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### <u>Research Perspectives on the Photocatalytic Activity of Titanium Dioxide:</u> <u>Catalytic Assessment Methods in Solution and Solid-State in Relation to Particle</u> <u>Surface Activity</u>

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#### **ABSTRACT**

A range of prepared titania nanoparticles were characterised by Brunauer-Emmett-Teller (BET) surface area, X-ray Diffraction (XRD), CPS Disc Centrifuge, Transmission Electron Microscope (TEM), Scanning Electron Micrographs (SEM), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Measurements (DRIFTS). In addition, the activities of the different catalysts were determined via rapid assessment methodologies like Microwave Dielectric Spectroscopy (MDS), Hydroxyl content, Phosphorescence and Chemiluminescence Spectroscopy and Isopropanol Oxidation Test and the data related to actual weathering properties of the pigments doped in metallocene polyethylene under dry and humid conditions. Quantum size effects, which lead to high surface areas and blue shifts and diminish electron-hole recombination, are used to explain the high activities of the nanoparticle products. In situ FTIR data and OH content determination show the presence of high contents of hydroxyl groups and large amounts of adsorbed water on TiO<sub>2</sub> nanoparticles. The Disc Centrifuge results and BET surface area combined with the XRD particle size results show that a careful distinction between the crystal and aggregate sizes must be made in order to properly interpret the activity of TiO<sub>2</sub> pigments. Aggregation of TiO<sub>2</sub> pigments affects not only the surface area offered by the TiO<sub>2</sub> but also the type of interaction between the light and the TiO<sub>2</sub>. The treatment conditions used for the crystallization of the primary material (precursor) in order to prepare the nanoparticle pigments, not only influenced the anatase crystal size but also other anatase properties (such as the surface hydroxylation, adsorbed water, recombination rate, aggregation state and type of structural defects). Chemiluminescence of the titania particles is discussed in light of potential surface active peroxidic species.

#### **INTRODUCTION**

Of the many pigments and fillers used commercially in polymers and coatings applications one of the most important and complex in this regard is titanium dioxide [1-35]. To date research activities into the photochemical properties of titanium dioxide relate to a number of areas. One current area of topical interest deals with studying the photocatalytic activity of titanium dioxide in order to convert harmful organic waste products into harmless environmentally acceptable materials [3,10,20,31] while another deals with minimising the photocatalytic activity of TiO<sub>2</sub> in order to enhance the durability of organic substrates such as polymers and coatings [1,2, 7-9,32-35]. In many plastics and coatings applications however, the prime use of titanium dioxide is as an opacifier and colourant.

The ability of pigments to catalyse the photooxidation of polymer systems has also received significant attention in terms of their mechanistic behaviour in various solution and solid media [1-35]. In this regard much of the information originates from work carried out on  $TiO_2$  pigments in both polymers and model systems [1,2]. To date their are three current mechanisms of the photosensitised oxidation of polymers by  $TiO_2$  and for that matter other white pigments such as ZnO [3,30]. These are:

1. The formation of an oxygen radical anion by electron transfer from photoexcited TiO<sub>2</sub> to molecular oxygen [14-17]. A recent modification of this scheme involves a process of ion-annihilation to form singlet oxygen which then attacks any unsaturation in the polymer [1,2,32-35].

 $\begin{array}{l} TiO_2 + O_2 - hv - - > TiO_2^{+} + O_2^{-} \ (I) \\ (I) - - - > TiO_2 + {}^{1}O_2 \ (ion-annihilation) \\ (I) + H_2O - - - > TiO_2 + HO^{-} + HO_2^{-} \\ 2HO_2^{-} - - - > H_2O_2 + O_2 \\ RCH_2 = CHR' + {}^{1}O_2 - - - > RCH = CHCH(OOH)R' \end{array}$ 

2. Formation of reactive hydroxyl radicals by electron transfer from water catalysed by photoexcited TiO<sub>2</sub> [1,2,31-35]. The Ti<sup>3+</sup> ions are reoxidised back to Ti<sup>4+</sup> ions to start the cycle over again.

3. Irradiation of  $TiO_2$  creates an exciton (p) which reacts with the surface hydroxyl groups to form a hydroxyl radical [1,2,10, 31-35]. Oxygen anions are also produced which are adsorbed on the surface of the pigment particle. They produce active perhydroxyl radicals.

 $\begin{array}{l} TiO_2 -----hv -----> e' + (p) \\ OH^- + (p) ------> HO \\ Ti^{4+} + e' -----> Ti^{3+} \\ Ti^{3+} + O_2 -----> [Ti^{4+} ----O^{2-}] \ adsorbed \\ [Ti^{4+} -----> Ti^{4+} + HO^- + HO_2 \\ \end{array}$ 

Titanium dioxide pigments (Titania) exist in three morphological crystalline forms which exhibit different photoactivities when incorporated into a number of commercial polymers [1,2,4,7,10-13]. Each modification exhibits 6:3 coordination but whereas the anatase forms a distorted octahedral structure the rutile form slender primatic crystals that are often twinned. Differences in the photoactivities of these two modifications of titania depends markedly upon the manufacturing history of the pigment. Anatase pigments are generally more photoactive than the rutile types [18-19]. However, more recent research has shown that the third intermediate polymorph Brookite is significantly more active [4] albeit has little interest in terms of its pigmentary use.

To improve pigment dispersion and reduce photoactivity the surface of the pigment particles are coated with precipitated aluminosilicates. Zirconates are also used in some instances while for other applications such as in nylon polymers and fibres the anatase is coated with manganese silicates or phosphates. Anatase will photosensitise the oxidation of a polymer the effect being dependent upon the nature and density of the coating and increases with pigment concentration. Uncoated rutiles are also photosensitisers but again the effect is reduced and proportional to the effectiveness of the coating. In this case stabilisation increases with increasing coated rutile concentration. Thus, the surface characteristics of the Titania pigment is an important factor in controlling photoactivity [21,23,25]. The surface is covered with hydroxyl groups of an amphoteric character formed by the adsorption of water. These groups are more acidic in character on the surface of anatase and less effectively bound than those on rutile. The surface carriers (excitons) therefore, react more slowly with the hydroxyl groups in the case of rutile.

Surface modifications of the TiO<sub>2</sub> particles with inorganic hydrates may reduce the photochemical reactivity of titanium dioxide pigments [35]. This can reduce the generation of free radicals by physically inhibiting the diffusion of oxygen and preventing release of free radicals. The often simultaneous chemical effects of surface modification can involve provision of hole and electron recombination sites or hydroxyl radical recombination sites. In addition to the latter effects, the surface treatment or coating as mentioned above can improve other properties such as improve the wetting and dispersion in different media (water, solvent or polymer), to improve compatibility with the binder and dispersion stability and colour stability. The photosensivity of titanium dioxide is considered to arise from localized sites on the crystal surface, and occupation of these sites by surface treatments inhibits photo-reduction of the pigment by ultraviolet radiation and hence the destructive oxidation of the binder is inhibited. Coatings containing 2-5% by weight alumina or alumina and silica are satisfactory for general-purpose paints [35]. If greater resistance to weathering is desired, the pigments are coated more heavily to about 7-10% weight. The coating can consist of a combination of several materials, eg. alumina, silica, zirconia, aluminium phosphates of other metals. For example, the presence of hydrous alumina particles lowers Van der Waals forces between pigments particles by several orders of magnitude, decreasing particle-particle attractions. Hydrous aluminium oxide phases appear to improve dispersibility more effectively than most of the other hydroxides and oxides [35].

During the weathering of commercial polymers containing white pigments such as titania oxidation occurs at the surface layers of the material which eventually erodes away, leaving the pigment particles exposed. This phenomenon is commonly referred to as "chalking" and has been confirmed by scanning electron microscopy [1,2,15,35].

Titania pigments absorb strongly in the near UV region with anatase having a cut-off point at 340 nm and rutile at 370 nm. Simply on this basis one may argue that the latter will screen more of the active UV radiation. Methods of assessing pigment photoactivities have attracted much interest from both a scientific and technological point-of-view. Artifical and natural weathering studies are tedious and very time consuming. Consequently numerous model systems have been developed to rapidly assess their photochemical activities. Most of these systems undergo photocatalytic reactions to give products which are easily determined, usually by UV absorption spectroscopy, HPLC or GC etc. Oxygen uptake [14], ESR [23], luminescence [5,6,24], hydroxyl analysis [25,35] and microwave spectroscopy [25,26].

Microwave photodielectric spectroscopy has been found by far to be one of the latest and interesting methods for ascertaining pigment photoactivity and photoconductivity [25,26]. Like all other spectroscopic methods one obtains an absorption spectrum in the microwave region as return frequency loss which is related to the polarisability of the pigment structure. The higher the initial absorption frequency the more polarisable the structure, hence greater activity with anatase being more active than rutile. Irradiation of the TiO<sub>2</sub> in a microwave cavity cause charge separation and increased polarisation. The absorption frequency then shifts with time providing a measurement of the extent of charge-generation. Upon switching off the light the charge carriers recombine. Fast rise and decays indicate shallow traps while the more slower decays indicate deep traps.

In recent years however, there has been extensive interest in ultrafine or nanoparticle fillers and pigments especially with regard to their properties as a UV "blocker" in coatings applications [27,28,35,36]. Thus, whilst for conventional pigmentary titania light scattering is governed by the Mie theory for ultrafine titania Rayleigh's scattering applies. Thus, the finer the particle the more effective will be the scattering of UV light below 400 nm. At an optimum particle size of 2-50 nm visible light will be transmitted and the system becomes essentially translucent. Recent work has also indicated that for ultrafine titania physisorption and chemisorption process are paramount and can significantly influence the performance characteristics of stabilisers in different ways [29] and this can in turn control the stability of the matrix. The overall photocatalytic performance of titanium dioxide particles is complex and highly dependent on quite number of parameters including preparation method, annealing temperature, particle size, the specific surface area, porosity and the ratio between the anatase and rutile crystal phases [3,4,35]. Although, photocatalytic activity of the particles themselves can be more easily understood and inter-related in more complex systems such as coatings and polymers the situation becomes complicated by numerous factors such as light intensity, humidity and the nature of the substrate to be degraded along with other formulative complexities such as antioxidants and light stabilisers [27,28,35,36]. For example, the photocatalytic activity of nano particles in polymers and coatings are not always consistent with particle size and concentration activity [35,36].

This study addresses the preparation, characterization, and catalytic activity of nanometer-sized anatase and rutile TiO<sub>2</sub> particles specially prepared in the industrial laboratory to control surface activity and crystallinity through the sulphate and chloride routes. Some of the rutile pigments have then been surface treated with increasing levels of silica. Comparative photoactive nano anatase samples have also been included coated with hydroxyapatite (Showa Denka) and P-25 (Degussa). The as prepared powders have been characterised by Brunauer-Emmett-Teller (BET) surface area, X-ray

Diffraction (XRD), CPS Disc Centrifuge, Transmission Electron Microscope (TEM), Scanning Electron Micrographs (SEM), Thermogravimetric a Analysis (TGA) and Fourier Transform Infrared Measurements (DRIFTS) in order to gain a complete picture of particle properties. In addition, the activities of the different catalysts were determined via rapid assessment methodologies including wide ranging Microwave Dielectric Spectroscopy (MDS), Hydroxyl content, Phosphorescence and Chemiluminescence Spectroscopy and Isopropanol Oxidation/oxygen uptake Test. In this way particle properties can be thoroughly interrelated with the different photoactive test methods in order to understand in more detail a wide ranging approach to linking the properties with a particular photocatalytic mode. In particular, the chemiluminescence analysis of the particles provides some very novel information on surface characteristics in relation to their activity. The study is then extended to a final evaluation of the titania particles processed into a stabilised metallocene polyethylene at different concentrations. An assessment is undertaken of their photocatalytic behaviour upon weathering in two types of exposure systems (QUV) and Microscal where different light sources (Fluorescent tubes (340nm) vs Coated Hg/Tunsten) and atmospheric conditions (Humid vs Dry) are shown to provide an interesting contrast when correlations are assessed with rapid laboratory test methods. Even though the QUV is a highly rated commercial weathering machine for lifetime assessments the photoactivity relationships of the nano-particles breaks down.

# **EXPERIMENTAL**

# <u>Materials</u>

The titania pigments used in this study were pigmentary and nanoparticle grades prepared in the laboratories of Tronox, Grimsby, UK and are listed by alphabetical codes in Table 1. For a representative estimation of their performance the Tronox have been compared to Degussa P-25, very often used as a world-wide reference photocatalyst. In addition, the Japanese product H was studied for comparison purposes. Conventional micron size anatase (pigment A) (uncoated) and rutile pigments (B-D) (coated) were also studied for comparison purposes with the nanoparticle pigments.

Sampla	Titanium Dioxide	Manufacturer	Preparation	Alumina	Other
Sample	%		Method	%	Treatments
A-Anatase (pigmentary)	99.0	Millennium	Sulphate route		
B-Rutile (pigmentary)	99.0	Millennium	Chloride route	1	
C-Rutile (pigmentary)	95.0	Millennium	Chloride route	2.8	
D-Rutile (pigmentary)	95.0	Millennium	Chloride route	3.4	
E-Nano anatase	>95	Millennium	Sulphate route		
F-Nano anatase	>95	Millennium	Sulphate route		
G-Nano anatase	>95	Millennium	Sulphate route		
H-Nano anatase	>95	Showa Denka	Sulphate route		Hydroxy Apatite
I-Nano rutile (untreated)	>95	Millennium	Sulphate route		
Degussa P-25		Degussa	Flame hydrolysis		

 Table 1: Nomenclature, manufacturer, preparation method and surface

 treatments of TiO2 catalysts

#### **Characterization of the samples**

The crystal structure, particle size, morphology and surface area of the  $TiO_2$  photocatalysts were characterised using Brunauer-Emmett-Teller (BET) surface area,

X-ray Diffraction (XRD), CPS Disc Centrifuge, Transmission Electron Microscope (TEM), Scanning Electron Micrographs (SEM), Thermogravimetric and Differential Scanning Calorimeter Analysis (TGA-DSC), Fourier Transform Infrared Measurements (DRIFTS), and UV-Visible spectroscopy. In addition, the photocatalytic activities of the different catalysts were determined via rapid assessment methodologies like Microwave Dielectric Spectroscopy (MDS), Hydroxyl Content, Phosphorescence, Chemiluminescence and Isopropanol Oxidation Test.

The Brunauer-Emmett-Teller (BET) surface area was determined using a Micromeritics Pulse Chemisorb 2700 nitrogen adsorption apparatus. The dried sample powders were analysed by XRD using a Rigaka D/MAX-rA powder diffractometer with a nickelfiltered CuKa radiation source or using a Shimadzu XRD-6000 X-ray diffractometer with a nickel-filtered Cu Ka radiation source [37]. The CPS Disc Centrifuge measures particle size distribution using sedimentation, a well-known and reliable method of particle size analysis. Particles settle in a fluid under a gravitational field according to Stokes' Law. The CPS disk centrifuge was used to measure the particle size distribution of the powder pigments. This technique measures the size of the aggregates that arrive to the detector assuming spherical size and gives an invaluable information about the aggregation/agglomeration state of the pigments. For TEM imaging, the sample powder was dispersed in isopropanol and a drop of the suspension was placed onto a carbon-coated copper grid. The excess liquid was removed using a paper wick and the deposit was dried in air prior to imaging. The deposited TiO<sub>2</sub> particles were examined with a Philips CM20 transmission electron microscope at an accelerating voltage of 200 kV. The size and morphology of the primary and secondary TiO<sub>2</sub> particles were measured from the TEM micrographs. Thermogravimetric experiments were carried out using a NETZSCH Thermische Analyse (TASC 414/3 controller and T6209 cell). 6 mg of pigment were analysed. They were prepared and heated from 25°C to 750°C under nitrogen (to avoid organic inferences) at a heating rate of 20°C/min and the % of mass loss was calculated. For the diffuse reflectance FTIR experiments, a Nicolet 510P FT-IR spectrometer was used. Spectra were made up to 150 co-added scans and Resolution was set to 4 cm<sup>-1</sup>.

Hydroxyl analysis is referred to elsewhere [40,41]. The photocatalytic activity of these catalysts was investigated for the gas-phase photooxidation of 2-propanol in a continuous flow annular photoreactor. 2-propanol was used as the reactant in the presence of air. Oxygen consumption was measured before and after UV exposure in a sealed glass tube and is representative of photocatalytic activity. Low temperature Phosphorescence spectroscopy is an important tool that can be used to study the electronic structure, optical and photoelectrical properties of TiO<sub>2</sub>. The analysis was undertaken on the pigments using a Perkin Elmer Model LS-55 luminescence spectrometer (Beaconsfield, UK) utilising liquid nitrogen as the coolant (77 K) and quartz tubes (5 mm diam.) as the sample cell. Chemiluminescence emissions of powder samples were obtained using a CL400 ChemiLUME apparatus developed by Atlas Electric Devices Co. 20 mg of each product was placed in the aluminium pan covering its surface as a powder layer and heated up with pre-test ramp  $(1 \, ^{\circ}\text{C min}^{-1})$  to the test temperature (170 °C), under constant flow (55 ml min<sup>-1</sup>) of dry gas, nitrogen or oxygen. software supplied with the instrument. This is a widely established test method for monitoring oxidation reactions and hydroperoxide activity [42]. Microwave photodielectric spectroscopy is the most novel and most informative method for characterising pigment photo-activity and photoconductivity [25,26]. In particular, the

application of microwave dielectric spectroscopy to nano-sized semiconductors in heterogeneous photocatalysis has been studied. In this study, a real time microwave cavity perturbation method was used to measure the response of the different titania samples. Microwave measurements were undertaken using a Marconi (6200A) 2 -20GHz programmable sweep generator and automatic amplitude analyser, coupled to a circular waveguide and cylindrical cavity. Powdered samples (0.2 g) were packed in the bottom of the cavity on a plastic dish (to ensure reproducibility) and were irradiated in the cell chamber with an ILC 302UV xenon source via an optical fibre set-up (Laser Lines Ltd., Beaumont Close, Banbury, Oxon, UK). This lamp has a 300W output power with a manual shutter control which allows the user to select the light type between Visible and UV light. The characteristics of these two settings are shown next:

- Vis: Visible only (320-700nm). 15000 lumens
- UV: Ultraviolet (260-400nm) 1.0W of UV output and 2.0W of IR leakage.

Changes in microwave cavity resonant frequency and attenuation of microwave power were monitored during 1800 s of irradiation and for 1800 s after switching off the light source. All measurements were carried out in triplicate, and at 25 °C. The uncertainty in the values of 'shift in microwave cavity resonant frequency ' is of the order 0.0004 GHz; while that for 'attenuated power 'is 0.05 dBm.

# **Polyethylene Film Preparations**

The titania pigments used in this study were the same pigmentary and nanoparticle grades characterised earlier. The polyethylene and 0.1, 0.5, 1, and 2% w/w of titanium dioxides were melt blended using a Brabender Plasticorder (Duisburg, Germany) fitted with W50E chamber and cam blades at 170  $\Box$ C for 10 min each and then compression moulded into film (100 –200µm thickness) for 1 min. During melt blending, 0.05% of Irganox ® 1010 was added to prevent excessive thermal degradation. The phenolic antioxidant, Irganox ® 1010 (pentaerythrityl tetrabis (3,5-di-tertbutyl-4-hydroxyphenyl) propanoate) was obtained from Addivant (UK) Ltd., Manchester, UK while the unstabilised polyethylene (in powder form) was supplied by Repsol (Madrid) with a number average molar mass of 156,000. A metallocene catalyst was used in the production of this material.

### Hydroperoxide analysis

Hydroperoxide determinations were carried out using the iodiometric method. [44]. Polymer film samples (1g) were cut into small pieces and placed into a 100 cm<sup>3</sup> pear shaped flask containing sodium iodide (0.1g), 'Analar' grade propan-2-ol, 9.5 cm<sup>3</sup> and glacial acetic acid, 0.5 cm<sup>3</sup>. The mixture was then refluxed vigorously for 30 min together with a control solution without polymer. The yellow I<sup>3-</sup> ion was then determined spectrophotometrically at 420 nm (Perkin-ElmerLambda-40 spectrometer) to avoid any additive absorbances and using a calibration curve set-up utilising 70% w/w cumene hydroperoxide as a standard (Aldrich, U.K).

### **Carbonyl index determination**

In infrared spectroscopy, IR radiation is passed through a sample when the resulting spectrum is related to vibrations of specific functional groups and thus creates a spectral fingerprint of the sample. Carbonyl groups are easily detected in the broad infrared

region at 1800 –1680 wavenumbers for oxidised polyethylene film. Carbonyl growth in this region of the spectrum was determined by the carbonyl index defined fully in the literature [44]. The rate of carbonyl group formation was compared by recording the ageing time required to reach carbonyl index value of 0.1 using the FTIR peak maximum at 1710 cm<sup>-1</sup>. This is often taken as the embrittlement time. Spectra were recorded and analysed using a Nicolet Nexus FTIR spectrometer.

### **Irradiation/Weathering**

The polymer films were irradiated in two light exposure units. The first was a Microscal Weathering Unit (Microscal Ltd., London) utilising a 500 W high pressure fluorescent mercury/tungsten source (wavelengths >300 nm, ambient humidity and temperature). The second was the fluorescent tube source QUV (Q-Panel company, Bolton, UK). The QUV tester consists of an array of eight UV 340 fluorescent tubes producing an energy spectrum with a maximum emission at 340 nm. This UVA 340 is the best available simulation of sunlight in the critical, short wavelength UV region between 365 nm and the cut off at 295 nm. The black body temperature of the specimens was set at 60 °C during the UV irradiation cycles and at 45 °C during the condensation cycles. A total of four hours were used for each cycle.

### **RESULTS AND DISCUSSIONS**

#### **Thermal Treatments**

Thermal treatments are useful for crystal growth and to improve the crystallinity of TiO<sub>2</sub> pigments. When TiO<sub>2</sub> powders are calcinated, apart from crystal growth, crystal structure transformations may also occur. The amorphous-anatase; anatase-rutile transitions depend strongly on the method of preparation, the nature of the precursor and calcinations conditions [3,4,35]. All the pigments named A, E, F and G were prepared by calcination of the same primary material: a sol-gel product formed by the hydrolysis of Ti(SO<sub>4</sub>)<sub>2</sub>. The pigment G was just washed and dried whereas the pigments F, E and A were calcined at increasing temperatures to produce nanoparticle product with different crystallite sizes and finally the pigmentary product pigment A. The noncalcined pigment G was expected to have the highest surface area of all the nanoparticles, consequently, the pigment A, calcined at the highest temperature was expected to have the lowest surface area. On the one hand, higher surface area implies more reactive sites to react with the reactant and this will obviously improve the activity. However, nanoparticle pigments produced at low calcination temperatures possess more structural defects [3,4,35]. Each one acts as a recombination centre when electrons and holes are generated under illumination, thus, decreasing the final activity.

#### Surface area measurements

The surface area measurements were carried out for all the  $TiO_2$  samples used in this study. Assuming spherical particles and a constant density of  $4.2g/cm^3$ , the particle size of the different particles can be estimated from the surface area measurements. Hence, the results for the BET surface area measurements and the crystallite size estimated from this area are depicted in Table 2.

Sample	BET Surface	Particle size	
	Area m²/g	from Surface area	
A-Anatase (pigmentary)	10.08	0.14microns	
B-Rutile (pigmentary)	5.5	0.26microns	
C-Rutile (pigmentary)	6.5	0.22microns	
D-Rutile (pigmentary)	12.48	0.11microns	
E-Nano anatase	4.436	32nm	
F-Nano anatase	77.92	18.33nm	
G-Nano anatase	329.07	4.32nm	
H-Nano anatase	52.1	27.4nm	
I-Nano rutile (untreated)	140.9	10.1nm	
Degussa P-25	50	28.57nm	

Table 2: BET surface area and estimated crystal size of TiO<sub>2</sub> catalysts.

The BET surface area is an excellent technique that allows us to identify the nanoparticle products. The superior surface area of the nanoparticle products E-I (up to 330 m<sup>2</sup>/g) in comparison with pigmentary TiO<sub>2</sub> (pigment A: 10 m<sup>2</sup>/g) is confirmed by this technique. This area measured by the N<sub>2</sub> adsorption is the maximum area that can be offered by these products if complete dispersion is achieved. In other words, if all the aggregates and agglomerates were broken during the dispersion step. In a real system, the dispersion method will not always be able to completely disperse the TiO<sub>2</sub> in order to offer the BET surface area measured by N<sub>2</sub> adsorption. Therefore, the BET surface area gives a value of the potential surface area of these TiO<sub>2</sub> products. However, the final area offered by a TiO<sub>2</sub> pigment in a determined application is dependent on two factors. Firstly, the dispersion state of the TiO<sub>2</sub> after the incorporation process used for that determined application. Secondly, it is dependent on the molecular weight of the molecule to be degraded or in contact with the TiO<sub>2</sub>. For example, high molecular weight compounds will not be able to enter the spaces between the aggregates and agglomerates of TiO<sub>2</sub> powders. The pores will also be too small for large molecules to enter. Therefore, a significant proportion of the measure BET surface area will not be accessible to large molecules.

The effect of the calcination temperature on the surface area is obvious from the data. The surface areas decrease with increasing calcination temperature from pigment G to pigment E. The particles of pigment G, as they have not been calcined are very small. Correspondingly, it has a high surface area. On the contrary, the pigmentary pigment A, calcined at the highest temperature has a very low surface area of  $10 \text{ m}^2\text{g}^{-1}$ .

#### XRD measurements

XRD is used for crystal phase identification and estimation of the anatase to rutile ratio as well as crystallite size of each phase present. The XRD peaks at  $2\theta = 25.25$  (101) and  $48.0^{\circ}$  in the spectrum of TiO<sub>2</sub> are easily identified as the crystal of the anatase form, whereas the XRD peaks at  $2\theta = 27.42$  (110) and  $54.5^{\circ}$  are easily identified as the crystal of the rutile form. The percentage of anatase in the samples can be estimated from the respective integrated XRD peak intensities using the following equation:

$$X(\%) = \frac{100}{(1+1.265 \,\mathrm{I_R/I_A})}$$

Where:

- $I_A$  represents the intensity of the anatase peak at  $2\theta = 25.25^{\circ}$
- $I_R$  is that of the rutile peak  $2\theta = 27.42^{\circ}$ .
- X is the weight percentage of anatase in the sample.

The crystallite size can also be determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula [36].

$$L = \frac{K\lambda}{\beta \cos\theta}$$

Where

- L is the crystallite size
- $\lambda$  is the wavelength of the X-ray radiation (Cu K<sub>a</sub> = 0.15418 nm)
- K usually taken as 0.89
- $\beta$  is the line width at half-maximum height

This is a generally accepted method to estimate the mean crystallite size of the nanoparticle. Because of the very small crystallite size of nanoparticles, the nanoparticle cannot be seen as an ideal crystal with in-numerous crystal faces. Thus, the diffraction spectrum of nanoparticles becomes wider and weaker. This feature was present in our results. The average crystallite size and the weight percentage of rutile phase of the nanoparticle TiO<sub>2</sub> powders calcined at different temperatures were analysed and the results are shown in Tables 3 and 4.

Table 3: BET surface area, estimated BET crystal size and XRD crystal size for MICnanoparticle products and Degussa P-25 pigment.

Sample	BET Surface	Particle size	Particle size
	Area m²/g	from Surface area	By XRD
A-Anatase (pigmentary)	10.08	0.14 microns	-
E-Nano anatase	44.359	32 nm	20-30 nm
F-Nano anatase	77.916	18.33 nm	15-25 nm
G-Nano anatase	329.07	4.32 nm	5-10 nm
Degussa P-25	50	28.57 nm	25-30 nm

It can be seen that the crystallite size of anatase increased with the increasing calcination temperature from pigment G to pigment A. A good correlation of the particle sizes found by XRD and the BET surface area was found. The  $TiO_2$  nanoparticles E, had similar composition and structure as well as morphology and particle size with P-25  $TiO_2$ , the latter one possessing an excellent photocatalytic activity. Table 4 shows the percentage of rutile measured by XRD. It has to be noted here that the percentage of rutile values for the anatase nanoparticle pigments (E, F and G) have to be treated with great care in order to interpret them properly.

Pigment	% Rutile measured by XR	
Pigment A	3.0	
Pigment C	99.2	
Pigment D	99.5	
Pigment E	7.0	
Pigment F	8.6	
Pigment G	31.7	
Pigment H	20.2	
Pigment I	79.2	

Table 4: Weight percentage of rutile phase measured by XRD.

The rutile values for pigmentary pigments A, C and D clearly indicate that pigment A is mostly anatase whereas pigments C and D are rutile. However, the increasing content in rutile from pigment E to pigment G are not due to an increase in this crystalline form but to the broadening of their signal as the particle size decreases. For pigment G, (non-calcined) with 31.7% of rutile does not make any sense as it has not been calcined. Its high value of rutile is due to its broadening of the anatase peak at 25.25 ° so as to cover the rutile signal at 27,42 °. As commented before, because of the very small crystallite size of nanoparticles the diffraction spectrum of nanoparticles becomes wider and weaker. Hence, the anatase XRD peaks broadens and is misled with the rutile one, measuring a rutile crystalline form, which is not actually present.



Figure 1: Bet surface area versus weight percentage of rutile phase measured by XRD.

The linear correlation between the rutile content for the nanoparticles and the BET surface area (Figure 1) proves that the misleading values of rutile measured are due to the broadening of their signal as the particle size decreases. However, the value for pigment H, above the linear extrapolation, proves that a mixture of anatase and rutile

phases is present in this pigment. The high value of rutile content for pigment I is expected as it was mean to be a rutile nanoparticle. Pigments I and H explains their off-alignment.

#### **TEM measurements**

TEM was used to measure the crystallite size of the pigmentary size  $TiO_2$  pigments (A-D). The crystallite size of the nanoparticle  $TiO_2$  pigments can also be measured using TEM but it is difficult to separate the particles so that they can be measured as individual particles. In addition, the number of particles to be measured is around 1000, therefore highly time consuming. TEM photographs of  $TiO_2$  pigments prepared by calcining the  $TiO_2$  dry gel at increasing temperatures are shown in Figure 2.





Pigment A



Figure 2: Transmission Electron microscopy images of titania particles calcined at increasing temperatures A, (G-E); note that pigment G was not calcined.

It is clear from the images that the size of the titania particles increases with increasing calcination temperature. All of the titania particles have a similar spherical shape. The images in Figure 2 also show that the titania particles are aggregated. Thermal treatment usually results in coarser  $TiO_2$  crystals. It is evident from the TEM micrographs that these  $TiO_2$  crystals or primary particles were aggregated into spherical ensembles with a porous and open structure. The structure of the pigment G, the one with the smallest particle size is quite different from the rest of the pigments. No crystalline phases or grain structure can be detected for the pigment G on the particles even at high magnification. As this pigment has not been calcined, it might be amorphous to some extent. In addition, more structural defects and less crystallinity are expected for this nanoparticle compared to pigments E and F.

During the thermal treatment of amorphous titania G condensation and polymerisation reactions occur, expelling water molecules and producing a denser structure. This eventually led to crystallization and growth of anatase crystals, as can be seen for pigment F. Thermal treatment is a common method used for obtaining crystalline TiO<sub>2</sub>. It is simple as well as convenient, and lends itself well to controlling the crystal size. However, great care must be exercised in order to ensure reproducibility and to avoid the formation of the rutile phase at high temperatures. TEM analysis was also used to determine the crystallite size of the pigmentary sized TiO<sub>2</sub>.

### **CPS Disc Centrifuge**

Although the crystallite size of TiO<sub>2</sub> can be estimated by XRD or BET surface area measurements, these crystals, as seen by TEM, aggregate and agglomerate in what is known as secondary particle sizes during the drying, calcination, and/or storage stages during the manufacturing process. The particle size of a TiO<sub>2</sub> pigment on a determined application is not fixed. For the same material depends on its state of dispersion. Depending on the milling that is applied to the titania pigments during the manufacturing process and during the dispersion process for the particular application, this secondary particle size will be reduced more or less to its primary or crystalline particle size.

The secondary particle size of a particular titania powder depends on the preparation method employed and also on the milling process applied to the titania. As will be explained later properties such us light absorption, light scattering, BET surface area and effective surface area can be affected by the secondary particle size. This parameter must therefore be considered when assessing the activity of titania pigments. For instance, the BET surface area of a photocatalyst is almost unaffected by the size of the aggregates and agglomerates. However, the "effective surface area" is directly proportional to the secondary particle size. Effective surface is the area that would be available to compounds with a molecular weight much higher than that of the N<sub>2</sub> molecule.

Another example of the complex dependence of different properties upon particle size is the band gap absorption. This absorption is almost unaffected by the size of the aggregates and is just dependent on the number of atoms present. However, light scattering is directly proportional to the effective surface area of the photocatalyst. The Disc Centrifuge technique can be used to determine the size distribution of a determined powder when dispersed in a liquid media. When all the pigments undergo the same dispersion process prior to the measurements (for instance: ultrasonic dispersion in water) it enables study of the particle size distribution and the aggregation state of titania pigments. The particle size for the nanoparticle products E, F and G obtained by disc centrifuge are shown in Table 5.

The average diameter of the aggregates is around 0.7µm and with a very broad distribution of particle sizes. From pigment E to pigment F there was a decrease in the distribution of particle sizes, however, surprisingly, pigment G, with the smallest crystallite size of all had a distribution very similar to pigment E. A possible explanation lies in the stronger attraction forces present in this nanoparticle product with the smallest particle size, producing aggregates of larger dimensions. Pigment H has a nanoparticle secondary size of around 70 nm with a narrow distribution of particle sizes compared to the highly aggregated E, F and G series pigments. The narrow distribution at 70 nm is very close to the particle size value obtained by the BET surface area method of 27 nm. This implies that pigment H is loosely agglomerated in secondary particle sizes of around 70 nm. The average particle size of the nanoparticle product Degussa P-25 and the pigmentary pigments A, C, and D are depicted in Table 5. The Degussa P-25 pigment has an average particle size of 0.15 µm compare to the 0.3 µm average of the pigmentary pigments. The particle size distribution of pigment Degussa P-25 was found to be broader compared to that of pigment H. Although its primary size measured by XRD is in the order of 25-30 nm, these crystals agglomerate into this broad distribution of secondary particles with a maximum at 0.15  $\mu$ m. On the other hand, the pigmentary products A, C, and D were found to have broad distributions of particle sizes centred at around 0.28 µm. This size is the optimum particle size for scattering the visible light (half the wavelength of visible light) and therefore to provide opacity which is the main purpose of pigmentary titania. In order to explain the different distribution of particle sizes for the different TiO<sub>2</sub> pigments the milling history and the preparation method of the different pigments have to be considered. Commercially available nanoparticle TiO<sub>2</sub> have significantly different dispersion characteristics depending on the production processes.

The nanoparticle products G-E were produced by calcination. It is well known that calcined nano-powders generally show high levels of agglomerates and that the large agglomerates formed during the calcination dominate the particle size distribution. This phenomenon was confirmed by disc centrifuge data. On the other hand, the pigmentary product A was also formed by calcination at the highest temperature but it has a particle size distribution centred at smaller particle sizes than the nanoparticles. This result might seem strange but it is most likely due to the more intense milling applied to this product during processing. In fact, the milling of the G-E nanoparticle series pigments during processing is poor; the nanoparticle are fairly coarsely ground. The only requirement during their manufacturing process is that they have to pass through a 0.85mm sieve. In contrast, the commercial pigmentary pigment A is dry ground and micro-pulverised; this milling process, breaks up a significant part of the aggregates and agglomerates producing a particle size distribution centred at particle sizes smaller that the nanoparticle. The same explanation applies to the pigmentary rutile pigments C and D. As they are commercially available pigments, they suffer a high energy milling step during the manufacturing process in order to break the aggregates and provide the product in a dispersed form free of aggregates.

The milling process for the Degussa P-25 and the Japanese product H are unknown. However, from their particle size distribution and knowing that they are a commercial product a milling step during their manufacture is quite likely. In addition, the Degussa P-25 pigment is produced by a flame hydrolysis technique, that is known to produce less aggregation and agglomeration than the calcination process. It has to be noted here that breaking up nanosized pigments is not a trivial task due to the strong attraction forces involved between these particles. However, this is not to say that these forces cannot be overcome. For the G-E nanoparticle products planetary ball milling was demonstrated to be an effective technique to break the aggregates. Figure 3 depicts the effect of 45 minutes of planetary ball-milling upon the particle size distribution for the pigments G and F. The high shear produced during ball milling, breaks the aggregates and agglomerates, therefore the particle size distribution moves to the nanoparticle size. Here, again pigment G shows a higher distribution of particles sizes than the pigment F with a bigger crystallite sizes, possibly due to its stronger attraction forces. To sum up all the results relating to particle size, the table below shows the particle size data obtained with the different techniques.

Sample	BET Surface	particle size	Particle size	Particle size	Particle size
	Area m²/g	from Surface area	By XRD	by TEM	Disc centrifuge
A-Anatase (pigmentary)	10.08	0.14µm	-	0.17 µm	Peak at 0.28 µm (broad)
B-Rutile (pigmentary)	5.5	0.26 µm	-	0.28 µm	Peak at 0.28 µm (broad)
C-Rutile (pigmentary)	6.5	0.22 µm	-	0.25 µm	Peak at 0.28 µm (broad)
D-Rutile (pigmentary)	12.481	0.11 µm	-	0.29 µm	Peak at 0.30 µm (broad)
E-Nano anatase	44.359	32 nm	20-30 nm	-	peak at 0.70 µm (broad)
F-Nano anatase	77.916	18.33 nm	15-25 nm	-	peak at 0.65 µm (broad)
G-Nano anatase	329.07	4.32 nm	5-10 nm	-	peak at 0.70 µm (broad)
H-Nano anatase	52.1	27.4 nm	-	-	peak at 70 nm (narrow)
I-Nano rutile (untreated)	140.9	10.1 nm	-	-	-
Degussa P-25	50	28.57 nm	25-30nm	-	peak at 0.19µm (narrow)

 Table 5: BET surface area and particle size data obtained by different methodologies for the titania pigment.

# **TGA-DSC** analysis

Thermogravimetric experiments were carried out to determine the percentage of mass loss. According to the TG curve, a mass loss at around 100 °C appeared, corresponding to the desorption of water. This mass loss was related to the amount of water adsorbed on the different TiO2 pigments. Mass loss percentage data are shown in Table 6 along with the surface area of each of the pigments. The amount of adsorbed water on the TiO2 pigments is very low (less than 5%) except for the pigments with the highest surface areas pigments G and H. The larger amount of water on these two nanoparticles is not just due to their high surface area but also to the fact that they were not calcined. They were just dried. There is a good linear correlation between surface area and adsorbed water for the nanoparticle pigments E-H as Figure 4 reveals.

# Table 6: BET surface area and percentage of adsorbed water for the different pigments

Sample	BET Surface area m <sup>2</sup> /gr	Mass loss %	
A- Anatase (pigmentary)	10.1	0.6	
B- Rutile (pigmentary)	5.5	0.34	
D- Rutile (pigmentary)	12.5	1.65	
E- Nano Anatase	44.4	1.99	
F- Nano Anatase	77.9	3.49	
G- Nano Anatase	329.1	15.867	
H- Nano Anatase	52.1	2.79	
I-Nano Rutile	140.9	9.92	
P-25	50	1.61	



Figure 3: Empirical correlation between BET surface area and adsorbed water.

For photocatalytic reactions proceeding in aqueous solutions, the effects of water concentration on reaction rates are miniscule since the catalyst surface is saturated with

water. For gas–solid and solid-solid reactions, however, reactivity of catalysts is strictly related to water. It was proposed that the adsorption of water onto TiO2 and ZnO causes structural changes in surface band bending, which unfavourably accelerates the recombination of photogenerated electrons and holes, and thus gives rise to low photo-efficiency [38]. In an alternative explanation, it is suggested that water is used to supply hydroxyl groups, which are consumed by trapping holes to generate OH radicals in the process of reaction [39]. Yet, water itself can compete with reactants for adsorption on active sites. In general, water can play multiple roles in photocatalytic reactions depending on the system.

### Diffuse reflectance (FTIR) spectra

Surface structure is important for photocatalytic purposes since the interaction of reactants with the surface active sites strongly influences the activity of the titania pigments. FTIR offers the possibility to study the surface structure of the titania pigments. DRIFTs studies of the titania samples in the region 4000 and 2500cm<sup>-1</sup> were performed in order to determine possible changes in the distribution of the hydroxyl and the water groups. The surface hydroxyl groups have been recognized to play an important role in photodegradation processes through their interaction with photogenerated holes. It is known that the preparation method of the catalyst affects the hydroxylation state of the catalyst surface. The FTIR spectra shown in Figure 4 shows a shoulder peak appearing at 3644 for the nanoparticle products and which is assigned to a free –OH stretching vibration. The Hydroxyl stretching vibration of molecular adsorbed water is found around 3283 and is represented by a very broad peak. Correspondingly, the strong absorption band at 1616cm<sup>-1</sup> corresponds to the bending mode of molecular water.



Figure 4: Diffuse reflectance FTIR spectra of titania pigments.

The linear correlation between BET surface area and adsorbed water is confirmed again by FTIR. If the amount of adsorbed water (in percentage) measured by TGA is plotted against the height of the FTIR water peak at 3283cm<sup>-1</sup>, a linear correlation is clear as shown in Figure 5.



# Figure 5: Empirical correlation between adsorbed water measured by TGA and water content measured by the water peak at 3276 cm<sup>-1</sup>.

The FTIR technique detects the presence of OH groups on the  $TiO_2$  at around 3644cm. These groups are especially evident for the nanoparticle pigments; however, its quantification is not possible due to the overlapping of the peak with the water signal.

### **Chemiluminescence**

The chemiluminescence of micron and nanoparticle titanium dioxide was examined in order to determine if they contain any surface active species. This fact could be due to the oxidation species produced during their manufacturing process. Unlike conventional techniques, Chemiluminescence can detect this phenomenon, which could have an effect on polymer properties. The chemiluminescence emission observed under nitrogen at 170 °C with the different titanium dioxide samples employed in this work (1 mg) are shown in Figure 6.



Figure 6: Chemiluminescence curves for the micron and nano titanium dioxide, in powder bulk obtained at 170 °C under nitrogen.

All the samples exhibited very low intensity of Chemiluminescence emission under this condition. The most interesting feature here is the high emission intensity from the Pigment F particles. In the presence of oxygen, the chemiluminescence emission was enhanced for all the titania pigments as compared to those obtained under a nitrogen atmosphere. The titanium dioxide is a well-known catalyst for polymer oxidation. Figure 7 shows the Chemiluminescence emission for  $TiO_2$  pigments under oxygen at 170 °C.



Figure 7: Chemiluminescence curves for the micron and nanotitanium dioxide, in powder bulk obtained at 170 °C under oxygen.

In general, the emission increases with particle size. Anatase and rutile micron size particles exhibit the highest values of chemiluminescence, and the emission is enhanced when the particles are coated. The surface treatments themselves may possess peroxides or hydroperoxides that could give chemiluminescence. Although the pigments and nanoparticles exhibit chemiluminescence in bulk, the emission may be considered negligible. It can only be assumed that traces of peroxides or hydroperoxides on the surface of the titania are responsible for the observed weak emissions. These could be present as weakly bound molecular oxygen complexes with acidic species.

#### **Luminescence Analysis**

The phosphorescence emission spectra have been widely used to investigate the efficiency of charge carrier trapping, migration and transfer, and to understand the fate of electron/hole pairs in semiconductor particles [6,45,46]. The low-temperature photoluminescence from the two common titania polymorphs is markedly different. In the case of anatase TiO<sub>2</sub>, a broad green emission has been attributed to the localised (self-trapped) exciton recombination [46]. For the rutile form, a broad emission band at 850 nm and 77 K is observed [6,45]. An additional band at 1015 nm, with the 815 nm emission only being detected from rutile prepared via the sulphate route has also been reported [6].

Motivated by a desire to investigate the dynamics of photocarriers in practical systems and their relevance to the durability of pigmented systems, the emission spectra of a series of industrially prepared nanoparticle and pigmentary titanium dioxide pigments with different particle sizes are examined here. Photoluminescence spectra from the anatase pigments and rutile pigments under near band gap excitation at 77 K are shown in Figures 8 and 9 respectively. All the samples of pigments gave rise to low intensity Stokes' shifted green emission in the wavelength region 450–750 nm. This reached a maximum intensity at about 580 nm. The spectral shape and position were not influenced by the excitation wavelength. Given that the charge carrier recombination for electrons and holes occurs in the 10–100 ns time domain, the luminescence centres observed here, are analogous of the long-lived states described [45] from rutile pigments.

Figure 12 shows the emission bands recorded under identical instrumental conditions for the nanoparticle pigments; a direct comparison is justified as all materials are derived from the same starting material (colloidal gel). The pigmentary grade A, exhibits the greatest emission intensity followed by the less intense nano-particle grade H. In the case of pigment H, the presence of the surface treatment will induce greater enhanced recombination of electrons and holes at the surface. The observed phosphorescence spectra can be attributed to the radiative recombination process of either self-trapped excitons or hydroxylated Ti<sup>3+</sup> surface ion/complexes from the charge transfer excited state of the highly dispersed titanium dioxide species.



Figure 8: Low temperature (77 K) emission spectra from the rutile pigments (excitation wavelength=340 nm).

For the uncoated nano-particles the intensity decreased in the order G > F > E, which follows the increase in particle size and decrease in surface area. The product resulting from the drying of the primary material, pigment G showed the highest luminescence of the uncoated nanoparticles. Indeed, this comportment is attributed to the poor crystallinity observed by X-ray analysis and TEM. The amorphous characters of compound G induces high concentration of defects, each one acts as a recombination centre when electrons and holes were generated under illumination. These defects are detected by luminescence spectroscopy. Thus the decrease in intensity with increasing particle sizes might be attributable to the lack of structural defects as the samples become more crystalline at higher calcination temperatures and therefore with less recombination centres. The reduction of phosphorescence intensity with the increase in the calcinations temperature (increase of particle size) indicates the decrease of radiative recombination processes. Hence, these results show that calcination is an effective treatment to increase the photoactivity of nanosized TiO<sub>2</sub> photocatalysts resulting from the improvement of crystallinity. Figure 12 shows the production of green emission, albeit weak, from the rutile pigments coupled with a longer wavelength weak infra-red emission at 712 nm.



Figure 9: Low temperature (77 K) emission spectra from the anatase pigments (excitation wavelength=340 nm).

The more heavily coated pigment D exhibits the greatest intensity due to enhanced recombination of electrons and holes at the pigment surface. The less well coated pigments B and C give lower intensities. In a practical sense, coating enhances pigmentary characteristics including durability, gloss and dispersibility in a polymeric system, where the inner surface oxide provides a physical barrier to photoredox reactions. The increased green emission intensity indicates that the coating process has introduced recombination centres into the material.

#### Microwave analysis

Real-time microwave measurements facilitate observation of both changes in conductivity and dielectric constant during irradiation of photoconductors In essence, the apparatus consists of a tuned microwave cavity, which concentrates the microwave field at the sample, with shifts in resonant frequency  $(f_0)$  and Quality factor (Q) being monitoring during ultra-band-gap exposure. Unlike time resolved microwave conductivity (TRMC) measurements, which monitor decay of conductivity following a high intensity pulse of irradiation, the real-time method adopted here permits simultaneous measurement of changes in the cavity resonant frequency and in the quality factor during sample illumination. These changes are proportional to changes in a real and in imaginary parts of dielectric constant according to a cavity perturbation theory. Usually (but not always) conduction band electrons cause a change in the conductivity of the material related to a change of cavity quality factor (photoconductivity). Trapped electrons cause a change in the real part of dielectric constant related to a shift in the resonance frequency (photodielectric effect). As a result, this technique registers both free and trapped electron kinetics. The link between cavity parameter and the photophysics of the samples applied here, was developed from the work of Hartwig and Hinds [47] and are summarised in Table 7.

# Table 7: Relative magnitude and sign of changes in resonant frequency (f<sub>0</sub>) and quality factor (Q) for a loaded microwave cavity under illumination.

	Free carriers	Trapped carriers (shallow)	Trapped carriers (deep)
$DF_0$	Small/+ve	Large/-ve	Small/- <sup>ve</sup>
DQ	Large/+ve	Small/- <sup>ve</sup>	Very small/- <sup>ve</sup>

These workers demonstrated that the cavity resonant frequency decreases due to trapped carriers which increases the dielectric constant and increases due to the decreased dielectric constant of delocalised carriers. Attenuation of microwave power may be attributed to delocalised carriers, which reduce the quality factor of the loaded cavity. Furthermore, it was concluded that shallow trapped carriers (with trapped depths < 100 meV) perturb both the cavity Q and the resonant frequency. A qualitative interpretation of the photoactivity of a pigment, on the basis of the microwave response requires a consideration of the interplay between charge carrier recombination, trapping and interfacial charge transfer. The initial attenuation of the microwave power and the initial shift in cavity resonant frequency for our pigment powders prior to the irradiation related to the empty cavity are given in Figure 10. The initial shift in frequency with respect to the empty cavity is dependent upon the polarisability of the material and it is proportional to the imaginary part of the susceptibility of the material. The higher the shift of the resonant frequency relative to the empty cavity implies being more polarisable and consequently a greater proportion of impurities/ traps. There is a pigment, which shows a much greater shift in frequency, pigment G, which would imply more impurities and traps. As commented before, the poor crystallinity of this uncalcined pigment is expected to contain more defects, which are apparently detected by microwave dielectric spectroscopy. On the other hand, it is interesting to note that there is linear correlation between the initial attenuation of power and the surface area of the anatase photocatalysts A, E, F and G with an R-squared value of 0.98. The initial attenuation of powder is proportional to the density of the material. Pigments with increasing BET surface area produce much greater attenuation in the power.



Figure 10: Initial cavity frequency and power shifts for the different pigments prior to the irradiation.



Figure 11: Shift of microwave cavity resonant frequency for titania pigments during consecutives periods of light exposure and darkness under visible light.

The photodielectric behaviour (shift in frequency Df) of the pigment samples in the cavity are summarised in Figure 11. For the anatase pigmentary pigment A, it was noted that the resonant frequency moved towards lower frequency values when this sample was irradiated. For the other samples, it was found that the shift was towards higher frequency values which are in the opposite direction to that obtained for the pigmentary

anatase. The positive values for Df for the nanoparticle anatase and rutile pigments are illustrated on Figure 12. The negative shift for the pigmentary pigment A is a consequence of its higher concentration of trapped carriers compared to the rest of the pigments. As displayed in Table 7 traps have a major effect upon the resonant frequency, they increase the dielectric constant and shift the resonant frequency towards negative values. On the other hand, free carriers decrease the dielectric constant and the shift that they produced is towards higher frequencies.

For the pigmentary pigment, pigment A, a small number of free radicals are produced due to its high recombination rate and trapping; therefore its frequency shift is determined by the trapped carriers centres present in this titania. This results correlate with the results obtained by phosphorescence spectroscopy where pigment A showed the highest luminescence. Luminescence is produced by the interaction of a hole with an impurity centre (trap). Luminescence results showed that pigment A had the highest luminescence signal, therefore more traps, this is consistent with the negative shift in frequency for this titania by Microwave dielectric spectroscopy found for pigment A.



# Figure 12: Shift of microwave cavity resonant frequency for titania pigments during consecutives periods of light exposure and darkness under visible light.

The positive shift of frequency Df (Figure 12) during sample irradiation is a consequence of the dominance of photoproduced free-carriers. The uncoated rutile pigment B exhibited a greater shift in the resonant frequency than the coated samples C and D. This lower shift in frequency for sample C and D might be associated with their lower photoactivity and is consistent with their higher phosphorescence values. Enhanced recombination of electrons and holes at the pigment surface for pigments C and especially D verified by phosphorescence, reflects on less free carriers as measured by Microwave Dielectric Spectroscopy.

Pigment A, quickly reaches the equilibrium between charge carrier recombination, trapping and interfacial charge transfer. The negative shift in the power and the frequency, proves that this pigment has many more traps that any of the other pigments. Its negative frequency shift means that the contribution of the trapped electrons is much higher than that of the free electrons, suggesting a very low concentration of free electrons for this pigment and therefore a low activity. The large number of traps present on this titania were also verified by phosphorescence. For the remainder of the titania pigments (Figure 14), the frequency shift and the quality factor shift is positive and originates from free electrons promoted from the valence up to the conduction band.



Time (Seconds)

Figure 13: Shift of cavity microwave power for titania pigments during consecutives periods of light exposure and darkness under visible light.

The data depicted in Figure 13 relates to the response of the titanium dioxide powders in terms of changes of the microwave power. Hence, higher values of DQ result from the generation of more free radicals by the pigment when exposed to visible light. The graph shows that, during irradiation, the change in microwave power is lower in the case of alumina coated rutile pigments B, C and D respectively. This is consistent with a reduction in free carrier population and enhanced trapping and recombination as in the case of the more heavily coated grade D. The nanoparticles E, F and G show an interesting behaviour. They all exhibit greater carrier generation than the rutile pigments hence greater activity. There are various factors that explain the higher activity of the nanoparticle products relative to pigmentary TiO<sub>2</sub>. To begin with, blue shifts caused by nanoscale effects enhance the band gap, which in turn increases the redox potential. One of the major limitations in semiconductor photocatalysis is the relatively low value of the overall quantum efficiency mainly because of the high rate of recombination of photoinduced electron-hole pairs at or near the surface. Some success in enhancing the efficiencies of photocatalysts can been achieved using nano-sized semiconductor crystallites instead of bulk materials [48]. Usually, electrons and holes need to diffuse to catalyst surfaces, where they are captured by electron and hole acceptors. If the dimensions of nanoscale particles are so small that the diffusion of electrons and holes

to the surfaces is faster than the recombination process, the photoefficiency would be enhanced by employing such ultrasmall particles. In comparison with bulk semiconductors, the nanoscale semiconductor retards the electron-hole recombination via charge carrier trapping. Moreover, the transport time for charge carriers to reach the surface from the interior can be estimated by the carrier diffusion equation. For large TiO<sub>2</sub> particle of 1 mm, the electron transport time is 100 ns, while for TiO<sub>2</sub> nanoparticles of 10 nm, the electron transport time is 10 ps. In other words, the smaller the particle size is, the shorter the electron transport time. In general, the recombination time is estimated to be a few nanoseconds Hence, the separation efficiency of photoinduced carriers is very high for semiconductor nanoparticles, so that the activity of semiconductor nanoparticles may be higher than that of conventional semiconductor particles, that is to say, the smaller the size of semiconductor particle is, the higher the photocatalytic activity may be. However, our experimental results are in contradiction with this speculation because crystalline structure is another factor influencing photoactivity. From our experimental results, there is an inverse correlation between activity and particle size where the nanoparticle with the highest particles size shows the highest activity and the nanoparticle with the highest surface area. Pigment G, after a fast initial rise in carrier production, displays a strong plateau due to strong trapping followed by a sharp dark decay to the valence state after extinguishing the light source, due to carrier recombination. Pigment G did not suffer any thermal treatment to improve its crystallinity, it was just dried. Hence, the amorphous characteristics of this compound induces a high concentration of defects that are able to trap out the carriers. No such rapid dark recombinations were evident in the case of the pigments E and F. The dark recombination process in pigments E and F suggests that excess carriers are trapped in deep lying states giving rise to the observed long lived residual component in the decay process. This would certainly account in part, for the apparent lower photoactivity of pigment G in the 2-propanol activity test than E and F as will be seen below. A high level of crystallinity compensates the lower specific surface area of pigment E. This crystallinity results in a higher efficiency generating free carriers. Again, the much rapid recombination rate of pigment G is evident. This will undoubtedly decrease its overall activity in real system as their carriers recombine much faster. Table 8 depicts the free carriers relaxation lifetime after switching of the light for comparison purposes by measuring the time it takes for the quality factor after 1800 seconds ( $Q_0$ ) to decrease to  $Q_0/e$ .

Pigment	Relaxation time Visible light	Relaxation time UV light
Е	1093	695
F	>1800	750
G	125	88
Н	480	340

#### Table 8: Free carriers relaxation lifetimes for nanoparticle pigments

It is evident from Table 8 that the relaxation times for the free carriers generated in pigment G are considerably lower than those in pigments E and F. These results prove that crystallite structure is a main factor influencing photoactivity. Poor crystallinity and defects on crystal planes are responsible for the relative low life of the free carriers of pigment G in comparison with pigments F and E.

# **Hydroxyl Content**

The hydroxyl content relates to the concentration of hydroxyl functionalities present on the pigment particles and is often related to activity. The increase in surface hydroxyl content will trap more photo-generated holes and thus prevent electron-hole recombination and consequently enhance the photocatalytic activity. The data for hydroxyl content are shown in Table 9 where it is noted that some of the pigments were pre-dried before the analysis for twelve hours at 150 °C to remove moisture. There are a number of trends within the data. Firstly, all the nanoparticle grades exhibit higher OH contents than the pigmentary grades. For the pigmentary pigments, anatase A has more hydroxyls than the rutile types B and D, the latter being the least active and most durable pigment.

Figure 13 depicts the OH content for each of the prepared nanoparticle products and the pigmentary pigment A against the surface area of each of the photocatalysts. Interestingly, there is a linear correlation between surface area and OH content for pigments A, E, F and I. However, pigment G does not fit as the OH content appears to reach a limiting value at surface areas higher than 150 m<sup>2</sup>/g. This will certainly account for part of the lower activity shown by this pigment.

Interestingly, although the water content followed a linear correlation with the surface area, the OH content of pigment G does not. In addition, the number of hydroxyl groups on the surface of the TiO<sub>2</sub> will undoubtedly affect the adsorption of reactants on the surface of TiO<sub>2</sub>, probably favouring the adsorption of hydrophilic compounds.

Pigment sample	OH content
A-Unheated	0.05
A-Heated	0.04
D-Heated	0.02
E-Unheated	0.35
E-Heated	0.32
F-Unheated	0.52
F-Heated	0.53
G-Unheated	0.78
G-Heated	0.78
H-Heated	0.20
I-Heated	0.82

# Table 9: Hydroxyl values for various micron and nanoparticle titanium dioxide pigments.



Figure 13: Dependence of the OH content versus the BET surface area for pigments A, E, F, G and I.

# **2-Propanol Oxidation**

Recent reports have shown that nanostructured anatase TiO<sub>2</sub> exhibited higher activity than the commercial Degussa P-25, for the gas-phase photocatalytic oxidation (PCO) of Volatile organic compounds (VOCs) [49]. The nanostructured TiO<sub>2</sub> provides a larger surface area for adsorption and decomposition of VOCs. Quantum size effect was also observed for the nanometer sized nanoparticles [38]. The oxidation of 2-propanol to yield acetone is a specific methodology to determine pigment photoactivity and here has been related to oxygen consumption during irradiation of the medium in the presence of the titania pigments [22]. Hence, the catalytic activity of the nanometer-sized TiO<sub>2</sub> was investigated using gas-phase photo-oxidation of 2-propanol as a probe reaction. Results for this test for oxygen consumption are shown in Table 10 and plotted against surface area in Figure 14.

# Table 10: Photoactivity tests on oxidation of 2-propanol and hydroxyl values for various micron and nanoparticle titanium dioxide pigments

Pigment sample	OH content	Oxygen consumption (%)
A-Unheated	0.05	1.3
A-Heated	-	1.0
B-Heated	-	0.6
D-Heated	0.02	0.3
E-Unheated	0.35	3.1
E-Heated	0.32	3.6
F-Unheated	0.52	4.1
F-Heated	0.53	4.9
G-Unheated	0.78	3.0
G-Heated	0.78	3.9
H-Heated	0.20	4.3
I-Heated	0.82	6.3
2-Propanol control	-	0.2



# Figure 14: Dependence of the surface area versus OH content and oxygen consumption for the different pigments.

It is clear from Figure 14 (contains the insert of Figure 13) that the photocatalytic activity of the TiO<sub>2</sub> is strongly influenced by crystal size. As the size of TiO<sub>2</sub> diminishes from A to I the oxygen consumption increases. For the photo-oxidation of 2-propanol, the reaction data indicates that surface area plays a dominant role for TiO<sub>2</sub> with primary particle size larger than 10 nm (pigment G). From the microwave dielectric technique, pigment E was found more active at generating radicals compared with pigments F and G. In other words, its intrinsic activity was higher. However, for this particular system (2-propanol oxidation), the smaller crystals of pigment F and I offer a larger surface area for the adsorption of reactants. This makes a positive contribution to the catalyst reactivity towards 2-propanol oxidation which results in a higher activity for these two photocatalysts. The subsequent drop in reactivity for pigment G indicates that in addition to the requirement of appropriate particle size, crystallinity is also important for the achievement of high photoefficiencies. The drop in reactivity for pigment G is attributed to structural and electronic defects as verified by Microwave and phosphorescence spectroscopy. By virtue of their high surface area, nanoscale particles possess a high concentration of active sites. In this study a surface area of 100 to 160  $m^2/g$  is the optimal value for the decomposition of 2-propanol. By relating surface area to photocatalysis data, these data indicate that appropriate surface areas are critical for high photoactivity of TiO<sub>2</sub> catalysts. Too high (pigment G) or too low (Pigment E) surface areas will result in poor photoactivity.

The different photocatalytic properties of  $TiO_2$  pigments must be due to different bulk and or surface properties for each of the photocatalysts. The bulk properties determine the process of charge carrier photogeneration and diffusion, whereas those of the surface influence both organic molecular adsorption and the generation of species necessary for photoreaction. The 2-propanol oxidation results might appear to be in contradiction with the results obtained by Microwave Dielectric spectroscopy and phosphorescence in which a higher intrinsic activity was attributed to pigment E rather than F or I. However, the catalyst efficiency is also related to the molecule to be degraded. This effect is not taken into account when assessing the activity by the Microwave Dielectric Spectroscopy, technique which measures the intrinsic activity of the pigments. In real application systems, the activities shown by the same pigment grades might vary depending on the pollutant studied. These variations in the photocatalytic efficiencies for different photocatalyst may be due to several factors listed:

- 1.Differences in the crystalline phase of the titania (anatase versus rutile- the latter known to be relatively inactive).
- 2.Differences in the size and shape of the particles, thereby affecting the extend of light scattered.
- 3.Differences in the density of OH- groups on the particle surface and in the number of water molecules hydrating the surface.
- 4.Differences in the numbers and nature of trap sites both in the lattice and at the surface.
- 5.Differences in the number of photogenerated free carriers.
- 6. Finally, the adsorption desorption characteristics of each surface, which might vary according to the nature of the photocatalyst material and also the nature of the organic substrate (pollutant).

All these factors are important when it comes to evaluate the photoactivity of TiO<sub>2</sub> pigments. Different tests can be performed to analyse the importance of each of the factors for different pigments. For instance, Microwave Dielectric Spectroscopy provides information mainly about factors 4 and 5 whereas FTIR spectroscopy gives us information about factor 3. However there is no universal test for approving one TiO<sub>2</sub> for photocatalytic purposes. In other words, different activity orders can be found for the same grades of TiO<sub>2</sub> depending on the technique and pollutant used for the analysis. As a results, the assessment of pigments activities using only one technique or only one molecule as a pollutant is not sufficient because the development of certain affinity occurs between the catalyst and pollutant.

When studying the degradation of organic pollutants (like 2-propanol) by  $TiO_2$ , the adsorption of the pollutant on the  $TiO_2$  surface is known to play an important role on the activity as the contact between oxidative radicals and the pollutants facilitates the reaction. Hence, adsorption plays a major role in the activity.

For example, in one study [50] with a range of  $TiO_2$  pigments with different particle sizes, the effect of the pollutant adsorption onto the  $TiO_2$  was studied. They reported that strongly adsorbed pollutants were more efficiently converted to non-toxic substances by pigments with high surface area. In this case, it was claimed that the process was more sensitive to texture (surface area). When low absorption pollutants were used, the best products for photocatalytic decomposition were the highly crystalline products. The process was then more sensitive to structure (crystallinity). Our experimental results seem to indicate that the oxidation of 2-propanol is more sensitive to texture (surface area) rather than to structure (crystallinity). In fact, a higher adsorption of the 2-propanol onto pigments with a higher content of OH groups (pigment F and I) will be facilitated due to interaction forces between the OH groups present in both pollutant and photocatalyst. The drop in activity for pigment G, the one with the highest surface area indicates that an optimum efficiency would be obtained with a surface area combining a large adsorption and a limited electron hole recombination.

#### **Polyethylene Oxidation**

In this section activity studies in a solid metallocene polyethylene matrix makes an interesting comparison. Taking the initial hydroperoxide levels in the polyethylene films make an interesting comparison (Table 11). One interesting feature is that the pigmentary grades of titania pigments (A –D) in conjunction with Irganox<sup>®</sup> 1010, results in enhanced suppression of hydroperoxide formation, relative to when Irganox<sup>®</sup> 1010 is used alone. For the more heavily coated grades, (C+D) the level of suppression activity increases with pigment loading.

Pigment	[ROOH] Unpigmented	[ROOH] 0.1%	[ROOH] 0.5%	[ROOH] 1%	[ROOH] 2%
None (PE control-unstabilised)	181	-	-	-	-
None (stabilised IRG 1010)	54	-	-	-	-
Pigment A	-	37	21	22	27
Pigment B	-	34	35	33	32
Pigment C	-	26	21	18	5
Pigment D	-	2	24	22	6
Pigment E	-	23	21	15	214
Pigment F	-	30	60	179	237
Pigment G	-	28	108	180	44
Pigment H	-	32	19	38	55
Pigment I	-	39	99	135	138

Table 11: Initial hydroperoxide values of metallocene polyethylene samples Brabendered with various titanium dioxide pigments (Mol/L). All pigment films have Irganox 1010.

On the other hand, all the nanoparticles E–I exhibited much higher levels of initial hydroperoxides. These higher values for the uncoated nanoparticles, coincides with a noticeable yellowing formation (data not shown) during processing due to an interaction between the pigment surface and IRG<sup>®</sup> 1010, this interaction destroyed in part, the stabilising effect of IRGANOX <sup>®</sup> 1010. This is normally due to the pigments catalysing the photooxidation of the phenolic antioxidant to quinones [50,51]. Most metal based photocatalysts are renown in this respect. Of the uncoated anatase grades pigments, E and F exhibited the highest values. It would appear that greater pigment particle contact with the matrix induces more oxidation/interaction during the processing. The anatase grade H gives much lower levels of hydroperoxides indicating the protective influence of the hydroxy apatite coating. On subsequent photo-oxidation prior levels of hydroperoxides can play a significant role in controlling post stability or activity in the polymer.

### **Photoageing**

In the absence of  $TiO_2$ , the initiation of the photodegradation of polymers is due to photolytic reactions that are dependent on the presence of chromophores that absorb UV light within the wavelength of sunlight. For most polymers these chromophores are hydroperoxides and carbonyls formed during polymerisation, storage or processing. When titanium dioxide is present in a polymer film, its photostability is going to be affected mostly by the nature of the pigment. For example if the pigment absorbs or screens light energy, the protection of the polymer will result, for instance in electrons and holes generated by the transitions from the valence to the conduction band in the  $TiO_2$  that could lead to the production of free radicals like OH• and HO<sub>2</sub>•, which sensitise the photochemical breakdown of the polymer. The extent of each reactions will determine whether the pigment protects or degrades the polymer. From the photooxidation rates of the polyethylene films with nano and micron scale titania

particles embrittlement times are collated in Table 11 for irradiation in the Microscal unit. All the films except for the control (unstabilised) contain a base phenolic antioxidant IRG<sup>®</sup> 1010.

The most significant feature of the results is the high photocatalytic activity of all the nanoparticle anatase pigments; the effect increasing with increasing concentration from 0.1 to 2.0% w/w. Thus, the finer nanoparticle clearly have a greater particle-matrix contact inducing more oxidation. Untreated nanoparticle rutile I is also photoactive but less effective than any of the anatase grades. The pigmentary anatase A is less active than any of the nanoparticle grades (E-I). Thus, the finer nanoparticles clearly have a greater particle matrix contact inducing more oxidation. Secondly, the rates of oxidation for the nanoparticle at loadings higher than 0.1% are all autocatalytic with no induction period prior to the onset of carbonyl formation. For the untreated anatase nanoparticles E, F and G there is no direct correlation between activity and particle size. Of the three types F (with an intermediate particle size) is the most active, followed by pigment E, while the smallest pigment, the one with the highest surface area, showed the lowest activity. It is interesting to note at this stage of the discussion that the 2-propanol oxidation experimental results confirms the order in efficiency found for the nanoparticles in the Microscal. Therefore, the photocatalytic oxidation of the polymer films seems to be more sensitive to texture (surface area) than to structure (crystallinity). The anatase pigment H exhibits the highest activity, which confirms the importance of surface area for the photocatalytic oxidation of polymer films. Pigment H was proved by Microwave Dielectric Spectroscopy to be intrinsically less active than the thermally treated nanoparticle pigments. However, here, its superior dispersability will enhance the pigmentmatrix contact inducing more oxidation in formulations containing this pigment.

As mentioned before, the photoactivity is dependent on previous thermal degradation. This effect could lead to erroneous assignments of photoactivities. For example, if the differences between pigments H and I are examined, it is evident that pigment I showed strong catalytic effects during processing resulting in very high levels of hydroperoxides (see Table 11) probably due to the interaction of IRG ®1010 with the OH groups of pigment I. Pigment H, however, inhibited hydroperoxide formation and low concentrations were detected.

When films containing these two pigments are exposed to UV light, they show photosensitisation relative to the control polymer; but for pigment I most of this apparent photoactivity is due to the photodecomposition of abundant hydroperoxides groups formed during melt processing, rather than photoactivation associated with the light absorption of this TiO<sub>2</sub>. On the other hand the photoactivity of pigment H has to be assigned to its own ability to absorb light generating radicals as the initial concentration of hydroperoxide groups are lower for pigment H than for that of the control sample.

Table 12: Time to 0.1 Carbonyl index (Taken as embrittlement time) for the titania
pigmented polyethylene films irradiated in the Microscal unit.

Pigment(%)	Control polymer	Control +Irganox 1010	A	В	С	D	Ε	F	G	Η	Ι
None	213	595	-	-	-	-	-	-	-	-	-
0.1	-	-	402	592	630	719	363	300	391	252	491
0.5	-	-	359	494	605	841	140	103	187	92	271
1.0	-	-	211	436	575	900	110	69	115	69	181
2.0	-	-	166	290	500	809	86	45	122	41	200

The pigmentary grades of rutile, B, C and D, exhibit a different activity. Here stabilisation increases with increasing levels of coating of alumina, D being the most stable pigment. It is common knowledge that the photochemical reactivity of TiO<sub>2</sub> pigments may be reduced by treating the surface of the particles, this treatment inhibits the photo-reduction of the pigment by UV-radiation and destructive oxidation does not take place. In the case of pigments B and C, with a lower alumina coating than for pigment D, the sensitisation increases with increasing pigment concentration while for the pigment D its stabilising effect increases when the pigment loading is higher. This suggests that pigment D yields an overall protecting effect when interacting with UV light while the overall effect of pigments B and C is as a prooxidant. Hence, pigment D absorbs, reflects or scatters potentially dangerous UV light for the pigment than for the control polymer without pigment.

The general behaviour of the pigments in the QUV resembles the Microscal data as embrittlement times given in Table 12 reveal. QUV photodegradation results confirm the higher activity of the nano-size TiO<sub>2</sub> compared with the pigmentary TiO<sub>2</sub>. Moreover, pigmentary grades of rutile, B, C and D exhibited the same stabilising effect as shown in the Microscal.

Table 13: Time to 0.1 carbonyl index (taken as embrittlement time) for the titani	ia
pigmented polyethylene films irradiated in the QUV.	

Pigment (%)	Control polymer	Control +Irganox 1010	A	В	С	D	Ε	F	G	Η	Ι
None	68	111	-	-	-	-	-	-	-	-	-
0.1	-	-	99.5	168	170	168	80	83.5	110	65	121
0.5	-	-	96	152	178	252	64	52	118	51	103
1.0	-	-	76	122	283	234	68	51	89	64	89
2.0	-	-	89.5	185	222	430	75	62	144	54	110

However, an important difference was observed for samples aged in the QUV weathering machine (Figure 13). Here, pigmented films showed no clear increase in activity with increasing loading of pigment from 0.1 to 2.0%w/w. In order to explain this behaviour, the difference in degradation conditions inside the QUV and the Microscal unit must be considered. First, the light intensity output for the QUV is higher than that for the Microscal unit. Secondly, the temperature of the QUV during the irradiation cycle is 60 °C while the temperature in the Microscal goes up to around 45 °C. However, the main difference between the two weathering machines is the condensation cycle in the QUV at 40 °C. Inside the QUV, half of the exposure time is under wet conditions. The effect of the presence of water in the degradation behaviour is multiple. First, the sensitising activity of the TiO<sub>2</sub> is enhanced, because water is an intermediate reactive of the catalytic generation of radicals by TiO<sub>2</sub>. Secondly these radicals must be transported from the TiO<sub>2</sub> surface to the organic binder molecules, and water is regarded as the medium for this transport. In addition, as the initial hydrophobic binder molecules become oxidized, their solubility in water increases and soluble products of partial degradation are removed by water.

Finally and most importantly, the presence of water during the condensation cycle was responsible for the severe chalking that was observed for the films aged in the QUV in

comparison with the Microscal aged films. Under these conditions, and mainly by the action of water, mass loss is occurring all the time. Liquid water removes the top layer of degraded material and the film surface is then coated with a layer of TiO<sub>2</sub>. These particles prevent further direct degradation by shielding the underlying polymer from UV light. At the same time, these particles do not contribute to photocatalytic degradation since they are no longer in close contact with the polymer. The polymer degradation starts again if this layer of pigment is washed from the surface (either by the water or mechanically).

In a polymer film, the amount of binder that has to be removed from the surface for the chalking to appear decreases when the pigment concentration is increased or when the particle size of the pigment is decreased. This is believed to be the reason why the carbonyl index does not follow the expected behaviour with concentration, in the QUV. For example for highly active pigments like E, F and H, the initial fast growth of the carbonyl index for 1 and 2% w/w concentrations is gradually attenuated by the appearance of the TiO<sub>2</sub> chalk layer which shields the light and by the removal of soluble carbonyl products of partial degradation. For the 0.1 and 0.5% concentrations, higher amounts of polymer are still available to be degraded prior to the appearance of the layer of chalk. Thus, their carbonyl index reaches the 0.1 value more rapidly because in this case, the rate of generation of carbonyl groups is higher than the rate of disappearance by washing.

# **CONCLUSIONS**

The nanoparticle TiO<sub>2</sub> powders were prepared via the sulphate route, this approach afforded a precise control over the primary particle sizes of TiO<sub>2</sub> catalyst along with their crystallinephase structure and morphology. The prepared powders were characterised using N<sub>2</sub> Brunauer-Emmett-Teller (BET) surface area, X-ray Diffraction (XRD), CPS Disc Centrifuge, Transmission Electron Microscope (TEM), Scanning Electron Micrographs (SEM), Thermogravimetric analysis (TGA) and Fourier Transform Infrared Measurements (DRIFTS). In addition, the activities of the different catalysts were determined via rapid assessment methodologies like Microwave Dielectric Spectroscopy (MDS), Hydroxyl Content, Phosphorescence, Chemiluminescence and Isopropanol Oxidation Test.

BET measurements and XRD patterns combined with the Scherrer equation showed that the catalysts have surface areas between 50-330 m<sup>2</sup>g<sup>-1</sup> and average diameters of 10- 0 nm, contain anatase, and show high activity. Quantum size effects, which lead to high surface areas and blue shifts and diminished electron-hole recombination, are used to explain the high activities of the nanoparticle products. In situ FTIR data and OH content determination show the presence of high contents of hydroxyl groups and large amounts of adsorbed water on the TiO<sub>2</sub> nanoparticle. The Disc Centrifuge results and BET surface area combined with the XRD particle size results show that a careful distinction between the crystal and aggregate sizes must be made in order to properly interpret the activity of TiO<sub>2</sub> pigments. Aggregation of TiO<sub>2</sub> pigments affects not only the surface area offered by the TiO<sub>2</sub> to react with the pollutants but also the type of interaction between the light and the TiO<sub>2</sub>. The treatment conditions used for the crystallization of the primary material (precursor) in order to prepare the rest of the nanoparticle pigments, not only influenced the anatase crystal size but also other anatase properties (such as the surface hydroxylation, adsorbed water, recombination rate, aggregation state and number of structural defects) that determine the photocatalytic properties of these photocatalysts. Nanoparticle pigments produced at low calcination temperatures possess more structural defects. Each one acts as a recombination centre when electrons and holes are generated under illumination, thus, decreasing the final activity. This

poor crystallinity and defects on crystal planes are responsible for the low photoactivity of the smallest nanoparticle pigment G. The photoactivities of the calcined nanoparticle catalysts E and F are higher than that of the catalyst G as the higher level of crystallinity compensates the lower specific surface area of pigments E and F. This crystallinity results in a higher efficiency generating free carriers. Hence, calcination is an effective treatment to increase the photoactivity of nanosized TiO<sub>2</sub> photocatalysts resulting from the improvement of crystallinity. The photocatalytic activity decreases significantly for the micron size pigment A, calcined at the highest temperature, since semiconductors in larger size particles results in the recombination of holes and electrons at a higher rate. The low temperature phosphorescence measurements of anatase TiO<sub>2</sub> pigments; show a sensitivity to coating and structural defects within the lattice. Hence, the intensity of the green excitonic emission correlates with the photoactivity of the pigments, recombination being enhanced in samples calcined at lower temperatures. Microwave Dielectric spectroscopy can be an effective method for quickly evaluating the photocatalytic activity of semiconductor materials since it can provide a rapid, non-destructive monitor of the charge carriers production, recombination and trapping with the aid of light. A clear correlation was found between the photoactivity prediction given by the Microwave spectroscopy (E > F > G > A) and the photoactivity order found by phosphorescence spectroscopy. Here, samples with less structural defects within the lattice determined by Phosphorescence correlate with more free radicals measured by Microwave dielectric spectroscopy. This, we believe is a useful application, which could form the basis of an effective characterisation technique for TiO<sub>2</sub> pigments. It is concluded that the assessment of activity using only one molecule or one rapid assessment technique is not sufficient because the development of certain affinity occur between the catalyst and pollutant. Finally, the titania pigments and nanoparticles themselves also give rise to CL which, although low, at this moment in time is being investigated further in relation to the surface activity of these commercially important materials but to date indicates the importance of probable surface active peroxidic groups.

Photooxidation studies on metallocene polyethylene containing nanoparticle and pigmentary grade titanium dioxide pigments show that anatase nanoparticles are more photoactive than conventional pigmentary micron size  $TiO_2$  and rutile nanoparticle pigments. Hydroxy apatite coated anatase nanoparticle H was also highly active, this activity being enhanced by its superior dispersability. The pigmentary grades of rutile B, C and D exhibit a different activity. Here stabilisation activity increases with increasing levels of alumina coating. The anomalous behaviour exhibited by the polymer formulations under QUV exposures, where there was no direct correlation between loading and activity, indicates the importance of erosion (chalking) related issues. Carbonyl index measurement is only valid in cases where chalking has not occurred. As such when weathering pigmented polymers its crucial that the setup in the ageing trials closely match those for the materials end-use and therefore, there is not universal test procedure for pigmented materials.

A clear correlation was found between the photoactivity prediction given by the 2-propanol oxidation tests and the photoactivity ranking of the polyethylene. This correlation shows that the main limiting factor determining the activity of  $TiO_2$  nanoparticle pigments on the polymer is the surface area of the photocatalyst. In other words, the process is more sensitive to the texture (surface area of the photocatalyst) rather than to the structure (crystallinity). However, the ability to interact with light and generate radicals of each photocatalyst has to be taken into account as well. Hence, during photodegradation there was no direct correlation between activity and particle size because pigment G although it has the highest surface area has very low efficiency generating free radicals. SEM analysis clearly shows the formation of

holes or pits formed as a consequence of oxidation of the polymer at the particle surface and subsequently spreading out from the particle. Untreated nanoparticle pigments induce oxidation of the polymer during processing. Such effects can play a major role in controlling the photoactivity of the pigments in a polymer matrix where initial hydroperoxide levels can be important.

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