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Role of Sodium Hexametaphosphate in Ultra-fine Grinding of Alumina-doped Titanium Dioxide

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Abstract

In wet stirred milling of Al-doped TiO_2, sodium hexametaphosphate (SHMP) is used as a small molecule dispersant to improve milling performance. In both acidic and basic conditions, SHMP interacts strongly with Al-doped TiO_2 and remains stable during milling. Considering the apparent and true particle breakage performance, at pH 10.3, the optimal dosing concentration was 0.16 wt% (0.33θ, sub-monolayer coverage), which is consistent for both dilute (5 vol%) and concentrated (≥ 19.1 vol%) suspensions. At higher SHMP concentration (0.77θ), the increased solution conductivity compromised milling performance by weakly destabilizing the Al-doped TiO_2 particles. At the optimal dose concentration of 0.33θ SHMP, particle dispersion is maintained through electrostatic and steric forces which contribute to moderating changes in suspension viscosity (~10% increase) as the particle size is reduced.

Introduction

With its superb light scattering properties, titanium dioxide (TiO_2) is widely used in inks, paints and plastics.[1–3] The excellent scattering properties result from the rutile polymorph having the highest refractive index of any colorless material. In the chloride manufacturing process, and during flame synthesis, aluminum trichloride ($AlCl_3$) is doped at concentrations up to 5 mol% to preferentially form the rutile polymorph.[4]

The scattering properties of TiO_2 depend strongly on the particle size distribution with a d_{50} between 0.2 and 0.3 μm being desired.[1,5] To achieve this particle size distribution, wet stirred media milling is frequently used to reduce the aggregate particle size.[6] The method involves a rotating spindle and a fixed grinding chamber filled with small media beads. The spindle induces flow of the slurry and media beads, with particle size reduction occurring between two colliding media beads through singular or cumulative stresses (fatigue).[7,8] The high energy demands of the milling operation can be partly offset by milling high concentration slurries, although there is an optimum to be achieved by balancing the solids throughput and the slurry viscosity; too high a viscosity and the kinetic energy by bead collision will be damped which results in poor energy transfer to the particles, significantly hindering milling performance.[9,10] The effect of suspension viscosity on the frequency of media bead collision was computationally studied by Strobel et al.,[10] demonstrating that more viscous fluids also reduce the frequency of media bead collision, with the suspended particles having a greater tendency to follow the flow perpendicular to the approaching media beads.

To overcome the effects of viscous dampening at high solids concentrations, small molecule dispersants are typically added to achieve milling with solids content greater than 50 wt%.[11,12] He et al.[11] stated the role of a dispersant was to lower or eliminate the suspension yield stress by modulating the particle-particle interaction force. Gao and Fossberg[13] studied the role of Dispex N40 (polycarboxylic acid) in the wet stirred milling of 70 wt% dolomite. Varying the dispersant concentration from 0.25 to 8 wt%, the optimum dosage to achieve the best milling performance was 0.5 wt%. This concentration lowered the suspension yield stress from 27 Pa to 1.5 Pa, but increased the high shear suspension viscosity from 0.18 Pa.s to 0.48 Pa.s. The increase in suspension viscosity was reasoned to be critical in maintaining friction between the media beads and particles, but contrasted the study of Strobel et al.[10]

Bernhardt et al.[14] studied the stirred media milling of limestone, evaluating the effects of solids concentration, from 20 to 60 wt%, with and without the addition of 0.5% sodium polyacrylate (SPA). Increasing the slurry concentration from 20 to 35 wt% and without SPA, an increase in the energy utilisation was observed, with the breakage performance increasing due to increased probability of particles being captured between media bead collisions. However, at higher solids concentrations, from 35 to 50 wt%, a decrease in energy utilisation was observed, a consequence of viscous dampening, and highlighted the balance between milling throughput and viscous dampening. With 0.5% SPA, the same parabolic relationship was observed but the maximum energy utilisation shifted towards a higher solids concentration (45 wt% from 35 wt%). At 35 wt% solids, the energy utilisation was shown to be greater without a dispersant (2.75 m^2 KJ^{-1}) than with SPA added (~ 1.8 m^2 KJ^{-1}). The viscosity reduction with SPA was found to be beneficial at high solids concentrations where viscous dampening occurs, while at lower solids concentrations, the low suspension viscosity was postulated to result in particles evading media bead motion.

Comparing the performance of organic (Dispex CP [Acrylic copolymer]; Dispex N40[polycarboxylic acid]) and inorganic (sodium hexametaphosphate [SHMP]; tetrasodiumpyrophosphate) dispersants in the wet stirred milling of dolomite, Wang and Forssberg showed enhanced particle size reduction and higher particle surface area when milling with organic dispersants at 0.5 wt% and solids content of 70 wt%.[15] Both organic and inorganic dispersants had readily ionisable functional groups, but the organic dispersants were much larger (Mw < 6500 g mol^{-1}) compared to the inorganic polyphosphates of TSPOP (P_n = 3, 265.9 g mol^{-1}) and SHMP (P_n = 6, 611.77 g mol^{-1}), with the enhanced performance attributed to the greater electro-steric forces of the organic dispersants. Comparing the two polyphosphates, SHMP outperformed TSPOP, and Farrokhpay et al.[16] showed that polyphosphates of $P_n \geq 4$ provided improved dispersion over shorter polyphosphates due to the significant steric barrier which prevented direct particle-particle contact. Such contribution was also verified by Liu et al.[17] who used ^{31}P NMR to confirm that the adsorbed polyphosphate (P_n = 6 and 21) extends from the particle surface with a steric barrier of > 5 Å needed to perturb the van der Waals forces.

SHMP is of particular interest in the wet stirred milling of alumina-doped TiO_2, yet there are few published studies on this system. Of note is the work by Elliot et al.[18], who milled Al-doped TiO_2 at a solids concentration of 40 wt %, using 0.14 % w/w SHMP as P_2O_5 on TiO_2. The isoelectric point (i.e.p.) of Al-doped TiO_2 with SHMP adsorbed was pH ~4.5 (at 1 min milling) and reduced to pH ~3.0 after milling for 32 min. It was suggested that the de-agglomeration process led to exposure of additional surface sites for SHMP adsorption, thus lowering the i.e.p.. This hypothesis was further supported by X-ray fluorescence (XRF) spectroscopy, which showed a ~95 % increase in the phosphorous content during milling. However, when washing the samples, the 32 min milled sample showed a reduction in the zeta potential from ~44 mV to 37 mV (at pH 7), and a reduced phosphorous content by 70%. Such changes were not observed for the sample milled for 1 min. The weakened adsorption of SHMP on the TiO_2 surface and/or partial hydrolysis of the polyphosphate, induced by the mechanical activation of the surface during milling, was postulated to explain this phenomenon. Furthermore, polyphosphates are known to be liable to degradation with heat.[16,19,20]

Adsorption of SHMP has been studied on a range of different particles/surfaces, including titanium dioxide,[15] alumina-doped titanium dioxide,[16] aluminium oxide,[17] kaolinite,[18] illite and montmorillonite.[19] Surface charge reversal is frequently shown with SHMP adsorption, and a range of critical concentrations are reported depending on the surface properties and SHMP molecular size; with larger molecules inducing charge reversal at a lower concentration.[21,22] Taylor et al. [17] studied the adsorption of polyphosphates (P_n = 10 to 12) on Al-doped TiO_2 at concentrations of 1.2, 2.0 and 2.7 mg/g. The i.e.p. of the Al-doped TiO_2 ranged between pH ~8.7 to 9.1, with variation attributed to slight sample heterogeneity resulting from different alumina contents (7.3 and 10.4 at%). With increasing concentration, the i.e.p. was found to decrease from approximately pH 5 to pH 3.

Using FTIR spectroscopy, Connor et al.[23] confirmed that orthophosphate (P_n = 1) binds to TiO_2 via two Ti-O-P bonds as a bidentate ligand. A more comprehensive study by Michelmore et al.[21] considered the adsorption of linear polyphosphates ranging from P_n = 1 to 4 and a poly-disperse polyphosphate of mean P_n = 10. The authors proposed that both the orthophosphate and polyphosphate molecules bind as bidentate ligands, but unlike orthophosphate which forms two Ti-O-P bonds from the same phosphate group, the polyphosphate forms two single Ti-O-P bonds, one from either terminal phosphate groups resulting in a flat-on conformation (parallel to the surface). This conformation was not found to change with pH (pH 4 and 9.1) when the surface potential changed from being strongly positive at pH 4 to negative at pH 9.1.

In the current study, the role of SHMP in ultrafine grinding of Al-doped TiO_2 is studied at a range of solids concentrations from dilute (5 vol%) through to more industrially relevant concentrations of 13.6 to 26.2 vol%. The SHMP dose levels were varied from 0.16 to 3.5 wt% to study the effect of SHMP surface coverage on the true (particle specific surface area) and apparent (aggregate size) milling performance. Zeta potential and viscosity measurements were used to correlate the meso-scale suspension behaviour to the macro-scale milling performance, therefore, elucidating the critical role of SHMP in the wet stirred milling of Al-doped TiO_2.

Materials and Experimental Methods

Research grade Al-doped TiO_2 was supplied as a ~50 wt% slurry by Venator Ltd., UK. Prior to use, the suspension was washed with excess deionized water (5 L), agitated for 1 hr and left to settle for 2 weeks before siphoning-off the supernatant and repeating the wash process a further two times. With the supernatant removed, the wet sample (~3 kg) was dried at 100 °C for 24 hr, during which it was frequently mixed to ensure homogeneous drying. The Al-doped TiO_2 was then aliquoted for suspension preparation and crushed with a mortar and pestle for 5 mins to break-up any large particle aggregates. All suspensions were dispersed in 10^{-3} M NaCl (analytical grade, Sigma-Aldrich) prepared with Milli-Q^{TM} water (< 18 MΩ/cm). Sodium hexametaphosphate (SHMP) of Mw = 611.8 g mol^{-1} (Sigma Aldrich, 98% purity) was used without further purification. The Al-doped TiO_2 suspensions were allowed to equilibrate for several hours prior to and after addition of the SHMP.

Wet Stirred Mill: A stainless steel grinding chamber (V = 365 mL excluding spindle) and ceramic spindle (Fig. S1) were fabricated for use with a Silverson high shear mixer (L5M-A, Silverson, UK). The mill was operated using zirconia coated silica beads (d = 500 µm) at a media fill ratio of 0.8. After each experiment the grinding media were washed in excess deionised water and sieved between 350 and 560 µm mesh to remove any potential fragmented/aggregated milling beads prior to reuse. Further details of the mill can be found in our previous publication.[6]

Al-doped TiO_2 suspensions were prepared at concentrations from 1.2 to 26.2 vol% in 10^{-3} M NaCl at pH 4 (approximately the natural suspension pH). To ensure ionic equilibrium, between the particle surface and fluid, these suspensions were gently agitated for several hours prior to use. For milling studies with SHMP, the dispersant was added at the desired concentration and the suspension gently agitated for several more hours prior to pH adjustment to the milling condition. Suspensions of 75 mL were transferred to the mill and the rotational speed of the spindle was initially set at 100 rpm for 1 min to ensure the suspension was dispersed in the milling media. For all experiments, the mill was operated at 6000 rpm with the milling times varied between 2 and 60 min as these were found to be the optimum conditions for the mill based on our previous findings.[6]

Zeta Potential: The pH-dependant zeta potential of the milled particles was measured using a Zetasizer Pro (Malvern Panalytical, UK), applying the Henry-Smoluchowski approximation.[24] The mill was stopped temporarily at the desired milling time with 150 µL aliquots of the sample pipetted into 15 mL Eppendorf tubes made up with 14.85 mL of 10^{-3} M NaCl. The suspension pH was adjusted using 10^{-3} M HCl or NaOH before ultra-sonicating for 5 min and pipetting into a zeta cell (DTS1070). All zeta potential measurements were conducted in triplicate, with the average values reported. To limit the influence of sample volume reduction on milling behaviour, a maximum of 5 samples were collected from one mill test. For zeta potential measurements, all samples were measured within 4 h of completing the mill test.

Particle Size: The particle size distribution (PSD) was measured using a Mastersizer 2000 (Malvern Panalytical, UK) with a Hydro 2000 SM dispersion unit. Samples were collected from the mill following the procedure outlined in the zeta potential section, and ultra-sonicated for 5 min before pipetting into the dispersion unit to increase the laser obscuration within the optimum range (15 to 20 %) at a stirrer speed of 2200 rpm. Prior to pipetting the suspension, the dispersion unit and flow cell were filled with 10^{-3} M NaCl at the sample pH (pH 4, 9 or 10.3) to ensure no change in pH when adding the suspension to the measurement cell. The particles were circulated through the measurement cell and the scattering intensity of the incident laser used to determine the PSD based on MIE theory.[25] The particle size distribution of the as-received Al-doped TiO_2 and a representative SEM image of the particles is shown in Fig. 1.

Figure 1. Particle size distribution of the as-received Al-doped TiO_2. A suspension of 0.05 vol% was prepared in 10^{-3} M NaCl, adjusted to pH 4. Inset: scanning electron microscope image of the dried Al-doped TiO_2 sample.

Particle Specific Surface Area: The Brunauer, Emmett and Teller theory (BET) was used to determine the particle surface area via adsorption of nitrogen gas. The mill was stopped at the desired milling time and the suspension carefully decanted from the milling chamber, followed by several rinses of the milling media and grinding chamber with DI water to ensure most of the sample was recovered. Approximately 6 to 8 g of milled sample (solid mass) was heated at 100°C in a vacuum oven overnight (< 10 mmHg, ~12 h), before nitrogen adsorption was conducted using a Tristar 3000 (Micrometrics, USA). A 6 point adsorption method was used between relative pressures (equilibrium pressure (p_e)/ saturation pressure (p_o)) of 0.04 and 0.1, where Langmuir-like, monolayer adsorption is observed.[26] Results are plotted in the linear format of the BET equation to determine the specific surface area (Eq. 1):

$$\frac{1}{v[\left({}^{p_0}/_{p}\right)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \qquad (1)$$

where v and v_m are the adsorbed gas volume and monolayer adsorbed gas volume respectively, and c the BET constant. Correlating v_m to the specific surface area is possible using the molecular area of the adsorbate, σ, and Avagadro's constant, N_a***Error! Reference source not found.***, (Eq. 2).[27]

$$SSA = \frac{v_m}{22414}\sigma N_a. \qquad (2)$$

Rheology: Suspension rheology was measured using a stress-controlled Discovery Hybrid Rheometer (DHR-2, TA Instruments, UK) equipped with a smooth bob (L = 41.94 mm; D = 28.02 mm) and cup (D = 30.4 mm) geometry. Shear rate sweeps were conducted from 1200 s^{-1} to 0.1 s^{-1} to 1200 s^{-1}. The first sweep was at 25 ^{o}C followed by 5 sweeps at increasing temperatures of 35, 45, 55, 65 and 70 ^{o}C. A final sweep at 25 ^{o}C was completed to provide comparison with the initial rheological data at 25 ^{o}C. The temperature range was selected to correspond with the measured temperatures in the milling chamber (~60 ^{o}C). Only the shear rate ramp down data is reported as no hysteresis was observed during the testing protocol.

Sampling issues were encountered when recovering the sample through the bottom sieve of the milling chamber. Due to the poor flowability of the sample (under gravity) and significant coating of the suspension on the milling beads, it was challenging to ensure the drained suspension concentration was consistent with the as-prepared concentration (19.1 vol%). To address this issue, samples were removed from the milling chamber following the procedure outlined in the particle specific surface area section. The dried Al-doped TiO_2 was then redispersed in pH adjusted 10^{-3} M NaCl to 19.1 vol%, stirred for 4 h and ultrasonicated for 10 min prior to rheological assessment. Measurements with SHMP followed the same protocol, but with SHMP being added after milling and drying, and during the redispersion-step. This method was taken as many studies had reported polyphosphate liability to degradation (hydrolysis) under mild heat, thus the drying-step may have led to changes in SHMP that may have limited the reliability of the rheology data and its comparison with the milling behavior.

To ensure the re-dispersion method was appropriate, 3 sample preparation protocols were compared: i) sample re-dispersion with gentle mixing; ii) sample re-dispersion with gentle mixing followed by ultrasonication for 10 min; iii) sample re-dispersion with gentle mixing followed by 10 min ultrasonication and 2 min with a sonic horn. These protocols were compared for fresh samples (un-milled) and those milled for 60 min in 10^{-3} M NaCl at pH 4 (Fig. S2). For the un-milled samples, the low shear rate (< 10 s^{-1}) viscosity was found to gradually increase with each sample preparation method (iii > ii > i) and was attributed to the breakup of weakly formed sintered aggregates from the flame synthesis process. However, for the milled samples, the measured viscosity was found to be almost equivalent and showed negligible effect of the sample preparation method. To ensure consistent sample history, all samples were prepared following protocol ii.

Suspension Conductivity: The conductivities of Al-doped TiO_2 and Al-doped TiO_2 + SHMP suspensions were measured using a conductivity probe (Seven2Go S3, Mettler Toledo). To ensure the conductivities were within the measurement range of the probe, samples were diluted 100 times with Milli-Q™ water. The conductivity results of Al-doped TiO_2 + SHMP samples were correlated to an equivalent NaCl concentration using a 3-point calibration curve.

Adsorption Isotherm: Using 200 mL plastic (PE) sample bottles, 100 mL SHMP solutions were prepared to concentrations from 5 mg L^{-1} to 1000 mg L^{-1} in 10^{-3} M NaCl at pH 4 or 9. 1 g of Al-doped TiO_2 was added to the SHMP solution and stirred gently while the pH was monitored for 4 hr. During the first 5 – 10 mins, the suspension pH would drift (more acidic when prepared at pH 9) and required careful pH control. After 20 mins the suspension pH stabilized, likely confirming the rapid adsorption of SHMP. The suspensions were gently agitated for 12 hr on an orbital shaker (SSL1 Stuart) before separating the supernatant from the particles by centrifuging the suspensions at 12,000 rpm for 2 hr (Heraeus™ Megafuge™ 16 Centrifuge). The supernatant was then further purified using a 0.22 μm syringe filter to ensure minimal transfer of any ultrafine particles. The supernatant was analyzed using ICP-OES (Thermo Scientific iCAP7600 ICP-OES) with a 5 point calibration of SHMP in 10^{-3} M NaCl. In addition to studying adsorption at pH 4 and pH 9, a further set of samples were studied by first adsorbing SHMP at pH 4, gently mixing for 12 hr, and then adjusting the pH to 9 before gently shaking for a further 12 hr prior to removing the supernatant and analyzing by ICP-OES.

Results and Discussion

SHMP Adsorption on Al-doped TiO_2. SHMP adsorption on Al-doped TiO_2 was studied at pH 4, pH 9, and pH 4 adjusted to pH 9, see Fig. 2. The data for pH 4 and pH 9 adsorption were well-fitted using the Langmuir adsorption isotherm model (see Table 1 for the model fitting parameters) and confirm a > 30% increase in the surface adsorption capacity (q_m) at pH 4 compared to pH 9. Enhanced adsorption at pH 4 partly corresponds to the strength of the electrostatic interaction between the particle and dispersant molecule, with the zeta potential of Al-doped TiO_2 at pH 4 equal to +38 mV which decreases to −38 mV at pH 9 (Fig. 4). Furthermore, pKa values for the bridging and terminal hydroxyl phosphate groups vary from ~0−3 and 7−9, respectively.[28]

Figure 2. Adsorption isotherms of SHMP on Al-doped TiO_2. Closed symbols represent SHMP adsorption at pH 4 (black) and pH 9 (blue), while open symbol represents SHMP adsorption at pH 4 and adjusted to pH 9. The lines show the Langmuir fits at pH 4 and pH 9.

Table 1. Langmuir adsorption isotherm fitting parameters.

In studying the adsorption of polyphosphates of increasing chain length (P_n = 2 to 10) on pure TiO_2, Michelmore et al.[21] observed a strong influence of pH with the q_m@pH4/q_m@pH9 ratio found to be between 4 and 10 for polyphosphates of P_n = 2 to 6, and no adsorption at pH 9 for the largest polyphosphate (P_n = 10). The authors commented that with increasing molecular size the total molecular charge increases, therefore, the interaction between the negatively charged particle surface and polyphosphate molecule becomes increasingly repulsive. For similarly large polyphosphates (P_n = 10 to 12) adsorbed on Al-doped TiO_2, Taylor et al.[28] reported q_m@pH4/q_m@pH9 ratios of ~3, with the lower ratio attributed to greater adsorption at pH 9 due to the surface heterogeneity of the Al-doped TiO_2, comprising Al-OH, Al-OH^{2+} and Ti-O^- surface sites. In the current study, the measured q_m@pH4/q_m@pH9 ratio for SHMP ($P_n = 6$) is 1.34. The lower ratio is in good agreement with published data and corresponds to small molecule adsorption onto heterogeneous surfaces. When adjusting the suspension pH from pH 4 to 9, the adsorption isotherm remained consistent with the pH 4 data and confirmed the stability (irreversible adsorption) of SHMP on Al-doped TiO_2 via a bidentate chelating chemisorption mechanism, as previously discussed.

For 10^{-3} M NaCl at pH 4, the zeta potential of Al-doped TiO_2 was +38 mV. Slightly increasing the SHMP equilibrium concentration (q_e) led to a significant reduction in the zeta potential and charge reversal was observed at ~22 mg/L (Fig. 3). At SHMP concentrations > 100 mg/L, the measured zeta potentials were shown to be stable around −35 mV. The reduction in zeta potential values inversely correlated to the adsorbed amount of SHMP, with the surface coverage (θ) calculated based on q_e/q_m. With adsorption of SHMP, particle charge reversal occurred at θ ~0.5, and the plateau in zeta potential was observed between $\theta = 0.85$ to 1.0.

Figure 3. SHMP adsorption isotherm on Al-doped TiO_2 at pH 4 in 10^{-3} M NaCl and the corresponding particle zeta potential at pH 4.

Milling of Al-doped TiO_2 with SHMP. A series of tests were developed to determine the effect of SHMP when milling Al-doped TiO_2, and included assessment of intrinsically related parameters: i) SHMP surface coverage (SHMP concentrations were varied from 0 to 3.5 wt%); ii) increased electrolyte conductivity by SHMP addition (comparable conductivity achieved by adding NaCl), and iii) electrostatic stabilization (adjusting the suspension pH to result in similar zeta potentials with and without SHMP).

As a consequence of milling and the increased particle specific surface area (SSA), SHMP surface coverage can reduce if not added in excess. Measuring the change in SHMP surface coverage during milling is not trivial, but can be approximated by measuring the particle zeta potentials before and after milling. The pH-dependent zeta potential curves for all three initial conditions (0.32θ, 0.76θ and 0.92θ) are shown in Fig. 4, and for all samples the two data sets are superimposed across the pH range, suggesting negligible change in θ for all SHMP dose levels, and no detrimental impact of the milling process on the SHMP adsorbed layer. Previous work by Elliot et al.[18] showed that conversely, high energy milling degraded adsorbed SHMP. However, the SHMP was added in significant excess, where it was hypothesized that secondary physiosorbed layers formed that were more easily degraded than the chemisorbed monolayer expected with little excess SHMP. Also included in Fig. 4 is the zeta potential curves for the pure Al-doped TiO_2 sample without SHMP before and after milling. While the shift in particle i.e.p. has been extensively discussed in our previous work,[6] the resulting zeta potential curves confirm that the increased particle surface heterogeneity has negligible influence on SHMP adsorption.

Figure 4. pH-dependent particle zeta potentials before (closed symbols) and after (open symbols) milling with SHMP dose concentrations of 0.16 wt% (0.33θ), 1 wt% (0.77θ) and 3.5 wt% (0.92θ). The mill conditions were 60 min at 6000 rpm.

Dilute Milling of Al-doped TiO_2. The mill-curves for 5 vol% Al-doped TiO_2 in 10^{-3} M NaCl at pH 4 (Fig. 5a and b) and pH 10.3 (Fig. 5d and e) are considered with respect to the particle-particle interaction energy (Fig. 5c and f). Although not discussed, the mill-curve at pH 9 is provided in the Supporting Information, Fig. S4, and showed similar behavior to milling at pH 10.3. The theoretical interaction energies were approximated using the DLVO theory which describes the total interaction energy (Eq. 5) as the summation of an attractive energy (van der Waals, Eq. 3) and repulsive energy (electrical double layer, Eq. 4). The vdW and EDL energies were modeled using the non-retarded Hamaker constant ($A_H = 6.05 \times 10^{-20}$ J) and the linear superposition-approximation model, within the Derjaguin approximation for two spherical particles.[24]

$$V_A = -\frac{A_H\, d}{24\, h} \tag{3}$$

$$V_R = \pi \varepsilon_o \varepsilon_r \zeta^2\, d exp^{\left(-h/\lambda_d\right)} \tag{4}$$

$$V_T = \pi \varepsilon_o \varepsilon_r \zeta^2\, d exp^{\left(-h/\lambda_d\right)} - \frac{A_H\, d}{24\, h} \tag{5}$$

where d is the particle diameter (taken to be the d_{50} value after milling for 60 min), ε_o the permittivity of free space, ε_r the permittivity of the medium, ζ the zeta potential, and λ_d the Debye length, which was calculated as $0.304/\sqrt{I}$, where I is the electrolyte concentration. Since the electrolyte concentration could not be directly determined, an approximation was made by comparing the measured solution conductivity to that measured in NaCl for an equivalent concentration. This is subsequently referred to as the equivalent NaCl concentration.

Figure 5. The apparent milling performance of 5 vol% Al-doped TiO_2 in 10^{-3} M NaCl at pH 4 and pH 10.3, milled at 6000 rpm for up to 60 min. The initial dose concentrations of SHMP were such that the adsorbed surface coverages were 0, 0.33, 0.77 and 0.92θ. The particle size is represented by the d_{50} value and the particle size distribution by the d_{90}-d_{10} value. The theoretical particle-particle interaction energies were calculated using Eq. 5, with the zeta potentials taken from Fig. 4, and the Debye lengths determined from the measured solution conductivity.

Apparent milling behavior: At pH 4, SHMP dosing was found to negatively impact the apparent milling performance of 5 vol% Al-doped TiO_2. For all dosing concentrations and milling times, the particle d_{50} with SHMP was larger than that without SHMP. The final particle d_{50} was found to increase in the order $0\theta < 0.92\theta < 0.77\theta < 0.33\theta$, with the smallest d_{50} of 0.275 μm for 0θ. Although the particle d_{50} was significantly affected by the SHMP concentration, the width of PSD (d_{90}-d_{10}) was only found to broaden at 0.33θ, with the higher SHMP concentrations showing a similar width of PSD at 60 min milling as compared to 0θ, but a slightly narrower width of PSD at shorter milling times. The observed reduction in milling performance (particularly the higher d_{50}) can be better understood from the approximated interaction energies for each suspension (Fig. 5e and f). When SHMP is dosed into the Al-doped TiO_2 suspension at pH 4, the large primary aggregation barrier (peak energy of ~120 KbT) is reduced, changing the interaction from being predominantly repulsive to attractive, with the strength of attraction increasing in the order $0.92\theta < 0.77\theta < 0.33\theta$. Although adding SHMP causes the Debye length to decrease, the greater effect is from the particle zeta potential which changes from 4 mV to –31 mV for 0.33θ to 0.92θ. At 0.33θ, the colloidal particles have a tendency to aggregate (Fig. 5a and c) due to the low zeta potential which results from the partial (in-homogeneous) surface coverage of SHMP on Al-doped TiO_2. As such, the induced particle aggregation would increase the suspension viscosity which negatively affects the milling performance.

At pH 10.3, the apparent milling performance was found to be slightly improved when adding SHMP (0.33θ, 0.77θ 0.92θ), although the differences between SHMP dose concentrations were negligible. The final d_{50} decreased from 0.271 μm (0θ) to 0.239 μm (0.33θ), with the respective widths of PSD equal to 0.297 μm and 0.274 μm. The final d_{50} for 0.77θ and 0.92θ were 0.246 μm and 0.265 μm. The reduced dependence on SHMP concentration resulted from the strongly negative zeta potential at pH 10.3 in the absence and presence of SHMP. Consequently, the particle-particle interaction energy is strongly repulsive, with a shallow secondary minima reducing with increasing SHMP concentration (Fig. 5f). This secondary minimum most likely contributes to the slight difference in the final d_{50} when milling with SHMP. Even though the particles remain strongly electrostatically-stable (with and without SHMP), the addition of SHMP remains to provide some benefit to the apparent milling performance, which translates to a slightly smaller particle d_{50} and width of PSD after milling for 60 min. This may result from an additional steric repulsive force induced by the adsorbed SHMP molecules,[16,19,22] with the steric interaction force possibly exceeding electrostatic forces at shorter separation distances.

True milling behavior: The effect of SHMP concentration on the true breakage (primary particle size) can be assessed by measuring the particle specific surface area (SSA) after milling. Figure 6a shows the particle SSA for Al-doped TiO_2 milled at pH 4 and pH 10.3, with varying initial concentrations of SHMP, 0, 0.33, 0.77 and 0.92θ. The pH 9 data is provided in the Supporting Information, Fig. S4. The largest particle SSA was measured for 0θ at pH 4, 9.60 m^2/g, and addition of SHMP decreased the particle SSA, with the effect dependent on suspension pH and SHMP concentration. At pH 10.3, increasing the SHMP concentration reduced the final particle SSA, while at pH 4, the particle SSA was smallest at 0.33θ. This outlier is likely attributed to the partial coverage of SHMP on the Al-doped TiO_2 and the strong aggregation potential at this condition. While not considered in the current study, previous research on the milling performance of Al-doped TiO_2 revealed the presence of many spherical ultra-fines ($\ll$ 50 nm), at extreme milling extents, which go undetected when measured by laser diffraction, but do contribute to a higher particle SSA.[6] It is thought that the higher particle

SSA for 0θ at pH 4 results from these ultra-fines that are formed by surface erosion of individual primary particles, which is a consequence of the high shear milling.

Figure 6. a) The particle specific surface area (SSA) of Al-doped TiO_2 milled at 5 vol% in 10^{-3} M NaCl at pH 4 and pH 10.3 for 60 min at 6000 rpm. The initial dosing concentrations of SHMP led to adsorbed surface coverages of 0, 0.33, 0.77 and 0.92θ. b) Comparing the particle SSA as a function of the equivalent concentration of NaCl ($\times 10^{-2}$ M). The data points with SHMP correspond to the samples in (a), and without SHMP the background electrolyte concentration (NaCl) was increased. The data are compared for milling at 6000 rpm and 60 min. The corresponding Debye length for the electrolyte concentration is shown on the X_2-axis. It is important to note the correlation between Debye length and equivalent electrolyte concentration is non-linear. Therefore, only at those Debye lengths plotted are the values absolutely correct.

The change in particle SSA with the equivalent concentration of NaCl is compared in Fig. 6b for suspensions with and without SHMP. With the bridging and terminal hydroxyl phosphate groups having pKa values of 0−3 and 7−9 respectively,[28] adding SHMP to the Al-doped TiO_2 suspension increased the solution conductivity which can negatively impact milling performance. With SHMP, increasing the dose concentration led to an s-shaped response in the true breakage performance, with a step-up in performance observed at ~0.018 M equivalent concentration of NaCl. Without SHMP, the concentration of NaCl was increased from 0.3 to 1.75×10^{-2} M to span the same conductivity range measured with SHMP. An s-shaped response was again observed, albeit with a shallower step-change, and the true breakage performance was found to be poorer than milling with SHMP (equivalent performance was only observed at very low equivalent concentrations of NaCl).

A similar s-shaped response has been observed by Knieke et al.[9] when comparing the energy transfer coefficient to the mean particle size of α-alumina during stirred media milling. The energy transfer coefficient represents the energy for media bead collision relative to the energy for fluid displacement. At all suspension concentrations, as the mean particle size was reduced, a critical condition was reached whereby the energy transfer coefficient abruptly transitioned from the significant energy contribution to media bead collision to that of fluid displacement. This critical condition was found to depend on the solids concentration, with the abrupt transition occurring at a higher mean particle size for increasing solids concentrations. Such dependence is expected since both the particle size and solids concentration can strongly influence the suspension viscosity. On this basis, the s-shaped behavior observed in the current study can also be attributed to changes in the suspension viscosity, which is also impacted by the solution conductivity. Herein, the critical step-change occurs at equivalent NaCl concentrations of ~1.8 and 0.7×10^{-2} M with and without SHMP, respectively. While the data confirms a reduction in the true breakage performance with increased conductivity of the suspension, it also highlights the added benefit of using SHMP, modulating the effects of the increased electrolyte concentration (retaining high particle SSA with increased solution conductivity).

Concentrated Milling of Al-doped TiO_2. Milling at solids concentrations more relevant to industry often means achieving a balance between solids throughput and suspension viscosity. The effect of Al-doped TiO_2 solids concentration on the milling performance is shown in Fig. 7a and b. When milling at 6000 rpm for 60 min, increasing the solids concentration without SHMP resulted in larger aggregate sizes, with d_{50} increasing from 0.257 µm to 0.292 µm from 1.2 to 26.2 vol%. The increase in aggregate size also corresponded to an increase in the width of PSD (d_{90}-d_{10}), with a significant reduction in the milling performance seen at 19.1 vol%. Similar behavior has also been reported for TiO_2 suspensions in the concentration range of 1.2 to 9.2 vol%.[29]

Figure 7. The effect of solids concentration on the apparent milling performance of Al-doped TiO_2 in 10^{-3} M NaCl at pH 4, milled at 6000 rpm for up to 60 min. The particle size is represented by the d_{50} value (a) and the width of PSD (d_{90}-d_{10}) (b). The solids concentration range was 1.2 vol% to 26.2 vol%, with the increments shown in the data legend. All samples were milled without SHMP. The data for 1.2 to 5.0 vol% are greyed-out as they represent solids concentrations below those of industry relevance, but are included to further demonstrate the milling behavior.

It should be noted that the sample at 26.2 vol% with no SHMP could not be milled due to the very high suspension viscosity. At high solids concentrations, the apparent milling performance was found to vary with SHMP concentration, see Fig. 8a and b. The poorest milling performance was observed without SHMP (Al-doped TiO_2 in 10^{-3} M NaCl at pH 4 - used as the control sample), and the best milling performance was measured at 0.33θ SHMP. At this condition, the final d_{50} was 0.257 µm, 0.263 µm and 0.265 µm, for 13.6, 19.1 and 26.2 vol%, respectively. These final aggregate sizes were comparable to those measured when milling dilute suspensions of Al-doped TiO_2 with SHMP (Fig. 7 a), confirming the potential to achieve equivalent milling performances at high solids concentrations when SHMP is added at the optimal concentration. The time-dependent milling curves for the data shown in Fig. 8a and b are provided in the Supplementary Information, Fig. S5.

The true breakage was assessed by measuring the particle SSA after milling for 60 min, see Fig. 8c. For dilute solids concentrations, increasing the SHMP concentration (@ pH 10.3) reduced the true breakage performance (13.6 vol% in Fig. 8c), while at higher solids concentrations, the effect of SHMP concentration was less consistent, especially at 19.1 vol%, where the particle SSA was highest at 0.33θ SHMP. For 0θ and 0.77θ SHMP, increasing the solids concentration decreased the final particle SSA, while for 0.33θ SHMP, the opposite trend was observed. For 0θ and 0.77θ SHMP, the decrease in true breakage can be attributed to higher suspension viscosities, resulting from the increased solids concentration, and for 0.77θ SHMP, the high solution conductivity (Fig. 6b) that promotes stronger particle-particle interactions which would increase the suspension viscosity.

Figure 8. The effect of solids concentration (13.6, 19.1 and 26.2 vol%) and SHMP dosing concentration (0, 0.33 and 0.77θ) on the apparent (a and b) and true (c) milling performance of Al-doped TiO_2 in 10^{-3} M NaCl at pH 10.3, milled at 6000 rpm for 60 min. The particle size data is represented by the d_{50} value (a), the particle size distribution (d_{90}-d_{10}) (b), and the particle SSA (c). N.b. the control sample without SHMP was milled at pH 4. Such comparison is valid as the magnitude of zeta potential at pH 4 (|38| mV) is equivalent to that at pH 10.3 (|45| mV), see Fig. 4.

Suspension rheology: At 19.1 vol% solids concentration, the effect of SHMP dose concentration on the milling performance could not exclusively be attributed to the changing electrical double layer forces, since 0.33θ SHMP led to the highest particle SSA. Further insight into the effect of SHMP was gained by studying the suspension rheology at pH 4 (no SHMP) and pH 10.3 with SHMP dose concentrations of 0.33 and 0.77θ. Samples were milled at 6000 rpm for 6, 15 and 60 min, the suspensions were then recovered from the milling chamber and prepared to a solids concentration of 19.1 vol% following the procedure outlined in the Methods section. All rheology measurements included a sequence of shear rate ramps from 1200 s^{-1} to 0.1 s^{-1}, and were conducted at several temperatures between 25 °C and 70 °C. Only the data at 25 °C, which is the first and last shear rate ramps are compared in Fig. 9. The complete set of data including the shear rate ramps at all temperatures is provided in the Supplementary Information, Fig. S3. With the rheology test protocol (consecutive shear rate ramps at increasing and decreasing temperatures) requiring 6 hr to complete, there was concern that solvent evaporation would modify the suspension viscosity. While the suspension viscosity with SHMP was found to change (first and last shear rate ramp comparison), no significant shift in viscosity was measured without SHMP, thus any affect from solvent evaporation was considered to be negligible.

Figure 9. The rheology of Al-doped TiO_2 suspensions in 10^{-3} M NaCl. The SHMP dose concentrations were equivalent to 0θ, 0.33θ and 0.77θ. Suspensions without and with SHMP were at pH 4 and pH 10.3. The solids concentration was fixed at 19.1 vol%. The milling times were varied: 0 min (a), 6 min (b), 15 min (c) and 60 min (d). The rheology data collected for the first and last shear rate ramp are shown by the closed and open symbols, respectively.

All samples showed a shear-thinning response with a slight increase in suspension viscosity at very high shear rates. This behavior is thought to be an artifact of the experimental method and indicates a transition to non-laminar secondary flow. For the un-milled samples (Fig. 9a), increasing the dose concentration of SHMP led to an increase in suspension viscosity, which results from the changing aggregation-state of the particle suspension, see discussion on the milling of dilute suspensions.

Without SHMP, the viscosity of the Al-doped TiO_2 suspension was observed to increase with increased milling times. This is attributed to the changing particle size, with the d_{50} decreasing from 1.230 μm to 0.403 μm to 0.366 μm and 0.292 μm for milling times of 0, 6, 15 and 60 min. For colloidally-stable suspensions, as the particle size decreases the effective volume fraction (ϕ_{eff}) of the suspension increases due its dependence on the ratio $(a_{eff}/a)^3$, where a is the particle radius and a_{eff} is the particle radius plus the Debye length. Based on the Krieger-Dougherty model,[30] increasing the solids volume fraction (ϕ_{eff}) equates to an increase in the relative suspension viscosity. However, the change in suspension viscosity is more significant without SHMP than with SHMP, hence, with longer milling times, the suspension viscosity with SHMP goes from being greater than to less than the viscosity without SHMP, demonstrating the critical role of SHMP in moderating the suspension viscosity as the particle size is reduced. In fact, for suspensions prepared to 0θ, 0.33θ and 0.77θ SHMP, the viscosity increase (taken at 100 s^{-1}) from those samples initially measured at 25 °C was 100, 1.1 and 1.5-times, respectively. Therefore, as the particle size is reduced, the role of non-DLVO forces become more significant in governing the suspension flowability. Without SHMP, the particle-particle interaction is strongly repulsive (Fig. 5c), yet the electrostatic repulsion is not sufficient to moderate suspension viscosity as the particle size is reduced. Therefore, we hypothesize that the small molecule SHMP, when adsorbed on Al-doped TiO_2, acts to lubricate particle-particle contacts via a steric barrier. Critically, the best milling performance at 19.1 vol% Al-doped TiO_2, and best rheology control, was achieved for 0.33θ SHMP, when SHMP partially coats the particle surface. At this condition the Debye length (4.10 nm) exceeds the steric barrier (SHMP molecular length = 1.5 nm)[22], whereas for 0.77θ SHMP, the adsorbed layer of SHMP on Al-doped TiO_2 is more homogenous, and the Debye length (2.61 nm) is similar to the steric barrier, although the steric barrier is also likely to be influenced by changes in salinity. Heeb et al.[31] showed that with end-tethered ethylene glycol-based monolayers, increasing salinity collapsed the molecules on to the surface and subsequently the lateral friction force increased (i.e. surface lubrication decreased). The rheology data confirms an optimal SHMP concentration where the contributions from electrostatic and steric forces lubricate particle-particle contacts to deaggregate and stabilize the fine particles for enhanced milling performance. Had it been possible to mill the suspension without SHMP, this optimal SHMP concentration would have also been likely observed at 26.2 vol% Al-doped TiO_2.

Although not considered in the current study, polyphosphates are known to be unstable at high temperatures (> 100 °C), in strongly acidic and basic conditions,[16] and in the presence of divalent salts (calcium);[20] with hydrolysis leading to the formation of shorter chains, which McCullough *et al.*[32] described via the i) splitting of end-groups, ii) random scission along the chain and iii) ring formation. It is noted that following the rheology protocol, the suspension viscosities increased relative to the initial flow curve, with the increase found to be greater for those samples which had been milled for longer times. The increase in viscosity likely indicates a reduced performance of the SHMP molecules, supporting the understanding that the adsorbed layer of SHMP undergoes partial thermal degradation, reducing the effectiveness of SHMP to lubricate particle-particle contacts and maintain a low suspension viscosity. It is reiterated that for these rheology tests, SHMP was added after milling Al-doped TiO_2 (black symbols in Fig. 9), hence, any changes in viscosity are purely a result of the rheology test protocol where samples were exposed to elevated temperatures for a longer duration than during milling. If significant thermal degradation of SHMP had occurred during milling, the superposition of the pH-dependent zeta potential curves would not have been observed (Fig. 4).

Conclusions

The critical role of sodium hexametaphosphate (SHMP) to efficiently mill suspensions of Al-doped TiO_2 has been studied. SHMP strongly adsorbs on Al-doped TiO_2 in both acidic and basic conditions, even though the zeta potential of pure Al-doped TiO_2 is oppositely charged at pH 4 (~40 mV) and pH 10.3 (~ -45 mV). With no SHMP, the Al-doped TiO_2 particles are electrostatically-stable. However, at pH 4 the suspension can be destabilized by adding SHMP, therefore increasing the formation of particle aggregates/clusters which negatively impact milling performance.

When milling Al-doped TiO_2 at pH 10.3, the negative zeta potentials without and with SHMP led to a weaker dependence of SHMP addition on particle stability, but a measurable effect on the milling performance; with the addition of SHMP decreasing the final d_{50} and reducing the width of PSD. The optimal SHMP concentration when milling dilute suspensions of Al-doped TiO_2 was 0.33θ SHMP, with higher SHMP concentrations increasing solution conductivity, thus destabilizing the particles as seen by a reduction in the particle specific surface area (SSA) beyond a critical solution conductivity, ~0.018 M equivalent of NaCl.

At higher solids concentrations (19.1 and 26.2 vol%), the milling performance was only maintained by adding SHMP. The optimal dosage was 0.33θ SHMP, and the apparent and true breakage performance worsened at 0.77θ SHMP. Since the electrostatic stabilization of Al-doped TiO_2 at pH 10.3 was similar with different SHMP concentrations, the enhanced milling performance is attributed to the contribution from SHMP steric forces when adsorbed on Al-doped TiO_2. The steric forces maintain a low suspension viscosity during milling, ensuring negligible dampening of the media beads kinetic energy.

Achieving good particle dispersion to maintain low suspension viscosity is of critical importance when milling at high solids concentrations. SHMP stabilizes the particles via steric and electrostatic forces, with the dispersion forces weakening at high SHMP concentrations due to increased solution conductivity caused by the dissociated Na-ions. Such understanding is essential to ensure efficient energy utilization in energy-intensive processes, such as wet stirred media milling.

Supporting Information

Fig. S1. Stirred wet mill used throughout the study. Images from left to right: stirred wet mill setup with attachment to the Silverson high shear mixer (L5M-A); zoomed image of the milling chamber showing the bottom outlet containing a removable sieve; zoomed image of the ceramic spindle showing attachment to the Silverson holder; schematic of the milling chamber and dimensions; **Fig. S2.** Rheology flow curve for 19.1 vol% Al-doped TiO_2 in 10^{-3} M NaCl at pH 4. Different sample preparation methods were assessed for the un-milled sample (a) and a sample milled for 60 min at 6000 rpm; **Fig. S3.** Suspension viscosity as a function of the shear rate from 1200 s^{-1} to 0.1 s^{-1}. All samples were prepared to 19.1 vol% in 10^{-3} M NaCl. The Al-doped TiO_2 suspensions were first milled without SHMP for varying times up to 60 min at 6000 rpm, and then SHMP was added at 0θ, 0.33θ and 0.77θ. The suspension at 0θ was at pH 4 and electrostatically stable, while the suspensions with SHMP were at pH 10.3; **Fig. S4.** The apparent (d_{50} [a] and width of PSD [b]) and true (particle specific surface area [c]) milling performances for 5 vol% Al-doped TiO_2 milled at 6000 rpm for up to 60 min with SHMP dose amounts of 0.77θ and 0.92θ at pH 9; **Fig. S5.** Apparent milling performance of Al-doped TiO_2 at pH 10.3 and solids concentrations of 13.6, 19.1 and 26.2 vol%. Two SHMP concentrations of 0.33θ (a and b) and 0.77θ (c and d) were considered and the milling performance is described by a) d_{50} and b) width of PSD.

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