



Surface properties of recycled titanium oxide recovered from paint waste

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ABSTRACT

Aluminium oxide coated rutile pigment was extracted from a paint matrix by means of a thermal recycling process. The objective was to investigate the effect of the recycling process on the surface properties of the pigment. The pigment was analysed using powder x-ray diffraction (XRD), surface area measurements (BET), laser diffraction for particle size analysis and X-ray photoelectron spectroscopy (XPS) before and after the recycling process. Investigations on the zeta potential and the surface charge were performed as well. It was concluded that the rutile crystalline core and the aluminium oxide coating of the pigment were still intact after the recycling process. The particle size distribution of the recycled pigment was slightly broader compared to the virgin pigment. The measured magnitude in zeta potential of the recycled pigment was lower than for the virgin pigment. This difference is thought to be caused by alteration in the surface hydroxyl concentration. Surface charge titrations showed differences between the virgin and the recycled pigment at alkaline pH and at low salt concentrations.

1. Introduction

Titanium minerals are of great technical importance in today's society. In 2011, the world production of titanium containing minerals was 6.7 million metric tonnes [1]. Of that, the vast majority was used to produce TiO₂ for use as a white pigment in paints, coatings, plastics and papers [2,3]. TiO₂ is the major white pigment used by the coatings industry [4] due to its abundance and its ability to scatter visible light while being chemically inert.

Typically, TiO₂ is produced using a sulphate or chloride route, both of which have a high carbon footprint per kilogram of TiO₂ produced. It has been reported that even if new innovative production routes are developed the carbon footprint per kg TiO₂ produced would still be high [5]. The European Union (EU) has recognized the environmental impact of TiO₂ production and has consequently set restrictions on the amount of TiO₂ allowed to be used in paint formulations if the paints are to qualify for the voluntary Ecolabel labelling [6]. In the future, waste management of old paint residues may also be included in the Ecolabel criteria [7].

Even before regulatory guidelines were in place, the coatings industry has strived to find a replacement for TiO₂ due to its relatively

high cost compared to other coating components [8]. One appealing approach is the recovery of TiO₂ from paint waste, as it could benefit the coatings industry in two ways. First, recovered TiO₂ may be a cheaper and more environmentally friendly replacement for virgin TiO₂ produced by conventional high carbon footprint routes. Second, a successful TiO₂ recovery process could be a cornerstone in the waste management of old paint residues and production waste from manufacturing plants.

TiO₂ is often mentioned as the major white pigment but commercial grade pigment is frequently not pure TiO₂. The crystalline TiO₂ core is the active ingredient that provides the pigment's optical functions. However, the surface of the TiO₂ particles does not consist solely of titanium and oxygen. As the TiO₂ crystals grow during manufacturing, insoluble components accumulate on the surface. The components can be impurities from the ore or additives introduced deliberately to control the crystal structure, crystal growth, and particle agglomeration [9,10]. Besides these contaminants, the surface of a pigment is deliberately altered to suit the final application of the pigment. For instance, to reduce photoactivity and to improve the compatibility between the pigment and the other paint components, the surface of the TiO₂ pigment is commonly treated with silicon, aluminium and zirconium

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oxides. The surface of uncoated TiO₂ pigment shows a complex behaviour with different active groups, but a coated pigment can have an even more complex surface that is chemically very different to the bulk TiO₂ phase [11]. For the optimum opacity and durability of a paint film, a well dispersed pigment is a must. So, although it is no uncomplicated task, the surface characterization of a coated pigment is of importance in understanding pigment-medium interactions and its performance the final application [12].

In a previous TiO₂ recycling study [13] a white paint was pyrolysed at 500 °C in order to recover the inorganic components. In that study, TiO₂ was extracted together with the mineral extenders present in the paint, generating a pigment-extender mix consisting of roughly 45% TiO₂ and 55% mineral extenders, mainly dolomite. The recycled material was then used in a new paint formulation. It was concluded that using pyrolysis as a means to recycle TiO₂ resulted in a pigment-extender mix that could be used in a low-quality, flat paint, formulation if it was not for the large, millimetre size, agglomerates present in the paint. Since the recovered fraction was a mix of inorganic components, it was not possible to study in detail the agglomeration mechanism or the effect of the recycling process on the properties of the TiO₂ pigment. Therefore, it was decided to perform the next step of the work using a model paint based on TiO₂ as the sole pigment.

In the present work, a paint formulation based on alumina coated TiO₂ pigment (rutile) was prepared. The pigment was extracted from the paint matrix through a pyrolysis based recycling process. The pigment was analysed prior to and after the recycling process in terms of surface chemistry, both with electrokinetic measurements and with direct titration of surface groups. Additionally, the pigment were characterized using powder x-ray diffraction (XRD), surface area measurements (BET), laser diffraction for particle size analysis and X-ray photoelectron spectroscopy (XPS). The main purpose of this study was to understand the effects of the thermal recycling process on the surface characteristics of the pigment and identify the changes caused by the process. The knowledge of the surface characteristics will be useful in future studies when evaluating the dispersion stability of the pigments and their interactions with other paint components, such as dispersants and binder.

2. Materials and methods

2.1. Model paint

A white model paint was produced according to the formulation shown in Table 1. A commercially available pigment quality TiO₂, rutile coated with aluminium oxide, and all other paint components were acquired from Akzo Nobel Decorative Paints, UK. Typically, waste paint streams do not only contain TiO₂ as the inorganic component. Inorganic extenders are used in paints to give the final coating the desired properties, such as gloss or scrub resistance. However, those components were excluded from the model formulation. A simplified version of a paint waste stream will allow for a more in-depth analysis of the

properties of the recycled TiO₂ and the effects of the recycling process on the TiO₂ pigment specifically. The formulation, mixing and paint preparation was performed at Akzo Decorative Paints in Slough, UK.

2.2. Recovery process

The TiO₂ was recovered from the model paint presented in Table 1 by means of a pyrolysis process. The temperatures chosen in the thermal recovery process were based on previously published results [13]. By heating the paint in an inert atmosphere, the organic fraction was volatilized, separating it from the inorganic fraction. The volatilized organics were cooled and collected as an oil with the potential to be used as feedstock for a chemical process or as an energy source. After pyrolysis, the inorganic fraction was oxidized in air to remove residual carbon and non-pyrolyzed material, improving the colour of the recovered pigment. To further purify the recovered material it was dispersed in water with a mixture of ion exchangers. To finalize the recycled pigment the ion exchangers were separated from the pigment dispersion, which was dried and homogenized into a fine powder. A schematic of the recycling process can be found in the supplementary information.

2.2.1. Pyrolysis

The pyrolysis experiments were conducted in a Rohde, ME 45-13 furnace, fitted with a pyrolysis retort in corrosion resistant steel. The inner dimensions of the pyrolysis retort were 300 × 300 × 150 cm. During the experiments, the temperature was controlled using a TC 504 temperature controller. In addition, an external thermocouple was used to monitor the furnace temperature in relation to the set temperature. Before each experiment, the retort was filled with nitrogen gas (purity 99.9%) to an overpressure of 0.5–1 bar, emptied, and refilled again with nitrogen to overpressure. This was repeated three times to create an oxygen free environment. The paint was dried at 150 °C, followed by pyrolysis done under atmospheric pressure at 500 °C. During the pyrolysis experiments, the retort was flushed with nitrogen, 0.85–0.95 L/min. The volatilized organics and liquid produced during the pyrolysis were led out through the retort outlet. In the present work, the focus was on the inorganic components of the sample materials and therefore the oil and gas fractions were not collected for analysis.

To reduce the exposure of hazardous volatile pyrolysis products, the sample was cooled to 50 °C, under continuous nitrogen flow, in the pyrolysis retort before being removed. Once cooled, the solid residue was collected and weighed. The solid product was finally homogenized with a mortar and pestle.

2.2.2. Oxidation

The pyrolysis product mainly contained the inorganic components in the paint formulation (in this case, TiO₂) and carbon residues from pyrolysis of the organics. To remove the residual carbon and non-volatilized organic material, the pyrolysis residue was oxidized by spreading the powder in a thin layer (< 4 mm thick) in an alumina crucible and heat treating it in 470–500 °C for 1.5 h in air. After cooling, the material was collected, weighed, and homogenized using a M20 universal mill from IKA.

2.2.3. Purification of pigment with ion exchanger resin

During the pyrolysis process all organic components of the paint are decomposed into smaller entities and volatilized, and were therefore separated from the inorganic fraction of the paint. This inorganic fraction would contain the inorganic pigments and unwanted salt residues from the original paint. In a later stage, when the recycled pigments were re-dispersed in an aqueous system, these ionic species would dissolve and increased the ionic strength of the solution. It is known that an increased ionic strength have negative effects on colloidal stability [14] and the performance of certain dispersing aids commonly used in paints [15]. Therefore a washing of the pyrolysis product was designed.

Table 1
Model paint formulation produced for the TiO₂ recovery process.

Raw Materials	wt. %
Water	22.92
Binder (vinyl acrylic)	44.25
Antifoam	0.51
Non-ionic surfactant	0.51
Anionic surfactant	0.46
Hydroxyethylcellulose (HEC)	0.51
TiO ₂	30.47
Incan preservative	0.12
pH modifier	0.25

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