Characterisation of polyphosphate coated aluminium-doped titania nanoparticles during milling

Laura N. Elliott\textsuperscript{a,b,*}, Juliette S. Behra\textsuperscript{a}, Nicole Hondow\textsuperscript{a}, Richard A. Bourne\textsuperscript{a,c}, Ali Hassanpour\textsuperscript{a}, John L. Edwards\textsuperscript{d}, Stephen Sutcliffe\textsuperscript{d}, Timothy N. Hunter\textsuperscript{a}

\textsuperscript{a}School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom
\textsuperscript{b}Centre for Doctoral Training in Complex Particulate Products and Processes, University of Leeds, United Kingdom
\textsuperscript{c}Institute of Process Research and Development, School of Chemistry, University of Leeds, United Kingdom
\textsuperscript{d}Venator, Titanium House, Hanzard Drive, Wynyard Park, Stockton-on-Tees TS22 5FD, United Kingdom

Highlights

\begin{itemize}
  \item Particle fines (10–20 nm) were observed after milling TiO\textsubscript{2} for 32 min, with no change in crystal phase.
  \item DLS data confirmed the hydrodynamic diameter is relatively unchanged with milling time.
  \item NMR relaxation rate enhancement is observed for longer milling times, due to phosphate content changes.
  \item Elemental analysis shows a difference in polyphosphate content for washed and unwashed samples.
\end{itemize}

Abstract

This paper investigates the characterisation of alumina-doped titania nanoparticles, milled under high-shear over time, in the presence of sodium hexametaphosphate (SHMP) dispersant. Transmission electron microscopy (TEM) indicated that prolonged milling times led to the formation of 10 nm particle fines which were electrostatically attracted to larger particles, where no change in the crystal structure was observed. Primary particle sizes measured by dynamic light scattering (DLS) and TEM were in agreement and showed no change in primary particle size (~250 nm) with respect to milling time, however, there was a clear reduction in the magnitude of the slow mode decay associated to aggregates. The TiO\textsubscript{2} was found to have an isoelectric point (iep) in the range of pH 3–4.5, where an increase in milling time led to a lower pH\textsubscript{iep}, indicative of an increase in SHMP coverage, which was further supported by an intensification in phosphorus content measured by X-ray fluorescence (XRF). Phosphorus content and zeta potential analysis before and after centrifugal washing showed that SHMP was partially removed or hydrolysed for the longer milled pigment samples, whereas no change was observed for shorter milled samples. Relaxation NMR was also performed, where enhanced relaxation rates at longer milling times were associated partially to increases in surface area and exposure of Al sites, as well as physicochemical changes to SHMP density and structure. It is thought that extended milling times may lead to hydrolysis or other structural changes of the dispersant from the high energy milling conditions, allowing easier removal after washing for longer milled pigments.

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1. Introduction

Titanium dioxide (TiO₂), commonly called titania, occurs in three abundant crystallographic forms, rutile, anatase and brookite [1,2], and is a key pigment used in a wide range of consumer products such as paints, cosmetics, pharmaceuticals and plastics [3–6]. The estimated market in 2014 was 6 million tonnes, worth approximately US$ 13.5 billion globally [7]. TiO₂ can be produced by two main routes, the chloride and sulphate processes. Commercial pigment type rutile titania is primarily produced by the chloride process, which was commercialised by DuPont in the 1950’s [6,8].

Dopants are regularly added during the chloride process. For example, small quantities of AlCl₃ are added to the reactor feed to control pigment aggregation and favour the rutile phase [2,8,9]. It has been proposed that some Al dissolves into the titania lattice which enhances the phase transformation rate [10,11]. Later in the production process, titania is subjected to various chemical surface treatments to improve durability and dispersibility, before being wet milled to control the particle size distribution and dried. The final quality of TiO₂ in consumer products is dependent on a number of these variables where, in particular, the size of the milled dispersed crystallite aggregates is a key physical parameter that dictates overall whiteness and brightness [6,8,12].

Polyphosphate salts are widely used as dispersants in mineral and material processing industries, due to their ability to adsorb onto metal-oxides and clay-particle surfaces including illite, montmorillonite, kaolinite and dolomite [13–16]. Hence, polyphosphates are also often added to the titania pigment suspension during processes such as milling, in order to improve the dispersion properties and reduce suspension viscosity [17]. Taylor et al. [17] investigated polyphosphate interactions with alumina doped rutile pigment particles, and showed under alkaline conditions (pH 9) the interactions are dominated by chemisorption, whilst at pH 4 a combination of chemisorption and electrostatic interaction occurs. Feiler et al. [18] and Michelmore et al. [19] both studied the adsorption of polyphosphates onto the surface of TiO₂ and SiO₂ particles. For TiO₂, it has been shown that increasing the concentration of polyphosphate [18] and/or increasing the chain length of the linear polyphosphate [19] led to a decrease in the magnitude of the zeta potential at pH 4, but no interactions were observed for SiO₂. Connor [20] studied phosphate adsorption onto titania dioxide films by in situ infrared spectroscopy and adsorption kinetics, and suggested that phosphate strongly binds as a bidentate surface species. Importantly, aqueous polyphosphate solutions are not stable under high temperature (above 120 °C), acidic pH, or in the presence of some metal ions [21], as covered in recent reviews by Cini [22] and Rashchi [23]. Farrokhpay et al. [24–26] have investigated the stability and the influence of polymeric and polyphosphate dispersants on titania pigment particles. They found that acidic conditions (pH 3.5 – 5.5), high calcium ion concentrations and elevated temperatures all decreased the polyphosphate dispersion properties of titanium pigment particles [26].

Although efforts have been made to understand the influence of dispersants on slurry rheology during milling (see review by He et al. [27]), there appears to be limited published research studying polyphosphates. Wang and Forssberg [16] studied the interactions of sodium hexametaphosphate (SHMP) with dolomite in a stirred bead mill. They found that the use of SHMP, compared to organic dispersants, led to particles of a larger mean size and lower surface area. However, to our knowledge, the influence of milling time on the structure and density of polyphosphate dispersants on the surface of titania pigment particles has not yet been explored, nor has there been any published research relating to the strength of the interactions through centrifugal washing.

A number of studies have been conducted on the milling of TiO₂ particles (without polyphosphates) to determine the optimum milling control parameters, such as agitation speed, mill ball size, filling ratio and suspension concentration [28–31]. Interestingly, Inkyo et al. [31] found that large beads (50 and 100 μm) did not effectively break up nanoparticle agglomerates, although the structure and morphology of the nanoparticles were altered with milling time, moving from rod-shaped to more spherical morphologies. Jeon et al. [32] compared the wet milling of titania with alumina, and they reported that increased milling times led to alumina aggregates becoming more worm-like, whereas titania particles remained fairly spherical.

Phase transformations have also been reported for high energy ball milling of anatase with prolonged milling times. Begin-Colin et al. [33] showed, using TEM, that polycrystalline particles formed with TiO₂-II grains at the surface of the anatase particles after 15 min of milling. Gajovic et al. [34] also reported a phase transformation from anatase to TiO₂-II, as investigated by Raman spectroscopy and TEM. Sen et al. [35] observed particle fines 40–50 nm in size after ball milling anatase for 32 h, and after milling for 100 h they observed disintegration of nanoparticles to sizes of ~13 nm. Both anatase and rutile have also been observed to transform into TiO₂-II with shear [36]. For example, Šepelák et al. [36] observed TiO₂-II crystallites of 10 nm in diameter on the surface of anatase particles using high resolution TEM. However, to date, formation of nanoparticle fines from milling of rutile phase titania has not been reported.

TiO₂ particle size is important, as this controls the amount of scattered light. The optimum mean size is around 200 nm because the sum of the light scattered at each wavelength reaches its maximum [6,8,12]. Currently, TiO₂ pigments are manufactured in a continuous process with concentrations up to 600 g/L, and the particle size is often monitored using dynamic light scattering (DLS) [37]. Concentrated slurries exhibit multiple scattering; which leads to significant errors in the measured sizes and cannot be accounted for by most of the commonly available DLS devices [38]. Thus, to monitor the size of TiO₂ particles by DLS during a production process, aliquots must be sampled and diluted to concentrations where no multiple scattering occurs. Not only is this time consuming, but samples may be misrepresentative of the bulk system if an insignificant amount of statistics is collected on the dilute system or if particle aggregation/agglomeration occurs.

Studying industrially relevant processes is often not straightforward, as the dispersions are commonly highly concentrated, opaque and may contain a variety of inorganic contaminants [9]. However, nuclear magnetic resonance (NRM) relaxometry can be used to determine particle specific surface area, even for highly concentrated slurries [39]. In contrast to DLS, surface area calculations from relaxometry data do not require any assumptions on particle size or shape [39,40]. Furthermore, the NMR technique allows particles to be measured in the wetted state, contrary to most surface area techniques such as Brauner-Emmett-Teller (BET), that are performed on dried samples which are often subjected to aggregation. Relaxation NMR is thus an ideal candidate for an online process control tool, and could, for instance, offer the possibility of continuously monitoring particle surface area during milling.

Solvent relaxation NMR has been used to study the adsorption of polymers and dispersants onto particles and shows changes in the relaxation rate of bound water at the particle interface [39,41–50]. The technique has been used to determine particle porosity [51–54]. However, its use for surface area measurements is limited [39,55–57]. Elliott et al. [58] demonstrated that relaxation NMR can be used to measure the surface area of TiO₂ samples of different crystal structures (with the use of a standard silica
reference material of a known surface area) and showed excellent agreement with BET. Cosgrove et al. [49] studied relative relaxation rates for alumina (surface charge density 0.42 μCcm⁻²) and latex (1.6 μCcm⁻²). They showed that the time bound water spends at the surface of a particle is not entirely determined by the surface charge of the particle. In the case of alumina particles, despite a lower surface charge compared to latex, a larger increase in relaxation rate is observed. Thus, indicating a faster relaxation of bound water at the alumina particle surface due to surface hydroxyl groups which causes the motional restriction of water through specific interactions. This type of unproportionable increase in relaxation rate is often called a relative relaxation rate enhancement. Thoma et al. [55] investigated two titania powders consisting of aluminosilicate coated rutile of pigment grade quality. They reported deviations for highly concentrated slurries due to a decrease in the signal to noise ratio from the NMR, because of a reduction in the number of protons present in the system.

This paper presents the characterisation of industrially produced alumina-doped TiO₂ pigment particles milled for different periods of time in the presence of a polyphosphate salt. It aims to understand how milling affects the aggregate size and morphology of alumina-doped rutile pigment particles through particle size characterisation by TEM, X-ray disc centrifugation (XDC) and DLS. Further we investigate how the surface density and structure of the polyphosphate salt change with milling time. The stability of the polyphosphate layer against centrifugal washing is investigated by studying changes in the zeta potential and phosphorus content using XRF. Additionally, we explore the use of NMR relaxometry as a novel technique to understand changes in surface area in real time during the milling process and understand the influence of the polyphosphate-alumina interactions on relaxation times.

2. Materials and methods

2.1. Materials

Unmilled and milled titanium dioxide pigment samples were supplied by Venator. Sodium hexametaphosphate (Univar), known by the trade name Calgon, and abbreviated as SHMP throughout this manuscript, was added prior to the milling process to control titania dispersion properties. Stock acid and base solutions were prepared to vary the pH of suspensions, where hydrochloric acid was used as background electrolyte for surface charge analysis. A copper sulphate solution (Xigo Nanotools) was used as received to calibrate the frequency prior to NMR resonant frequency measurements. Ethanol absolute was purchased from Fisher Scientific and used as received for TEM sample preparation.

2.2. Methods

The industrially produced pigment samples were firstly adjusted to pH 10–10.5 with NaOH and sodium hexametaphosphate (SHMP) was added prior to milling at 0.14% w/w as P₂O₅ on TiO₂.Suspensions were milled at concentrations of 400 g/L in a stirred wet lab-scale mill (60 mL total volume) using a rotor speed of 12,000 RPM. The conditions in the mill were designed to mimic industrial-scale media mills commonly used in commercial exploitation of TiO₂. Suspensions were milled at concentrations of 400 g/L for different periods of time. Some of the milled samples were washed post-milling in an attempt to remove poorly adsorbed SHMP, and these are stated as washed herein. For these samples, 2.5 wt% dispersions were prepared in ultrapure water and centrifuged using a Heraeus Megafuge 16R Centrifuge (Thermo Scientific). Two wash cycles were performed. The first one was carried out at 6000 RPM for 20 min, after which the supernatant was removed and conductivity measured using a Seven2Go S3 (Mettler Toledo). The concentration of the centrifuged samples were adjusted back to 2.5 wt% using ultrapure water and washed for the second time at 8,000 RPM for 20 min. Once again the supernatant was removed, conductivity was measured, and the washed particles were re-dispersed to 2.2 wt%.

2.2.1. Transmission electron microscopy (TEM)

Samples of TiO₂ milled for 1 and 32 min were prepared for TEM by suspending in ethanol and vigorously shaking, before a drop of the suspension was placed onto a copper grid coated with a holey carbon film (Agar Scientific Ltd.) and left to dry. TEM analysis was used to investigate primary particle size and crystal structure on FEI Tecnai F20 FEGTEM operating at 200 kV. Bright field TEM was used to investigate particle size and morphology with images collected on a Gatan Orius CCD. Particle size analysis was conducted using Image J [59] by measuring the Feret diameter of primary particles. High magnification TEM images were used to obtain distances between atomic planes using a fast Fourier transform (FFT) function, from which d-spacings were then measured.

The dispersion state of TiO₂ nanoparticles after 32 min of milling was further investigated by dispersing in water, and using the plunge-freeze and vacuum dry method, as previously described by Hondow et al. [60]. Briefly, this involved rapidly freezing a blotted 3.5 μL drop onto continuous carbon coated TEM grids which had been plasma cleaned (1020 Fischione) for 10 s. The droplet was blotted using an FEI Vitrobot, with prior conditions set to 100% relative humidity and 21 °C in the chamber. After a wait time of 10 s, the droplet was blotted once for 4 s. The blotted droplet was rapidly plunged into liquid ethane, stored in liquid nitrogen, then transferred into a vacuum desiccator and allowed to sublime.

Energy dispersive X-ray spectroscopy (EDS) was used as elemental analysis for TiO₂ before and after milling for 32 min (plunge-frozen and vacuum dried) to check for potential bead contamination from milling media, and to confirm the presence of the polyphosphate species on the alumina-doped pigment surface. EDS was performed using the SuperX (4 detector) system on the FEI Titan™ G2 operated at 300 kV. High angle annular dark field (HAADF) scanning TEM (STEM) images were recorded using a probe current of ~450 pA, with analysis performed using the Bruker Esprit (v1.9) software.

2.2.2. X-ray diffraction (XRD)

Titanium dioxide samples were analysed after 1 and 32 min milling. The X-ray powder diffraction patterns were obtained to investigate the nature of the crystalline phase and calculate the crystallite sizes, using a D8 X-ray Diffractometer (Bruker) and CuKα radiation source. The titanium dioxide samples were prepared as powders and deposited onto a silicon holder. The samples were heated at 105 °C. The so-obtained dried titania powder was heavily agglomerated due to capillary forces, and in order to handle the samples for dispersion characterisation, they were gently crushed using a mortar and pestle for 5 min. All suspensions were made in milli-Q water and dispersed using an ultrasonic bath (Clifton Sonic) for 30 min, unless otherwise stated. Samples were then further dispersed using an ultrasonic probe, a Sonic Dismembrator (Fisher Scientific), at 20% amplitude for 1 min using a 6 mm horn tip.

Some of the milled samples were washed post-milling in an attempt to remove poorly adsorbed SHMP, and these are stated as washed herein. For these samples, 2.5 wt% dispersions were prepared in ultrapure water and centrifuged using a Heraeus Megafuge 16R Centrifuge (Thermo Scientific). Two wash cycles were performed. The first one was carried out at 6000 RPM for 20 min, after which the supernatant was removed and conductivity measured using a Seven2Go S3 (Mettler Toledo). The concentration of the centrifuged samples were adjusted back to 2.5 wt% using ultrapure water and washed for the second time at 8,000 RPM for 20 min. Once again the supernatant was removed, conductivity was measured, and the washed particles were re-dispersed to 2.2 wt%.
were scanned from 2θ angle 10° to 70° with a step size 0.0490° at 304 ms per step. The obtained pattern was matched against ana-
tase [61] and rutile [62] crystal structures, which were also used to
index the d-spacing measured from TEM analysis.

Crystallite size, L (Å), was obtained using the Scherrer equation

\[ L = \frac{K \lambda}{B \cos \theta} \]  

(Eq. (1)), where \( B \) is the line broadening in the XRD peak at the
full width half maximum intensity (FWHM) after subtracting instrumen-
tal line broadening (radians). Here, the line broadening of the instru-
ment was taken as 0.06°, and the FWHM was obtained by fitt-
ing a Gaussian distribution to the two most intense peaks observed
in the XRD patterns. \( K \) is a dimensionless shape factor; a value of 0.89 was used as this relates to spherical particles
[63]. \( \theta/2 \) is the Bragg angle (radians) which was obtained from
the peak position at the FWHM, and \( \lambda \) the wavelength of the inci-
dent x-rays taken as 1.5406 Å for the CuKα radiation source.

\[ B = \frac{K \lambda}{L \cos \theta/2} \]  

2.2.3. Zeta potential characterisation

A Zetasizer Nano ZS (Malvern Instruments) was used to mea-
sure the zeta potential of the unmilled and milled dispersions. Dis-
persions of TiO₂ in 0.1 mM KCl background electrolyte were
prepared at 100 ppm and dispersed as per Section 2.2, where the
pH was measured using a HI-208 pH meter (Hanna Instruments),
before pipetting into DTS1070 folded capillary cells (Malvern
Instruments). Stock base (KOH) and acid (HCl) solutions were
prepared at 0.01, 0.1 and 1 M, to increase and decrease the pH of the
particle dispersions respectively. The pH of the dispersion was
either reduced from neutral with acid or increased with base. All
dispersions were kept mixing with a magnetic stirrer for approxi-
ately 10 min after altering the pH. The zetasizer standard operat-
ing procedure (SOP) was set for 3 measurements with a maximum
of 100 profiles, and measurements automatically terminated when
10 stable profiles were sequentially collated. A total of 6 measure-
ments were collected for each pH point on the zeta potential curve,
and averaged data were recorded with associated standard devia-
tion and error.

2.2.4. Dynamic light scattering (DLS)

Titanium dioxide suspensions were prepared from the milled
powder at 2 wt% in ultrapure deionised water and dispersed, as per
Section 2.2. 25 μL aliquots were sampled and diluted in 20 mL of
ultrapure deionised water and re-dispersed, before diluting by ten. The dispersions were filtered using 0.8 μm
sorpt-facet-free cellulose acetate filters (26 mm Minisart® Syringe
filters; Sartorius), unless otherwise stated. This sample preparation
was also used for TiO₂ milled for 1, 16 and 32 min after centrifugal
washing. The DLS measurements were performed at 25 °C also
using a Zetasizer Nano ZS (Malvern Instruments, 173° backscatter-
ing angle and 633 nm laser excitation wavelength). For each
measurement, thirty 30 s measurements were carried out.

For all the investigated milled suspensions, the collected inten-
sity auto-correlation data exhibited two relaxation modes. As seen in
Fig. S1(a) of the Supplementary Material, the fit of the data per-
formed by the commercial Zetasizer code did not properly account
for the second, longer, relaxation mode. The intensity auto-
correlation data were thus fitted in MatLab with a sum of two
stretched exponentials (Eq. (S1)) using the Levenberg-Marquardt
algorithm. An example of such a fit is provided in Fig. S1(b). It is
worth noting that the few measurements for which the intensity
auto-correlation data had an intercept higher than 1 were excluded
from the data set, while the remaining intensity auto-correlation
data were normalised to an intercept of 1. Assuming that the inves-
tigated relaxation mode is diffusive (see a more detailed explana-
tion in Section 3.2 and in the Supplementary Material),
corresponding hydrodynamic diameters \( D_H \) were calculated using

\[ \text{Eqs. (S1)–(S5)}. \]  

More information on DLS fitting and analysis procedures can be
found in Behra et al. [64].

Care must be exercised when characterising TiO₂ suspensions
with light scattering as they can exhibit multiple scattering
because of the TiO₂ high scattering index (i.e. 2.410). Multiple scat-
tering leads to significant errors in size measurements if it is not
accounted for and can be avoided by diluting TiO₂ suspensions.
To determine the optimum TiO₂ concentration at which DLS mea-
surements should be performed [37,38], dilution trials were
attempted. The results are shown and discussed in the Supplemen-
tary Material (Fig. S3), where the influence of filtration is also dis-
cussed. The concentration corresponding to the dilution described
at the beginning of this section (i.e. \( \sim 2.5 \times 10^{-7} \text{ wt%} \)) was found
to be optimal. To confirm that this concentration was appropriate, a
number of additional measurements were performed using a light
scattering device equipped with a ‘3D mode’ (instrument details
provided in the Supplementary Material), which allows to correct
for multiple scattering [37,64]. There was no significant difference
between the data collected with the ‘3D mode’ (data not shown)
and those collected with the standard ‘2D mode’, thus confirming
that the selected TiO₂ concentration allowed DLS measurements to
be performed in absence of multiple scattering.

There was a concern that the amount of energy brought into the
system during sonication could break the aggregates that may be
present in the TiO₂ milled samples. Hence, DLS measurements
were also performed on samples prepared using a lower energy
intensive dispersion method (compared to sonication). The results
are displayed in Fig. S4 and show that sonication does not break
the aggregates that may be present in solution, but successfully
breaks the agglomerates formed when the TiO₂ milled particles
are dried. These experiments are discussed in detail in the Supple-
mentary Material. Characterisation of the unmilled TiO₂ sample is
also detailed in the Supplementary Material, Section 1.6, Fig. S5.

2.2.5. X-ray disc centrifugation (XDC)

Milled slurries obtained at \( \sim 400 \text{ g l}^{-1} \) were diluted to \( \sim 40 \text{ g l}^{-1} \)
and the titanium dioxide particle size was determined by X-ray
disc centrifugation using a BI-XDC Particle Size Analyzer (Brookha-
ven), run at a disc speed of 1200 rpm for 40 min.

2.2.6. Brunauer–Emmett–Teller (BET)

Brunauer–Emmett–Teller (BET) surface area and pore size mea-
surements were obtained for milled titanium dioxide samples by
the nitrogen adsorption-desorption method at 77.3 K, using a TriS-
tar 3000 (Micromeritics) surface analyser. TiO₂ samples were
degassed to remove moisture using a vacuum oven at 120 °C for
24 h under a vacuum of 10 mmHg. To determine the reproducibil-
ity of the results, two TiO₂ samples (1 and 2 min milled) measure-
ments were repeated using the same experimental conditions. No
significant difference was observed for the 1 min milled sample (a
0.02% variation) or the 2 min milled sample (a 0.16% variation),
with repeated results within the experimental error. The obtained
\( N_2 \) adsorption isotherms were used to calculate the BET parame-
ters for TiO₂ surface area, whilst the desorption isotherms were
used to calculate the average pore size by the Barrett-Joyner-
Halenda (BJH) method.

2.2.7. NMR relaxometry

All relaxation measurements were obtained using an Acorn
Area (Xigo Nanotools), 13 MHz desktop NMR spectrometer. Prior
to any operation, the instrument was thermally equilibrated for
24 h, after which the resonance frequency was measured using a
copper sulphate solution. A resonance frequency of approximately
13.07 MHz is regarded as adequate for a measurement to proceed.
A 90°-pulse length of 5.67 μs, 180°-pulse length of 11.33 μs and a gain value of 10 dB were used for all relaxation measurements. The $T_1$ inversion recovery pulse sequence was used to measure the spin–lattice relaxation rate coefficient, and a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence was used to measure the spin-spin $T_2$ relaxation. Typically, a series of four replicate scans were averaged to produce the CPMG trace, and the Xigo Nanotools software fitted the collected signal to a single exponential to extract the relaxation rate coefficient. A recycle delay of 5 s was fitted the collected signal to a single exponential to extract the relaxation rate coefficient. A recycle delay of 5 s was used for all relaxation measurements.

Fig. 1. (a) TEM image of TiO₂ particles after milling for 1 min. (b) High magnification image of a TiO₂ nanoparticle after 1 min of milling to show the lattice fringes. (c) Fast Fourier transform (FFT) generated from the red square shown in (b), with measured d-spacings in nm and corresponding hkl planes shown referenced to the rutile crystal structure [62].

### 2.2.8. X-ray fluorescence (XRF)

Washed and unwashed TiO₂ dispersions at 2 wt% were prepared as described in the introduction of Section 2.2. The dispersions were poured into plastic holders ensuring that there was enough volume to cover the surface of the cup. Cup holders (40 mm Spex Unicell) were covered with a polypropylene film to contain the sample before securing with the plastic ring counterpart, creating a taut smooth film on the surface of the sample cup. XRF measurements were performed in a helium atmosphere using a Rigaku Primus II WD XRF. The following settings were used: analysis: EZ scan, sample type: liquid, component type: metal and balance component: H₂O.

### 3. Results and discussion

#### 3.1. Microscopy, elemental characterisation and crystal structure

Transmission electron microscopy (TEM) images (Figs. 1 and 2) were obtained for TiO₂ particles in order to understand primary particle size and morphology changes within the two extreme milling times (after 1 min and 32 min respectively). It is noted that a large proportion of primary particles are rod shaped, while there is certainly some considerable variation in their shape factors. Jordan et al. [65] analysed the self-assembly of rutile TiO₂ during initial stages of crystallization, where they reported elaborate structures of rutile TiO₂, such as rutile fibre networks and twinning branched clusters [65,67], although it should be emphasised that an alternative synthetic route is used for the samples in this study. Klein et al. [66] stated that synthesis acidity is important in determining crystal morphology of rutile titania when produced by the precipitation method, and detailed structures including rods, broomlike agglomerates and cauliflower spherical agglomerates. Clearly, the morphology of the nanoparticles depends on the conditions used, however observed in this study are spheres and rod shaped nanoparticles limited to TiO₂ produced in a flame reactor. It is assumed that the variation in shape-factors evidenced in Figs. 1 and 2 are likely from a distribution in growth rates, rather than differences in the underlying crystalline structure, which will be discussed in detail in the forthcoming section.

It should be noted that throughout this discussion the term ‘aggregate’ is referred to as an assembly of particles which are sufficiently strongly bound that they require bead milling to break the particle-particle bonds. This contrasts to the term ‘agglomerate’...
which is referred to as a collection of aggregated particles which has formed upon drying, these are softer bound and as later discussed can be broken by sonicating the suspension.

The average particle size was calculated using the Feret diameter of the TiO$_2$ primary particles, with over 100 particles measured for the unmilled material and both the 1 and 32 min milled samples, as given in the Supplementary Material, Table S1. Little change is observed in the average primary particle size between the unmilled pigment and size with increased milling time. A small number of aggregates (10) were analysed which had an average spherical diameter equivalent of $\sim$1100 nm after 1 min milling and 900 nm after 32 min milling. While it is expected that there may be some level of particle aggregation in TiO$_2$ slurries [67], the observed aggregates could also have formed during sample drying on the TEM grid. Hence, the measured aggregate sizes are unlikely to be representative of the aggregates that may be present in the wet dispersions.

Critically, titania samples milled for 32 min showed evidence of particle fracturing (Fig. 2), resulting in fines of $\sim$20 nm, which appear to cluster together (Fig. 2a) and are also attached to larger particles (Fig. 2c), probably due to electrostatic attraction [35]. Sen et al. [35] found particle fines in the order of 40–50 nm in size after high energy vibrational ball milling of anatase nanoparticles for 32 h, where further milling for 100 h caused disintegration of nanoparticles to sizes of $\sim$13 nm [35]. They suggested that particle breakage is caused by critical stresses that generate plastic deformation. It has also been observed that high energy ball milling results in the formation of uncommon metastable TiO$_2$-II phase. Gajovic et al. [68] also showed that milling times of more than 10 h for the anatase polymorph induced particle breakage towards 10 nm, while primary particles of larger sizes were still present [68]. Therefore, it appears that for the current system, 32 min milling supplies an excess milling energy, which not only is inefficient on time/energy costs, but negatively impacts the properties of the pigment particles. It is likely that the observed nanoparticle fines will lead to a reduction in the optical purity and whiteness. This is the first time, to the authors’ knowledge, that such breakage has been published for the harder rutile morphology (hardness scale anatase 5.5 – 6, compared to rutile 6–6.5) [69]. Although the milling conditions are fairly severe, such large milling RPM are required in order to scale down the milling process from production plant-scale to lab-scale. Therefore, the appearance of fractured TiO$_2$ fines is significant, as many pigment production processes will have similar unit operations, and thus it could be assumed that many TiO$_2$ samples may contain these fractured fines, when the TiO$_2$ reactor discharge is milled for long times.

The crystal structure of primary particles was investigated by analysis of lattice fringes in high magnification TEM images (Fig. 1b), and a fast Fourier transform (FFT) was generated to measure the d-spacing (Fig. 1c). The TiO$_2$ sample milled for 1 min had primary particles of the rutile crystal phase, as observed by the d-spacing corresponding to the (0 1 1) and the (1 2 0) planes of rutile [62], as shown in Fig. 1c. Due to crystal phase transformations reported in the literature after milling anatase TiO$_2$ [35], the crystal phase of the particle fines were also investigated for the 32 min milled sample. Fig. 2c shows three locations where the FFT was generated, either on the primary particle surface or on the fractured fines attached to the primary particle. The FFT generated from the primary particle (inset Fig. 2c, point A) again indicates d-spacings corresponding to the rutile (1 1 0) and (1 2 0) planes [62], and the fractured fines (inset Fig. 2c, points B and C) also have planes corresponding to the rutile (1 1 0) and (0 1 1) planes [62]. The dispersion behaviour of fractured fines was investigated for the 32 min milled TiO$_2$ sample, using the plunge-freeze and vacuum dry method described by Hondow et al. [60], allowing a closer in situ assessment of aggregation unaffected by sample drying. The fractured fines appear to either attach to the primary particle surfaces (Fig. 2d) or cluster together (Fig. 2e), thus suggesting that the fractured fines are not well dispersed in the suspension, which may significantly impact on the overall optical properties of the bulk material.

It was suspected that the ball milling media (glass ballotini) may contaminate the titania samples for extended milling times up to 32 min. Additionally, due to the industrial nature of the samples, other contaminants may also be present. Energy dispersive X-ray spectroscopy (EDS) was used as elemental analysis for the plunge-frozen 32 min milled sample, as presented in Fig. 3. It confirms the presence of silicon from the ballotini which is heterogeneously distributed across the particle. As the TiO$_2$ were milled in a slurry of sodium hexametaphosphate (SHMP), phosphorus and sodium are also evident, and appear to be evenly distributed on the surface. Dopants are regularly added during the chloride process. For example, small quantities of AlCl$_3$ (between 0.01 and 10%, although 0.5–2% is more typical), are added to the reactor feed.

**Fig. 2.** (a & b) TEM images of TiO$_2$ particles after milling for 32 min (particle fines electrostatically aggregated highlighted by the arrow in (b)). (c) High magnification TEM image at the point of the arrow in (b), with inset FFT taken from A, B and C sections indicated by the red box insets, with measured d-spacings and corresponding hkl planes shown [62]. (d & e) TEM images indicating the dispersion state of TiO$_2$ after milling for 32 min, dispersed in water and prepared using the plunge-freeze method.
to control pigment aggregation and favour the rutile phase [2,8,9] and hence aluminium is also clearly evidenced on the particle surface. Finally, zirconia is also observed in Fig. 3, which is a result of contamination from degradation of the impeller used in the mill. Fig. 3(b) shows a TEM of the particles from which the EDS was mapped. Here, observed fines are again attached to the larger primary particle surface. Fig. 3(c) shows the FFT generated from an area on the fines that also confirms the rutile crystal phase with the d-spacing and hkl planes [62]. Additional EDS maps of the unmilled TiO2 and 32 min milled particles are displayed in the Supplementary Material Figs. S6 and S7, which also shows an even coverage of the elements associated with the presence of SHMP on the TiO2 particles.

Fig. 4 presents the XRD pattern of the TiO2 samples after milling for 1 min and 32 min. Peaks again matched the rutile powder diffraction pattern [62], where no additional peaks were observed in the XRD pattern for both TiO2 samples, further confirming phase and sample purity, although line broadening and a small shift in the peaks are detected. The peak broadening in the XRD was used to determine crystallite size for the two samples. Therefore, the two most intense peaks in the XRD pattern, (1 1 0) and (1 2 1), were fitted to a Gaussian distribution, as shown in Fig. 4 (b and c). Table 1 shows the full width half maximum (FWHM) obtained from the Gaussian fit and the calculated crystallite size using the Scherrer equation (Eq. (1)) [63]. The primary crystallite size marginally decreases with milling time from ~39–48 nm after milling for 1 min to ~35 nm after milling for 32 min, and this decrease suggests that stresses within the crystal structure leads to a broadening of the peaks.

The (1 1 0) peak at 2Theta = 27° for rutile relates to the crystal size of the shortest dimension, and the (0 0 1) or (0 0 2) plane corresponds to the longest dimension [70]. Length to width ratios of 2:1 are common for rutile crystals [70], which would give rise to crystallite lengths of ~100 nm. Although this is in closer agreement...
with the primary particle sizes obtained from TEM, there is still a large discrepancy in the average crystal size. However, there are critical differences between direct primary particle size determination from TEM and crystal size characterisation by XRD, where primary particle sizes can only be measured by XRD if lattice planes are perfectly orientated [70]. Hence, under-estimation of particle sizes by XRD can occur, while it is clear that individual particles observed in the TEM do represent primary particles. In conclusion, no change in the primary particle size was observed with increased milling time, however there may be changes in the aggregate size. Longer milling times were found to induce particle fracturing resulting in nanoparticle fines 10–20 nm in size, although despite this, no change in the crystal structure was observed.

3.2. Particle surface charge and size changes through milling and washing

Zeta potential values for 1 and 32 min milled alumina doped TiO2 in the presence of SHMP are presented in Fig. 5(a). Fig. 5(b) shows the evolution of the pigment zeta potential with milling time at neutral pH, before and after centrifugal washing. The investigated TiO2 was found to have an isoelectric point (iep) between pH 3–4.5. With an increase in milling time leading to a lower pHiep, Taylor et al. [71] previously reported a change in rutile iep with alumina doping, with pure rutile pHiep at 4.9. This contrasts to alumina doped rutile which they reported had a pHiep in the range of 8–9, dependent on the surface concentration of alumina. The change in iep is due to the domination of aluminium hydroxide surface groups [71]. However, while these values appear higher than those seen in Fig. 5, Taylor et al. [17], in other work, also reported the pHiep of pigmentary titanias to vary significantly with the addition of SHMP, which even at low concentrations had a strong effect on the surface chemistry [17]. Indeed, they showed that the zeta potential decreased with polyphosphate concentration, which was pronounced at low pH (pH 4) and altered the reported pHiep to between 3 and 5, dependent on the dispersant concentration, consistent with values reported in Fig. 5 [17]. Further, Michelmore et al. [19] have shown that increasing the concentration of phosphate and increasing the chain length of the linear polyphosphate decrease the magnitude of the zeta potential of titanium dioxide.

Fig. 5(a) therefore suggests that increasing milling time leads to the presence of more SHMP on the alumina-doped pigment surface. It is expected that milling will lead to an increase in agglomerate breakage, potentially leaving more alumina-rich surface sites exposed. Thus, any non or poorly adsorbed dispersant remaining in the aqueous phase may adsorb to these newly exposed sites, leading to a reduced (more negative) zeta potential at low pH, because of the high charge density of the SHMP. Above pH 8 however, the zeta potential values remain constant near –50 mV regardless of milling time, consistent with Taylor et al. [17], and is indicative of the maximum potential magnitude of an adsorbed surface with SHMP.

Fig. 6 shows the XRF phosphorus elemental analysis for both washed and unwashed TiO2 samples milled for different times. It is important to note that the data has been first normalised to 100% Ti content, then the relative change in phosphorus calculated by setting the 1 min milled sample to 100% phosphorus content. The full elemental analysis obtained from XRF (which is also normalised to 100% Ti content) is given in the Supplementary Material (Fig. S8). There is a clear difference in phosphorus content for unwashed TiO2 milled for 1 min, compared to 16 and 32 min of milling where the phosphorus content is relatively unchanged. Whilst it is clear that more phosphorus is in the samples milled for longer time periods, the exact quantity of phosphorus on the surface of TiO2 is unknown due to the semi-quantitative nature of the technique. However, this change in phosphorus content supports the previous hypothesis that more SHMP is present on the pigment surface when milling time is increased. It is important to note that we cannot be certain from the XRF results alone that phosphorus is on the surface of the pigment. However, as previously discussed in terms of the EDS analysis as shown in Fig. 3, it is evident that phosphorus is spread over the particle surface rather than in the bulk solvent. Additionally, there are important differences between washed and unwashed samples. From the XRF data (Fig. 6), washing does not induce a change in phosphorus content for the 1 min milled sample, while it leads to a significant decrease in the phosphorus content for the 16 and 32 min milled samples, inferring a partial

| Table 1 |
| --- |
| Crystallite sizes calculated from Gaussian fitting of the (1 1 0) and (1 2 1) XRD peaks for 1 and 32 min milled TiO2. |
| | 110 | 110 | 121 | 121 |
| Milling time (min) | 1 | 32 | 1 | 32 |
| Position (°) | 27.7 | 27.6 | 54.7 | 54.5 |
| FWHM (°) | 0.2 | 0.3 | 0.3 | 0.3 |
| Crystallite size (nm) | 48 | 36 | 39 | 35 |
loss of the SHMP dispersant for samples milled at longer times. These results are consistent with zeta potential changes presented in Fig. 5(b), where, again, washing does not induce any change in the zeta potential for the 1 min milled sample, while it leads to a reduction in the magnitude of zeta potential for the 16 and 32 min milled suspensions. Hence, it appears that whilst milling increases the surface density of the dispersant, the SHMP that is additionally adsorbed is more easily removed upon washing.

The interaction of SHMP and titania can be complex, with both chemisorption (considered irreversible) and electrostatic physisorption (considered reversible) are possible [17]. It may be that the high energy of the mill induces some re-structuring and increases physisorption of the dispersant which is more weakly bound. Farrokhpay et al. [26] found that acidic pH, high calcium ion concentrations and elevated temperatures all decreased the ability of polyphosphate (Calgon T) to disperse titanium pigment particles of average primary particle size 230 nm. They concluded that the reduced dispersant performance, at least under high acid conditions and temperature, was due to the hydrolysis of the polyphosphate chains, which was observed through infra-red analysis. Furthermore, they reported that the reduction of the polyphosphate chain length from hydrolysis leads to a decrease in steric stabilisation, but the shorter chains still allowed electrostatic stabilisation to occur. Thus, we propose that mechanical activation at the pigment surface and high temperatures occurring during the milling process could either weaken the interaction between the adsorbed polyphosphate and the pigment surface, and/or cause the hydrolysis of the linear phosphate chains into shorter ones, thus allowing removal through centrifugal washing for the 16 and 32 min milled samples.

Fig. 7 presents the intensity auto-correlation data from DLS measurements of TiO₂ suspensions for the unmilled sample as well as for each sample (auto-correlation data for the unmilled sample is shown in Fig. 5S). For all samples, two relaxation modes are observed: (i) a relaxation mode characterised by a short relaxation time of ~7 x 10⁻⁵ s at 173° scattering angle, independent from the milling duration, and (ii) a relaxation mode characterised by a significantly longer relaxation time varying from one measurement to another. Owing to their relaxation times, no further calculation was performed for the slow relaxation mode. The diffusive nature of the fast relaxation mode was confirmed with a light scattering device allowing DLS measurements to be performed at different scattering angles (see Supplementary Material). Hence, the hydrodynamic diameter Dₜₕ associated with the fast relaxation mode could be calculated from the fast relaxation time using the Stokes-Einstein equation (see Eqs. (S4) and (S5) in the Supplementary Material) and are shown in Fig. 8. Fig. 8 also compares the particle diameters obtained from X-ray disc centrifugation, TEM and DLS measurements. The hydrodynamic diameters determined from DLS measurements compare very well to the primary particle sizes measured from TEM (with measured diameters of ~250 nm almost unchanged with milling time) thus suggesting that the fast relaxation mode probed by DLS can be assigned to the primary TiO₂ particles. Fig. 8 also shows the ratio between the relative amplitudes of the fast and the slow modes (A_fast/A_slow) decreasing with milling time (and is greatest for the unmilled sample) thus suggesting a decrease in the proportion of aggregates with milling time compared to the primary particles.

Particle size determination from XDC, based on terminal settling described by the Stokes law, can be used to probe a wider...
Fig. 8. Particle diameter of unmilled and milled TiO₂ particles measured using dynamic light scattering (DLS). Also shown is the particle size measured by x-ray disc centrifugation (XDC) and transmission electron microscopy (TEM). Additionally, given is the ratio \( A_{2}/A_{1} \) of fast and slow mode relative amplitudes (from DLS measurements) as a function of milling time (inset). It should be noted that the amplitude of the slow mode for the unmilled sample was calculated by \( (A_{2} + A_{3})/A_{1} \), where \( A_{1} \) is the fast mode and \( A_{2} \) and \( A_{3} \) were the two additional slow modes present due to an increase in polydispersity.

range of sizes (i.e., \( \sim 0.01–50 \mu \text{m} \)) than light scattering [72]. XDC results shown in Fig. 8 suggest an exponential-type decrease in particle or aggregate size with milling time. After 1 min milling, the measured size is \( \sim 450 \text{ nm} \), which is assumed to be an average of the sizes of both primary particles and aggregates (considering that the primary particle size is \( \sim 250 \text{ nm} \), as determined from TEM images). As the milling time is increased, the number of aggregates in the dispersion decreases, and the average particle size determined by XDC decreases towards that expected of the primary particles (\( \sim 250 \text{ nm} \)). It is noted that, given the influences of particle shape [73,74] and aggregation [75] on sedimentation rate, XDC results must be taken with caution.

The hydrodynamic diameters of the washed and unwashed milled TiO₂ samples were determined using DLS and can be found in the Supplementary Material (Table S2), alongside the values of the \( A_{\text{slow}}/A_{\text{fast}} \) ratios. The hydrodynamic diameter associated with the fast relaxation mode does not change upon washing; consistent with the fact that the size of the primary particles is not expected to be affected by washing. For the 32 min milled TiO₂ sample, the value of \( A_{\text{slow}}/A_{\text{fast}} \) is not affected by washing, suggesting also that the proportion of aggregates are not considerably affected by washing. Such an observation would be consistent with partial hydrolysis of the polyphosphate during milling, maintaining the electrostatic stability of the system after partial removal of poorly bonded physisorbed dispersant with washing. Thus, the maintained layer is sufficient to continue to prevent primary particles from significant aggregation. Taylor et al. [17] state the SHMP molecular weight to range between 1082 and 1286 Daltons which would be a sufficient length to induce steric stabilisation.

3.3. Surface area determination and NMR relaxometry of milled samples

Fig. 9 presents the BET surface area plotted against the milling time. The specific surface area increases due to milling, from \( \sim 5.7 \text{ m}^{2}/\text{g} \) after 1 min milling to \( 7.5 \text{ m}^{2}/\text{g} \) after 32 min milling, corresponding to calculated spherical equivalent diameters of 248 nm to 188 nm, respectively (as shown on the right-hand axis). The equivalent sizes calculated from BET surface areas are in relatively good agreement with the sizes estimated from TEM and DLS. Measuring shear-dependent aggregates is complex and it is important to use a variety of techniques to characterise the system. Gesenhues [76] also monitored surface area of rutile TiO₂ using BET, observing an increase in surface area from 6 to \( 8 \text{ m}^{2}/\text{g} \) after 65 min milling. Other reported pigment TiO₂ surface areas are in the range of \( 8–9 \text{ m}^{2}/\text{g} \) [17], \( 12–19 \text{ m}^{2}/\text{g} \) [77,78] and can be as high as \( 28 \text{ m}^{2}/\text{g} \) [79]. Mestl et al. [80] milled molybdenum oxide and showed crystal size to be fairly constant in the first hour of milling, with a small decrease in particle size and an increase in BET surface area, suggesting the breakage of agglomerates and larger particles [80]. In the second phase of milling (milling times up to 600 min) the particle size drastically decreased, primary crystals were broken down and amorphization occurred on their surface [80], all associated to an increase in the BET surface area. Thus, the results reported in Fig. 9 suggest that the increase in the specific surface area comes from aggregate breakage. The mean pore size obtained from BET measurements and the total pore volume (Supplementary Material, Table S3) remain constant ranging from 16 nm to 19 nm, further suggesting that the change in surface area is largely accounted for by the decrease in aggregate sizes. Some of the increase in surface area may also be accounted for by the formation of the nanoparticulate fines, although, as they are adsorbed on the dried agglomerated samples, it is likely that their influence on surface area changes is masked.

Changes in specific surface area, as measured by BET (in the dry state) were also compared to wet dispersion results from the NMR relaxometry measurements. Differences are observed in the NMR relaxation rate enhancement (\( R_{\text{sp}} \); in reference to water) for the alumina-doped pigment particles as the milling time is increased, as shown in Fig. 10(a) (for unwashed dispersions). It is well known that the liquid bound at a particle surface has a relaxation time orders of magnitude shorter than the comparative bulk (2–3 s) due to molecular motion becoming anisotropic and restricted at the surface, thus increasing the relaxation rate [39,42]. Therefore, the increase in \( R_{\text{sp}} \) with respect to milling time also suggests an increase in surface area, which can be calculated from \( R_{\text{sp}} \) using a standard reference material of known surface area (see Section 2.2.7).

For dispersant-free suspensions of particles with identical surface chemistry, the relaxation rate scales linearly with increasing surface area [42]. However, adsorption of a dispersant at the particle surface may also lead to an increase in the relaxation rate, from the decrease in the mobility of water at the particle surface [42]. Due to the complexities of correlating the interactions of the dispersant to a separate calibration system of known surface area, the BET surface area for the 8 min milled samples was used to find \( K_{\text{sp}} \) (the
specific relaxation constant) allowing $R_{sp}$ to be converted to particle surface area for the other milling times [58]. The 8 min milled sample was used as the reference system as it corresponds to the onset of the plateau observed in the zeta potential with increased milling time (Fig. 5(b)), consistent with an increase in concentration of SHMP at the particle surface. Therefore, it was thought that after 8 min of milling, the $R_{sp}$ would be most significantly enhanced due to the contribution of SHMP at the particle surface rather than the increased surface area available from aggregate breakage. Thus, the $K_a$ for milled TiO2 was calculated and correlated to the surface area obtained from the BET measurement for the 8 min milled sample, giving a $K_a$ of $3.93 \times 10^{-4} \text{ g/m}^2/\text{ms}$.

Fig. 10(b) shows the calculated surface area as a function of milling time, which compares relatively well with the BET results (Fig. 9) obtained at low milling times. However, at long milling times (16 and 32 min milling) the calculated surface areas continue increasing significantly, rather than beginning to plateau (as observed with the BET data). The deviation observed in the NMR could be due to a number of factors. Importantly, BET measures the particle surface area as a dried powder, compared to NMR where surface area measurements are performed on the dispersed suspension. Therefore, it is likely that the surface area is smaller by BET due to the presence of agglomerates compared to NMR where these are broken during sonication (see Fig. S4). However, it should be noted that the increase in surface area from agglomerate breakage is likely to be small and therefore alone cannot account for the differences. An additional explanation is the influence of the nanoparticle fines evidenced after long milling times from TEM, which at ~20 nm may contribute to much greater dispersion surface areas. Whilst the effect of these nanoparticle fines would be masked in the dried powder BET, they would be more evident in dispersion conditions. Also, as it was evident from TEM that these fines largely adsorbed onto the primary particles, it is assumed that they would increase the surface area primarily through roughening of the primary particles surfaces. Nevertheless, given the magnitude of the changes in relaxation rate after 16 and 32 milling times, it is still difficult to attribute the differences to actual surface area increases alone.

In an attempt to better understand relaxation changes with milling time, it was decided to consider both $T_1$ and $T_2$ relaxation measurements. Although both $T_1$ and $T_2$ can be used to determine particle surface areas using one or the other has both advantages and disadvantages [39]. Whilst $T_2$ measurements are faster, which is advantageous if samples are not stable (for example, if sedimentation occurs) the relaxation time can become very small at high suspension concentrations, leading to potential measurement errors. Furthermore, $T_2$ is more sensitive to changes in available surface area, and to the presence of ferromagnetic or paramagnetic impurities. Due to the differences in sensitivity of $T_1$ and $T_2$, it can be advantageous to measure both relaxation times, as shown in Fig. 10(c). Here, a clear inflection in the data arises between the 4 and 8 min milled samples, correlated to the change in zeta potential for pigment samples (Fig. 5(b)), which plateaus after 8 min of milling, as previously conversed this is suggestive of monolayer SHMP coverage.

While it is evident that longer milling times lead to an increase in adsorption density of the SHMP, it was assumed that the adsorption plateaus post 8 min, limiting further surface chemistry contributions (as discussed). However, given the potential for extended milling times to lead to hydrolysis or other structural changes of the dispersant because of the high energy milling conditions, we may have to consider the influence of the dispersant structure in addition to the influence of its density on NMR relaxation. It may be that hydrolysed SHMP has a greater influence on NMR surface relaxation than un-modified SHMP, although, due to the convoluted nature of the overall response, it is very difficult to further define the interactions between SHMP and the bound water.

After centrifugal washing, an increase in $R_{sp}$ was observed, as shown in Fig. 10(a), where the increase is minimal and within the measurement error for the 1 min milled sample, but this increase becomes significant with increased milling time. The first explanation is that the removed or hydrolysed polyphosphate (observed from the changes in zeta potential and phosphorus content determined using XRF; see Section 3.2) which occurs for samples milled for longer periods of time, leads to an increase in exposed alumina surface sites. Aluminium ($^{27}\text{Al}$) is a quadrupolar nucleus and can cause enhancements in relaxation rates of bound solvent molecules at the colloid surface [50]. However, if this was simply the case, one would expect the relaxation rate of the 1 min milled sample (unwashed or washed) to show the largest enhancements, as these samples have the lowest phosphorus content according to XRF, and should therefore have more exposed Al surface sites. For both the unwashed and washed samples milled for 16 and 32 min, the surface area increases, and the number of fines increases leading to a faster relaxation rate than the one of the washed or unwashed 1 min milled samples. As previously stated, the ball mill energy might be altering the surface structure of the dispersant or exposing further Al sites, whilst some dispersant can be washed off, this is most likely weakly interacting salt that might not contribute to the large relaxation enhancements. The remaining chemisorbed polyphosphate salt may have an altered surface structure, and this, coupled with the increase in exposure of Al surface sites, may be the reason for the enhanced relaxation rates upon washing. While it is difficult to state for certain what changes in the dispersant structure are occurring without additional surface analysis and this is an area of ongoing investigation, the degradation of an ammonium salt of poly(methacrylic acid) used during wet ball milling of alumina has previously been reported [81].
4. Conclusions

The effect of milling time on the interactions between aluminium doped titania pigment particles and polyphosphate (SHMP) dispersant has been studied using multiple characterisation techniques. TEM highlighted the presence of ~20 nm fractured fines in samples milled for 32 min that were found to have d-spacings correlating to a rutile crystal structure, implying that milling did not induce changes in crystal structure. Although the milling conditions that induced these breakage events are under high-shear, such large milling RPM, are required in order to scale down the milling process from production plant scale to lab scale. The appearance of fractured TiO₂ fines is even more significant, as many pigment production processes have similar unit operations and thus it could be assumed that many TiO₂ pigment samples may contain these fractured fines if the TiO₂ reactor discharge is milled for long times.

The TiO₂ samples were found to have an isoelectric point (IEP) in the range of pH 3–4.5, with an increase in milling time leading to a lower pH_{IEP}. It was proposed that increasing the milling time leads to the presence of more SHMP on the alumina-doped pigment surface, due to the breakage of agglomerates/aggregates. DLS measurements probed two relaxation modes: (i) a mode characterised by a fast relaxation time, assigned to primary TiO₂ particles, and (ii) a mode characterised by longer relaxation times, subject to inter-measurement variability, and assigned to the aggregates present in the suspensions. The hydrodynamic diameter associated with the primary TiO₂ particles did not change upon milling time, while the DLS data suggested that the proportion of aggregates in the suspensions decreased upon milling time. Interestingly also, phosphorus content and zeta potential analysis after centrifugal washing showed that SHMP was partially removed for the longer milled pigment samples, whereas no change was observed for the shorter milled samples. It was assumed that either additional SHMP adsorption or structural changes promoted with milling, resulted in a more weakly bound surface adsorbed layer that could be removed, whereas chemisorbed dispersant was stable to repeated wash cycles.

Relaxation NMR data was also used to estimate surface area changes as a function of milling time. It showed a close to linear increase in surface area, and no plateau was detected, due to either the increase in surface area from fractured fines in the samples milled for longer times, or due to the increase in SHMP concentration and/or dispersant restructuring at the surface of the titana particles. It was hypothesised that hydrolysed SHMP has a greater influence on the NMR relaxation rate of bound water molecules leading to an enhancement in R_{1p}, although it is difficult to state for certain without further surface analysis of the SHMP with milling. Additionally, washed samples also resulted in larger NMR R_{1p} values for longer milling times, in comparison to the unwashed samples. Such changes were explained from either the exposure of surface alumina sites or hydrolysed SHMP after wash cycles having a greater relaxation rate than non-hydrolysed SHMP, however future work is suggested to further investigate this area. Importantly, this paper demonstrates the difficulties of characterising shear-dependent milled aggregates and the need for multiple characterisation techniques, alongside the potential of NMR relaxometry as an online-process control tool for not only detecting changes in surface area but also surface chemistry.

Data statement

The article metadata is available in the University of Leeds repository. Laura Elliott (2019): Characterisation of polyphosphate dispersant interactions with aluminium-doped titania nanoparticles during milling data set. University of Leeds. [Dataset], https://doi.org/10.5518/576. Article metadata is available under a Creative Commons Attribution licence (CC-BY).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2019.04.009.

References

[1] M. Gordon, J.M. Guiulmeny, Milestones in functional titanium dioxide thermal spray coatings: a review, J. Therm. Spray Technol. 23 (2014) 577–595.
[2] T.-H. Wang, A.M. Navarrete-Lopez, S. Li, D.A. Dixon, Hydrolysis of TiCl₄, initial steps in the production of TiO₂, J. Phys. Chem. A 114 (2010) 7561–7570.
[3] L. Zhao, Y. Liu, L. Wang, H. Zhao, D. Chen, B. Zhong, J. Wang, T. Qi, Production of rutile TiO₂ pigment from titanium slag obtained by hydrochloric acid leaching of vanadium-bearing titanomagnetite, Ind. Eng. Chem. Res. 53 (2014) 70–77.
[4] X. Xiong, Z. Wang, F. Wu, X. Li, H. Guo, Preparation of TiO₂ from ilmenite using sulfuric acid decomposition of the titania residue combined with separation of Fe₃+ with EDTA during hydrolysis, Adv. Powder Technol. 24 (2013) 60–67.
[5] W. Zhang, Z. Zhu, C.Y. Cheng, A literature review of titanium metallurgical processes, Hydrometallurgy 108 (2011) 177–188.
[6] G.S. McNulty, Production of Titanium Dioxide, IAEA, International Atomic Energy Agency (IAEA), 2008.
[7] Zion, Titanium Dioxide Market for Paints & Coatings, Plastic, Paper and Other Applications: Global Industry Perspective, Comprehensive Analysis, Size, Share, Growth, Segment, Trends and Forecast, 2014–2020, 2016, pp. 110.
[8] J.H. Braun, A. Baidins, R.E. Marganski, TiO₂ pigment technology: a review, Prog. Org. Coat. 20 (1992) 105–138.
[9] A. Hartmann, Process for the use of rutile promoter and control additives in the manufacture of titanium dioxide by the chloride process, Google Patents (1996).
[10] M.K. Akhtar, Y. Xiong, S.E. Pratsinis, Vapor synthesis of titania powder by titanium tetrachloride oxidation, AIChE J. 37 (1991) 1561–1570.
[11] K. Akhtar, S. Pratsinis, S. Mastrangelo, Vapor phase synthesis of Al-doped titania powders, J. Mater. Res. 5 (1994) 1241–1249.
[12] J.P.B. Manuel, Jesús Gázquez, Rafael García-Tenorio, Federico Vaca, A review of the production cycle of titanium dioxide pigment, Mater. Sci. Appl. 5 (2014) 441–458.
[13] E. Castellini, C. Berthold, D. Malferrari, F. Bernini, Sodium hexametaphosphate interaction with 2:1 clay minerals illite and montmorillonite, Appl. Clay Sci. 83–84 (2013) 162–170.
[14] E. Castellini, G. Lusvardi, G. Malavasi, L. Menabue, Thermodynamic aspects of the adsorption of hexametaphosphate on kaolinite, J. Colloid Interface Sci. 292 (2005) 322–329.
[15] Y. Han, W. Liu, J. Zhou, J. Chen, Interactions between kaolinite AOH surface and sodium hexametaphosphate, Appl. Surf. Sci. 387 (2016) 759–765.
[16] Y. Wang, E. Forssberg, Dispersants in stirred ball mill grinding, Kona Powder Part. J. 13 (1995) 67–77.
[17] M.L. Taylor, G.E. Morris, R.S.C. Smart, Polyphosphate interaction with aluminium-doped titania pigment particles, Colloids Surf., A 190 (2001) 285–294.
[18] A. Feiler, P. Jenkins, J. Ralston, Metal oxide surfaces separated by aqueous solutions of linear polyelectrolytes: DLVO and non-DLVO interaction forces, PCCP 2 (2000) 5678–5683.
[19] A. Michelmore, W. Gong, P. Jenkins, J. Ralston, The interaction of linear polyelectrolytes with titanium dioxide surfaces, PCCP 2 (2000) 2985–2992.
[20] P.A. Connor, A.J. McQuillan, Phosphate adsorption onto TiO₂ from aqueous solutions: an in situ internal reflection infrared spectroscopic study, Langmuir 15 (1999) 2916–2921.
[21] C. Rulliere, L. Perenes, D. Senoço, A. Dodi, S. Marchesseau, Heat treatment effect on polyelectrolyte chain length in aqueous and calcium solutions, Food Chem. 134 (2012) 712–716.
porous ceramics: a 1H NMR relaxation correlation study, Appl. Magn. Reson. 46 (2015) 1159–1178.

[52] X. Li, Y. Li, C. Chen, D. Zhao, X. Wang, L. Zhao, H. Shi, G. Ma, Z. Su, Pore size variation from low field NMR spin–spin relaxation measurements of porous microspheres, J. Power Mater. 22 (2015) 11–20.

[53] D.P. Gallegos, D.M. Smith, C.J. Brinker, An NMR technique for the analysis of pore structure: application to mesopores and micropores, J. Colloid Interface Sci. 124 (1988) 186–198.

[54] D.P. Gallegos, K. Munn, D.M. Smith, D.L. Stermer, A NMR technique for the analysis of pore structure: application to materials with well-defined pore structure, J. Colloid Interface Sci. 124 (1988) 265–281.

[55] S.B. Thoma, D.M. Smith, J. Broughton, R. Davies, On-line surface area measurement of concentrated slurries using low field spin-lattice relaxation NMR, Part. Part. Syst. Char. 10 (1993) 246–251.

[56] P.J. Davis, D.P. Gallegos, D.M. Smith, Rapid surface area determination via NMR spin-lattice relaxation measurements, Powder Technol. 53 (1987) 39–47.

[57] C.L. Glaves, P.J. Davis, D.M. Smith, Surface area determination via NMR: fluid and frequency effects, Powder Technol. 54 (1988) 261–269.

[58] L.N. Elliott, R.A. Bourne, A. Hassanpour, J.L. Edwards, S. Sutcliffe, T.N. Hunter, Salt enhanced solvent relaxation and particle surface area determination via rapid spin-lattice NMR, Powder Technol. 333 (2018) 458–467.

[59] C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH Image to ImageJ: 25 years of image analysis, Nat. Meth. 9 (2012) 671–675.

[60] N. Hondow, R. Brydon, P. Wang, M.D. Holton, M.R. Brown, P. Rees, H.D. Summers, A. Brown, Quantitative characterization of nanoparticle agglomeration within biological media, J. Nanopart. Res. 14 (2012) 977.

[61] M. Horn, C.F. Schwerdtfeger, A.R. Meagher, Removal of the structure of anatase at several temperatures, Zeitschrift für Kristallographie (1972) 273–281.

[62] M.S.U. Okrusch, R. Hock, A. Brummer, H. Theisinger, M. Baier, Intergranular transport in rutile phases with Sc- and W-rich ferrocolumbite: an electron-microprobe and Rietveld study, Am. Mineral. (2003) 986–995.

[63] A.L. Patterson, The Scherrer formula for X-ray particle size determination, Phys. Rev. 56 (1939) 978–982.

[64] L.S. Behra, J. Mattsson, O.J. Cayre, E.S.J. Robles, H. Tang, T.N. Hunter, Characterization of sodium carboxymethyl cellulose aqueous solutions to support formulation: a rheology and light scattering study, ACS Appl. Mater. Inter. 1 (2009) 344–358.

[65] W. Jordan, U. Javornik, J.C. Plavec, A. Rečnik, Self-assembly of multilevel branched rutile-type TiO2(2) structures via oriented lateral and twin attachment, Sci. Rep. 6 (2016) 24216.

[66] D. Klein, J.H. Choi, D.J. Pine, F.J. Lange, Synthesis of rutile titania powders: agglomeration, dissolution, and reprecipitation phenomena, J. Mater. Res. 18 (2003) 1457–1464.

[67] N. Mandy, E. Grulke, T. Druffel, Breakage of TiO2 agglomerates in electrostatically stabilized aqueous dispersions, Powder Technol. 160 (2005) 121–126.

[68] A. Gajovic, K. Furic, S. Music, Ball-Milling of TiO2 and ZrO2, Rudjer Boskovic Institute, Biunica, 54 10000.

[69] J. Cooper, Manual of Mineralogy, Durrie & Peck, 1855.

[70] T.A. Egerton, I.R. Tooley, Physical characterization of titanium dioxide nanoparticles, Int. J. Cosmet. Sci. 18 (1996) 315–322.

[71] T. Cosgrove, Y. Espidel, I. Howell, P. Revell, Sodium polyacrylate: a novel polymer derivative for the stabilization of TiO2 nanoparticles, J. Nanopart. Res. 1 (1999) 223–234.

[72] C.L. Cooper, J.S. Van Duijneveldt, M. Murray, C. Flood, Characterization of multiple hindered settling regimes in aggregated mineral suspensions, J. Nanopart. Res. 1 (1999) 143–150.

[73] C.L. Cooper, T. Cosgrove, Y. Espidel, I. Howell, P. Revell, Sodium polyacrylate adsorption onto anionic and cationic silica in the presence of salts, Langmuir 23 (2007) 6191–6197.

[74] C.L. Cooper, T.M. Obey, M. Taylor, Solvent relaxation NMR: bound fraction determination for sodium poly(styrene sulphonate) at the solid/solution interface, Colloids Surf. 64 (1992) 311–316.

[75] G. Mestl, B. Herzog, R. Schloegel, H. Knoezinger, Mechanically activated MoO3. 1. Particle size, crystallinity and morphology, Langmuir 11 (1995) 3027–3034.

[76] D.P. Gallegos, D.M. Smith, Simple rheology is a wet ultrafine grinding of TiO2, J. Mol. Struct. 563 (2001) 315–320.

[77] D.P. Gallegos, D.M. Smith, Rapid surface area determination via NMR spin-lattice relaxation measurements, Powder Technol. 53 (1987) 39–47.