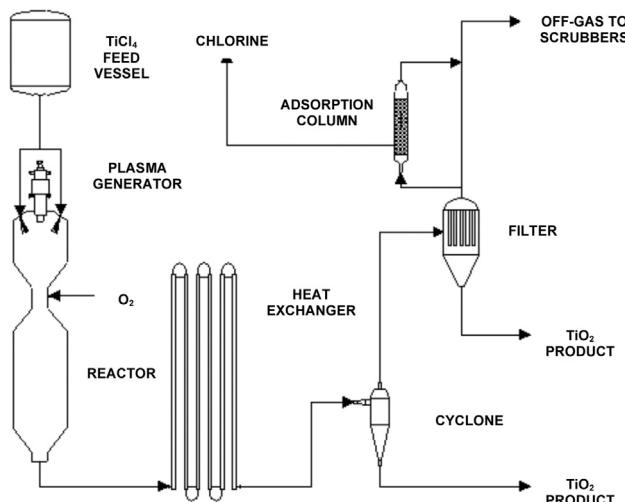


Figure 1—Process flow diagram of the plasma oxidation of $TiCl_4$ to produce TiO_2

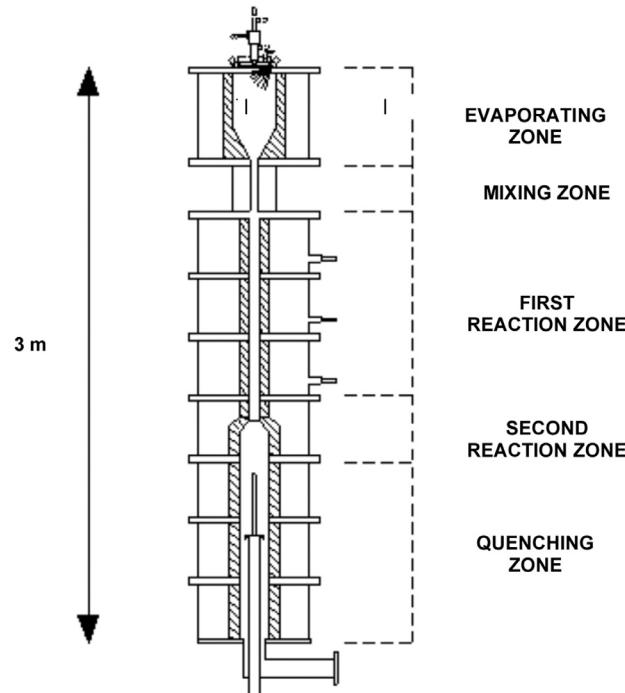


Figure 2—Schematic presentation of the TiO_2 plasma reactor

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valve system. The remainder of the TiO_2 is collected by suitable filter bags. The combined efficiency of the cyclone and filter system is such that less than 1% of the product accumulates in the off-gas scrubber. Brilliant white, free flowing powder was produced in all cases.

Analytical methods

The powder that was collected at the bottom of the cyclone was characterized according to the general requirements to which a typical titania pigment must conform. The whiteness of the produced titania pigments is assessed on the basis of L^* , a^* and b^* parameters that are calculated from the diffuse reflectance spectra according to the method recommended by the Commission Internationale de l'Eclairage (CIE).⁵ These measurements were conducted on a Hunterlab colourmeter supplied by Hunter. The CIE parameters have the following significance:

- L^* represents the brightness of a sample. $L^* = 100$ indicates a pure white colour, while $L^* = 0$ corresponds to a pure black colour
- a^* represents the green (-) → red (+) axis and
- b^* represents the blue (-) → yellow (+) axis.

Particle size and particle size distribution were determined by a scanning electron microscope (SEM) supplied by Zeiss. Standard sample preparation methods for analysing powders with a SEM was used and the particle size and particle size distribution were calculated by the internal software and algorithm supplied with the SEM. The specific surface area of the powders was determined by the BET method on a Tristar 3000 apparatus supplied by Micromeritics. The crystallographic phases of the powder were determined by X-ray diffractometry (XRD) on an X'PertPro apparatus from PanAnalytical. The chemical impurities were determined by the Pelindaba Analytical Laboratories at Necsa with inductive coupled plasma optical emission spectroscopy (ICP-OES) on a Spectro Flame EOP apparatus, using certified standard solutions for calibration purposes.

Results and discussion

The analytical results are summarized in Table I.

In Table II, the CIE L^* , a^* , b^* values of the primary produced TiO_2 pigment that were produced in runs 17, 18 and 19 on the pilot plant, are presented and compared with four different samples of commercially available primary TiO_2 pigment, indicated as Com 1–4 in Table II. Although the pilot plant samples have greater b^* -values (indicating a slightly more yellow tint) than those of the commercial samples, the average L^* -values (>95) for these samples were higher than for the commercial samples (ranging from 93.24–94.62), indicating a 'whiter and brighter' product.

X-ray diffractometry (XRD) showed the product to consist of >60% rutile and <40% anatase (see Figure 3). Rutile is usually preferred in the pigment industry for most applications. Samples that were heat-treated subsequent to the plasma oxidation showed a rutile content of 80–100%. This is consistent with the findings of Won *et al.*⁶ who discuss the transformation of anatase to rutile by post-annealing.

Al_2O_3 and SiO_2 are usually the main contaminants in TiO_2 pigment and influence the crystal and coating properties for pigment applications. The levels of Al_2O_3 (0.08%) and SiO_2 (0.50%) measured in the product are well below the acceptable limits of 4% and 2% respectively.² Impurities that have a detrimental effect on the colour (or whiteness) of TiO_2 pigment (V, Fe, Cr, Ni, Cu, Mn, Zr, Zn, P) amounted to a total of less than 0.1%. It must be appreciated that the purity of the final product is highly dependent on the purity of the TiCl_4 feed. In this project, distilled TiCl_4 was used. The low values of especially the Fe, Cr, and Ni indicate very little corrosion of the stainless steel parts of the equipment and consequent contamination of the final product.

SEM analysis (Figure 4) shows that the TiO_2 particles are agglomerated, which helped with the removal of the particles from the product gas stream by the cyclone and filter bags.

Chlorine recovery

One of the main advantages of the plasma process is the formation of Cl_2 instead of the problematic and very corrosive HCl as in the case of conventional methane combustion processes. Chlorine can be recovered from the off-gas and recycled with the consequent benefits for process economics and waste minimization. This was demonstrated experimentally by diverting a portion of the process off-gas stream

Table I
Results of the TiO_2 pigment powder

Physical characteristics	
Whiteness (Hunterlab; CIE L^* , a^* , b^*)	$L^* > 95$
Particle size (d_{50}) (SEM)	125 nm
Particle size distribution (SEM)	50–250 nm
Specific surface area (BET)	8–20 $\text{m}^2 \cdot \text{g}^{-1}$
Crystallographic phases (XRD)	>60% rutile; <40% anatase
Crystallographic phases after heat treatment (XRD)	>80% rutile
Chemical impurities (ICP-OES)	
Al_2O_3	0.08%
SiO_2	0.50%
ZrO_2	0.05%
Zn, Cr and Cu (total)	<0.01%
V, Fe, Mn and P (total)	<0.001%

Table II
CIE L^* , a^* , b^* values of the titania pigments

Sample	L^*	a^*	b^*
Run 17	95.66	-1.12	3.81
Run 18	95.38	-0.84	4.26
Run 19	95.37	-0.74	4.00
Com 1	93.59	-0.82	2.85
Com 2	93.24	-0.68	3.65
Com 3	94.62	-0.99	3.05
Com 4	93.51	-0.78	2.79

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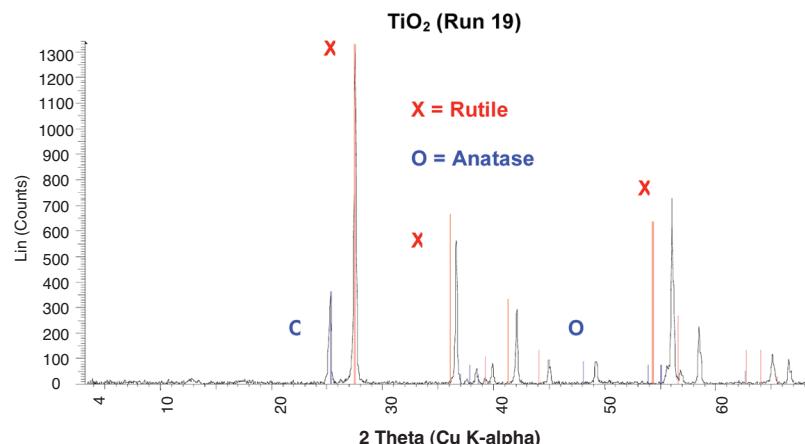


Figure 3—XRD spectrum of the TiO₂ plasma pigment

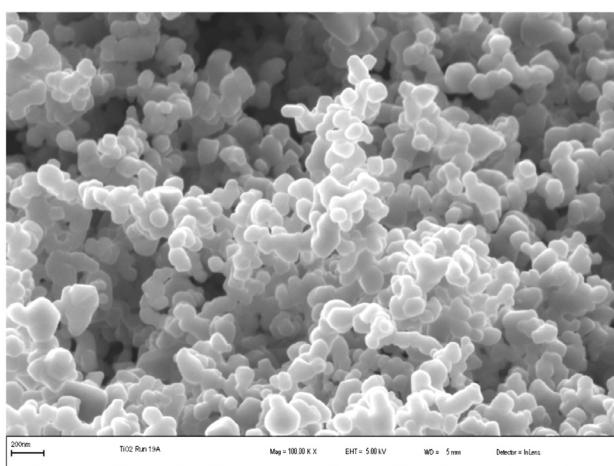


Figure 4—SEM image of the TiO₂ product with $d_{50} = 125$ nm

through a zeolite bed followed by a trap containing a 10% KI/starch solution. The solution in the trap remained clear as long as the zeolite capacity was not exceeded, indicating that Cl₂ had been adsorbed quantitatively. Titration and mass balance calculations showed that >95% of the Cl₂ was recovered by desorption from the zeolite bed.

Nano-titania

SEM analyses revealed particle-size d_{50} values of 50–250 nm for TiO₂ produced in several experiments under different conditions in the pilot plant (Figure 4). Observed trends show an increasing particle size with increasing TiCl₄ feed rate. This is consistent with an increased TiCl₄:N₂ mass ratio, which means that less dilution of TiCl₄ in the reactor gases and consequently resulting in the formation of larger particles. It was also found that the nozzle size and the position of the TiCl₄ spray nozzles have a significant influence on the particle size as well as the quench rate of the product-gas mixture and effective residence time of particles in the reactor. In general, the higher the quench rate, and the shorter the residence time, the smaller the particle size. Therefore, nano-titania can also be produced on this plasma pilot plant by careful selection and controlling of the process parameters.

Scale-up and economic factors

There is no technical reason why this process cannot be scaled up to a production plant. Plasma processes can be scaled modular, which has the advantage that the production plant capacity can gradually be increased according to market growth and demand. Plasma systems in the order of 450 kW were being run successfully at Necsa. The auxiliary pigment plant equipment is standard in the titania pigment industry.

A preliminary techno-economic evaluation for a 100 000 tonnes per annum TiO₂ pigment plant has indicated a favourable internal rate of return (IRR) and return on Investment (ROI).⁷ The economics are positively influenced by the potential direct recovery and recycling of gaseous chlorine instead of HCl. No techno-economic comparison was made between the plasma-based and conventional flame processes. Nano-titania can achieve very high selling prices, up to several thousand dollars per kilogram, depending on characteristics and applications. It is, however, a very smaller market in terms of volume than that of the titania pigment market. No techno-economic study was done on the nano-titania part of this project at this stage.

Conclusions and recommendations

A primary pigment grade TiO₂ was successfully produced on a plasma pilot plant. TiO₂ particles with a d_{50} of 125 nm were continuously produced at rates of 7–10 kg.h⁻¹ without any clogging of downstream process equipment. Specialized equipment and innovative reactor and pilot plant design allow for control over experimental parameters and conditions. The white TiO₂ product revealed properties conforming to the basic specifications for a primary titania pigment. Plasma parameters can be changed to manipulate the particle size and it was demonstrated that nano-titania can also be produced on the same pilot plant. Parameters that can be changed in order to achieve this are

- The TiCl₄ feed rate
- The spray nozzles size and configuration
- The dilution of the TiCl₄ with the plasma gas and
- The quench rate of the product-gas mixture.

The plasma oxidation of TiCl₄ by O₂ in the above-mentioned pilot plant allows for the successful recovery of Cl₂ for recycling, which will contribute greatly to waste

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minimization and the overall economics of a fully integrated commercial plant. Preliminary techno-economic evaluation for such a pigment titania plasma plant showed a favourable IRR and ROI.

The following approach is recommended for further development of the process:

- Proving operability and reliability of the present pilot plant facility by continuous production runs of 24 hour duration
- Scale-up to at 100 kg.h⁻¹ capacity
- Refinement of the techno-economic evaluation
- Further exploration of nano-titania opportunities.

Finally, it was proved that it is possible to establish a plasma titania pigment plant and a nano-titania plant in South Africa, fulfilling the South African government ideal for more local beneficiation and value adding of our minerals.

Acknowledgements

This work was partially funded by the Innovation Fund of

South Africa, a business unit of the Department of Science and Technology, as part of its mandate of promoting South African technological innovations.

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