

Selection of Suitable Dispersants for Aqueous Suspensions of Zirconia and Titania Powders using Acoustophoresis

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(Received 21 February 1998; accepted 15 August 1998)

Abstract

Acoustophoresis was used to study the effect of adding various commercially available dispersants onto aqueous suspensions of two zirconia and two titania powders. These powders were characterised for elemental composition by X-ray fluorescence (XRF) spectroscopy and for surface area by BET single point nitrogen adsorption. From the maximum value of the zeta potential, it was possible to select the most promising dispersants. From the shape of the curve the minimum amount of dispersant required to stabilise the powder particles was noted. The iso electric point (i.e.p) of the powders was also identified. Several dispersants can be recommended for the first titania powder, whilst none can be recommended for the second titania as the final zeta potentials on addition of the dispersants were low. The two powders had different surface chemistries which was reflected in a large difference in their i.e.p; the first at pH 7.5 and the second at pH 6.1. This was due to different coatings on the powder surfaces; alumina and an organic material respectively. Removal of this organic coating by calcination then enabled the dispersants to fully adsorb. Similarly dispersants for the first zirconia powder could be identified and the i.e.p identified at pH 5.4. However, no dispersants can be recommended for the second zirconia powder as yttria dissolves out of the powder under the naturally occurring weakly acidic conditions. The i.e.p was estimated to be pH_{i.e.p} 7–7.5. © 1999 Elsevier Science Limited. All rights reserved

Keywords: TiO₂, ZrO₂, suspensions, acoustophoresis, powders

1 Introduction

In the colloidal processing of ceramic powders it is essential that the powder particles are completely dispersed so that no aggregates form. It is these aggregates that give rise to flaws in the final sintered product causing reductions in strength and reliability.^{1–3} These aggregates form in sub micron powders due to the ubiquitous attractive van der Waals force. Traditionally, in colloidal processing this attractive force can be countered by a greater repulsive force separating the particles from one another. This can be achieved in two ways; either by the addition of charge to the particles so that they repel one another—termed electrostatic stabilisation and is achieved by altering the pH; alternatively by the addition of a polymeric molecule, which when adsorbed onto the powder surface prevents the particles physically coming close enough for the attractive force to cause flocculation; this is termed steric stabilisation. A combination of these two effects is termed electrosteric stabilisation and is the probable stabilisation mechanism when polyelectrolytes are adsorbed onto the particles.^{4–7}

As many dispersants used in the ceramic industry are polyelectrolytes it is essential to know which ones lead to suspensions with the greatest stability. It is also vital to know how much dispersant to add to each system for economic reasons as well as to avoid problems associated with unadsorbed dispersant in the suspension, i.e. compression of the double layer as a polyelectrolyte acts as just like an electrolyte. A polyelectrolyte can be considered to be a polymer chain with numerous dissociable groups. The degree to which these groups dissociate is a function of the pH. Most polyelectrolyte dispersants are based on polyacrylic acid, which is fully dissociated at pH 8.5–9.^{8,9} Previously techniques such as adsorption isotherms, electrophoresis,

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sedimentation tests and rheology have been used to estimate the amount of dispersant required.¹⁰

Electrophoresis techniques, however, can only be applied to extremely dilute systems and there is an inherent danger in extrapolating the results from the dilute system to the concentrated one especially in systems where dissolution of material is a reality.¹⁰ Adsorption isotherms can be tedious and sedimentation tests can often take several weeks to supply an answer. Using the technique of acoustophoresis it is then possible to measure the zeta potentials of concentrated suspensions which are more representative of the real concentrated suspensions used within industry. The added advantage is that the experiment is relatively quick and straight forward, the only possible disadvantage being the large volume of sample required for the measurement.

Generally speaking the larger the magnitude of the zeta potential then the greater the repulsive force that has been introduced into the system and the smaller the probability of flocculation occurring. The stability of ceramic suspensions against flocculation is determined by the surface charge density. So in any study of colloidal stability it is vital to have an indication of the amount of surface charge present, however, this is relatively difficult to measure. Fortunately, the zeta potential can be easily measured instead and this is a reasonable approximation for the surface charge density. The zeta potential is then defined as the potential at the plane of shear. When a charged particle in aqueous media is subjected to an electric field it moves. In doing so it moves with an adsorbed layer of counterions, the zeta potential is then the potential at the plane of shear, which is approximately one hydrated ion diameter away from the particle surface.

In electrophoresis techniques an alternating electric field is applied to a dilute suspension and the mobility of the particles is recorded. This is defined as the velocity of the particle/electric field strength. This mobility is then related to the zeta potential by the von Smoluchovski equation or the Huckel equation depending on the prevailing conditions (particle size and ionic strength).⁴⁻⁷

Acoustophoresis is a relatively new but similar technique in which again an alternating electric field is applied to a concentrated suspension.¹¹⁻¹³ Instead of measuring the mobility of the particles the amplitude of the generated acoustic wave is measured-called the electrosonic amplitude. This is then measured as a function of frequency (300 kHz-11.5 MHz) to generate a mobility spectrum, which can then be related to the particle size and the zeta potential. The technique also allows for automatic titration of acid and base to identify the iso electric point (i.e.p) The i.e.p is the pH

value where the zeta potential is zero. At the i.e.p there are no repulsive forces in the system such that the van der Waals forces are totally dominant and the particles are flocculated. If it were possible to measure the viscosity simultaneously then at a given shear rate the viscosity would be a maximum at the i.e.p.¹⁰ Previous work by Bergstrom and Greenwood¹⁰ also successfully correlated zeta potential measurements with independently obtained adsorption isotherms and rheological measurements. The plateau region from the plot of zeta potential against amount of added dispersant directly correlated with the plateau region of the plot of adsorbed amount of dispersant against the equilibrium dispersant concentration of the suspension. This also correlated with a minimum in the plot of suspension viscosity against the amount of dispersant added.

Thus, it is the initial objective of this study to use the Acoustosizer to see if the two zirconia and two titania powders are suitable for colloidal processing and if so which dispersants could be suitable for the production of aqueous, concentrated, aggregate free suspensions. This then would form the basis of any future work relating the strengths of the final products to that of the microstructure. It should be noted that not all the dispersants studied here are polyelectrolytes several are small highly charged molecules that adsorb onto the powder surface, e.g. Tiron, citrate, hexaphosphate. Hence, their stabilisation mechanism is purely electrostatic, whereas that of the polyelectrolytes is electrosteric. Unfortunately the acoustophoresis technique gives no information about the steric component to this type of stabilisation or how the polyelectrolyte adsorbs onto the surface. In his book Hunter,⁷ states that a non ionic polymer of molecular weight 10 000 Daltons has a spatial extension (the r.m.s end to end distance of the chain) of 6 nm. Hence, as we have several polyelectrolytes of molecular weights in the order of 10 000 Daltons and above, then it can be assumed that in these cases the steric component alone will impede coagulation in the primary minimum. So it is the degree to which the groups on the polyelectrolyte dissociate that will control how good a deflocculant the polyelectrolyte is.

2 Experimental

In this study two titania powders (G1, Rhone Poulenc, Watford, UK and RTC90, Tioxide, Billingham, Cleveland, UK) and two 3 mole% yttria stabilised zirconia powders were studied (Mandoval HSY3, c/o Bernard Myers Shipping, Staines, UK and Tosoh TZ-3Y c/o Whitfield and Sons, Stoke on Trent, UK) These four powders were characterised by BET single point nitrogen

adsorption (Strohlein Area meter II) and XRF spectroscopy (Phillips PW1606) at CERAM, Stoke, UK. For the acoustophoresis experiments approximately 850 ml of suspension at a volume fraction of approximately 0.07 were prepared. Previous experiments have revealed that this is a reasonable volume fraction to obtain a good mobility spectrum yet does not waste potentially expensive powder.¹⁴ The electrolyte strength was kept constant at 10 mM KCl (BDH, Butterworth, UK) in all cases. Under these conditions there is no overlap of the double layers. The titania suspensions were prepared with spherical alumina grinding media, (approx. diameter 2.5 cm) and the zirconia suspensions with zirconia grinding beads (approx. size 1 cm). Preparation of the suspensions involved adding the known mass of powder to a 1 l polyethylene bottle containing 800 ml of 10 mM KCl solution and 100 g of the respective grinding media. The suspension was then placed on a vibro mill (Sweco, Nivelles, Belgium model M18 -5) for 30 minutes to disperse the powder without generating new surface area. All water used was double distilled. The suspensions were then allowed to stand for 1–2 h prior to the acoustophoresis experiments to allow the system to reach equilibrium.

The Acoustosizer (Colloidal Dynamics, MA,) was calibrated daily in air and with the standard solution at 25°C. First, 400 ml of the suspension was placed into the chamber and allowed to come to equilibrium at 25°C, which typically took 20–30 min depending on the ambient temperature. For the experiments where the zeta potential was recorded as a function of the amount of dispersant added, the dispersants were diluted down so to allow more accurate measurements of the optimum concentration. Approximately 1–2 g of dispersant was diluted with approximately 30 ml of distilled water. Some dispersants were supplied as powders whilst others were diluted down liquids. To allow

comparison of the effectiveness of the dispersants the activity must be taken into account, for example, Darvan 7 was supplied as a solution containing 25% by weight active material. So this must be allowed for in calculating the amount of dispersant adsorbed onto the powder surface. The dispersants used, their manufacturer, their activity and molecular weight (if known) are listed in Table 1. The amount of dispersant adsorbed per unit surface area of powder was then calculated. This can be simply converted to a percentage weight adsorbed onto dry powder by knowing the volume fraction, total volume of the suspension, density and surface area of the powder.

With the Acoustosizer it is also possible to automatically measure the iso electric point (i.e.p) of the suspension. Suspensions of volume fraction 0.07 and background electrolyte strength of 10 mM KCl were prepared as per usual. The titrating syringes were then filled with 3M HCl (Timstar Laboratory Supplies, Crewe, UK) and 1 M KOH (BDH) and the automatic titration software set such that the zeta potential every 0.4 pH unit was recorded over a suitable pH range for each powder. Initially the pH of the suspension was reduced from the natural pH of the suspension to a set point. The pH of the suspension was then increased to another set point, such that two estimates for the iso electric point could be obtained and any hysteresis noted. In all the experiments the stirrer speed was kept constant at 300 r.p.m. Again all measurements were at 25°C.

3 Results

3.1 Powder characterisation

The surface areas of the four powders are listed in Table 2, alongside the d_{50} value for the particle size as measured on the Malvern Mastersizer E. The

Table 1. List of dispersants used, manufacturer, molecular weight and activity in percentage weight

<i>Dispersant</i>	<i>Manufacturer</i>	<i>Molecular weight (Daltons)</i>	<i>Percentage activity</i>
Darvan 7 (sodium polymethacrylate)	R. T. Vanderbilt, USA	16 000	25
Darvan 821 A (ammonium polyacrylate)	R. T. Vanderbilt, USA	6 000	40
Polyacrylic acid (sodium salt)	Fluka, Germany	2 100	100
Polyacrylic acid (sodium salt)	Fluka, Germany	5 100	100
Triammonium citrate (NH ₄) ₃ C ₆ H ₅ O ₇	Fisons, UK	243	100
Tetrasodium pyrophosphate Na ₄ P ₂ O ₇ ·10H ₂ O	Hopkin and Williams, UK	446	100
Tiron (disodium salt of 4,5 dihydroxy 1,3 benzenedisulphonic acid)	Aldrich, UK	332	100
Ambergum 3021 (sodium carboxymethylcellulose)	Hercules UK	8 000–12 000	50
Dolapix CA	Z & S, Germany	36 750	25
Dolapix PC21	Z & S, Germany	56 220	25
Dolapix PC33	Z & S, Germany	38 600	25
Sodium hexaphosphate (NaPO ₃) _{12–13} Na ₂ O	Fluka, UK	1286–1388	100
Dispex A40 (ammonium salt of polyacrylic acid)	Allied Colloids, UK	10 000	40
Daxad 19 LA (ammonium naphthalene sulphonate)	Hampshire Chemicals, UK	—	42

Note: Z & S = Zschimmer and Scharz; all three products are described as synthetic polyelectrolytes free from alkalis.

Table 2. XRF and surface area results for the zirconia and titania powders

	<i>Tosoh zirconia TZ3Y</i>	<i>Mandoval Zirconia HSY3</i>	<i>Tioxide Titania RTC90</i>	<i>Rhone Poulenc Titania G1</i>
d ₅₀ (microns)	0.9	0.9	0.4	1.4
Surface area (m ² g)	13.2	10.5	16.8	254.2
SiO ₂	<0.02	0.14	0.08	<0.02
TiO ₂	<0.01	0.13	94.2	94.5
Al ₂ O ₃	<0.02	0.25	4.32	<0.02
Fe ₂ O ₃	<0.01	0.01	<0.01	<0.01
CaO	<0.01	0.02	<0.01	0.02
MgO	<0.05	<0.05	<0.05	<0.05
K ₂ O	<0.01	<0.01	<0.01	<0.01
Na ₂ O	<0.1	<0.1	<0.1	<0.1
P ₂ O ₅	—	0.03	0.10	0.11
ZrO ₂	92.5 by difference	92.3 by difference	—	0.03
HfO ₂	1.85	1.66	—	—
Y ₂ O ₃	5.31	5.24	—	—
Nb ₂ O ₅	—	—	<0.01	0.21
Loss on ignition at 1025°C	0.29	0.21	1.25	5.15

surface areas of the two zirconia powders were similar which is also reflected in their similar mean particle sizes. But the two titania powders were widely different with the Rhone Poulenc titania powder having a massive surface area (254 m² g⁻¹, manufacturers value 250 m² g⁻¹) indicating that it has either a very fine particle size or is extremely porous. However, as the d₅₀ value of the particle size is 1.4 microns (manufacturer's value 1.5 microns), it is not a particularly fine powder, hence it must be porous. The Tioxide powder had a d₅₀ value of 0.4 microns which was in agreement with the manufacturers reported value. The difference between the two powders was also demonstrated when trying to prepare concentrated suspensions of the powders. It was possible to produce suspensions with weight fractions of 76% with the Tioxide powder, but only 43% with the Rhone Poulenc powder.

The XRF results are also listed in Table 2. The zirconia powders were similar with yttria contents of 5% by weight, but the Mandoval powder had higher impurity levels of silica, titania and alumina. The Mandoval powder also had a trace of phosphorous oxide which is not found in the Tosoh powder. There was also a high percentage of hafnium oxide present (about 1.5%) in both samples, which was expected as it is quite often a by product of zirconium refining.

The titania powders were again quite different. The Tioxide powder has a very large alumina impurity and greater levels of silica, which is consistent with the manufacturers data sheets., These state that the powder has a surface coating of alumina and other organic materials, e.g. alcohols, siloxanes and alkanolamines. Both powders also displayed small traces of phosphorous pentoxide. The Rhone Poulenc powder also revealed trace amounts of zirconia and niobium pentoxide and also had a large ignition loss of 5%, which is due to

the organic coating that had been applied to the particles.

3.2 Zeta potential of the zirconia suspensions against amount of dispersant added

A typical measurement of zeta potential against amount of dispersant per unit surface area is plotted in Fig. 1 (Dolapix CA on the Mandoval zirconia powder). Initially the particles have a small negative zeta potential of -20.1 ± 1.4 mV at a pH of 7.30 ± 0.07 . These relatively small variations in the pH and zeta potentials (averaged over all the samples) indicate that the suspension has reached equilibrium. With such a small zeta potential the particles are flocculated as the repulsive force is insufficient to overcome the Van der Waals attraction. However, addition of a small amount of dispersant increased the zeta potential as it adsorbs on the particle surface. Further addition of dispersant increases the zeta potential further until a plateau region was reached where addition of more dispersant does not effect the zeta potential. Hence the minimum amount of dispersant required to stabilise the powder can be identified as 0.15 mg m². The plateau value of the zeta potential obtained gives an indication of the suitability of the dispersant to stabilise the powder.

The greater the zeta potential the smaller the tendency to form the unwanted aggregates. It is worthwhile to remember that this final zeta potential has two contributions, one from the charge on the particles themselves and secondly from the charges on the polyelectrolyte. The magnitude of the plateau value of the zeta potential and the minimum amount of dispersant required to stabilise the Mandoval zirconia powder were listed in Table 3. The following dispersants can then be recommended for the Mandoval zirconia powder:

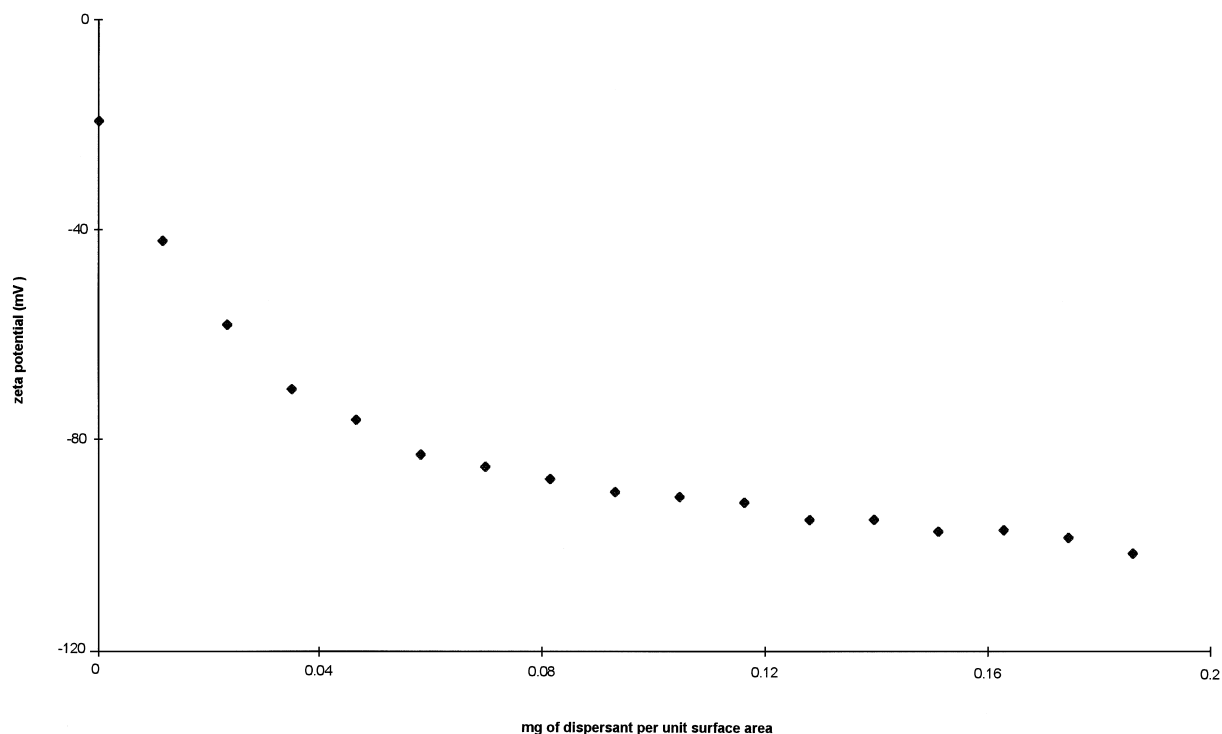


Fig. 1. Zeta potential against the amount of Dolapix CA added to a suspension prepared from the Mandoval zirconia powder.

Table 3. Adsorption isotherm summary for Mandoval zirconia powder

Dispersants	pH initial	pH final	Zeta initial (mV)	Zeta final (mV)	Optimum amount (mg m^{-2})
Darvan 7	7.30	8.71	-20	-105	0.15
Darvan 821A	7.27	8.17	-18	-92	0.22
Polyacrylic acid 2 100	7.26	8.75	-18	-92	0.15
Polyacrylic acid 5 100	7.25	8.64	-19	-92	0.12
Triammonium citrate	7.34	8.05	-22	-102	0.15
Tetrasodium pyrophosphate	7.28	9.93	-21	-108	0.28
Tiron	7.18	7.04	-19	-84	0.14
Hercules 3021	7.26	8.20	-19	-81	0.26
Dolapix CA	7.25	8.52	-19	-99	0.15
Dolapix PC21	7.34	8.45	-21	-103	0.16
Dolapix PC33	7.38	8.94	-21	-92	0.10
Sodium hexaphosphate	7.34	8.75	-22	-120	0.22
Dispex A40	7.48	8.24	-22	-96	0.16
Daxad	7.29	7.30	-21	-63	0.26

Dispex A40, Darvan 7, Dolapix CA, Dolapix PC21, triammonium citrate, tetra sodium pyrophosphate and sodium hexaphosphate. These last three molecules are not strictly speaking polyelectrolytes, but small highly charged molecules that adsorb onto the powder surface and hence have no or very little steric contribution to the stabilisation.

However, different results were obtained for the Tosoh zirconia powder. It was noted that although the natural pH of the suspensions was consistently 6.1, the initial zeta potential varied considerably, indicating that possibly an impurity was dissolving out of the powder. It is known that yttria dissolves out of zirconia powders under acidic conditions.^{15,16} So an experiment was established in which the zeta potential and particle size distribution of a freshly prepared 0.05 volume fraction

suspension was followed with respect to time. The first reading was taken 30 min after mixing, as this was the minimum time for the suspension in the Acoustosizer to come to equilibrium at 25°C. Subsequent readings were taken every 15 min for approximately 6 h. The results are shown in Figs 2 and 3.

The zeta potential increased by 5 mV over a period of 6 h, this was accompanied by a slight fall in conductivity of the sample from 0.144 to 0.132 S m^{-1} , and a small decrease in pH from 6.11 to 6.04. (Note that this natural pH is a pH unit lower than the natural pH of the Mandoval powder). The particle size distribution (Fig. 3), also changed with time. The general trend for the d_{10} , d_{50} and d_{90} values was to decrease with time. However, for the first 240 min the particle size distribution was narrow but

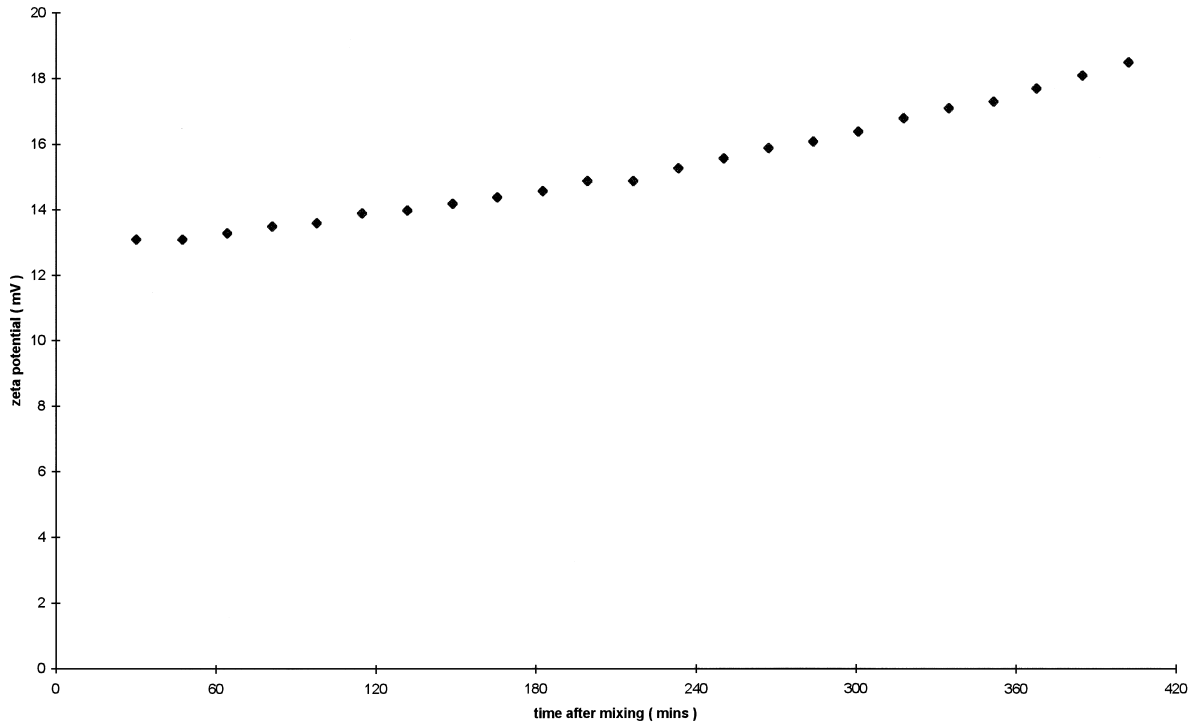


Fig. 2. Effect of time on the zeta potential of a suspension prepared from the Tosoh zirconia powder.

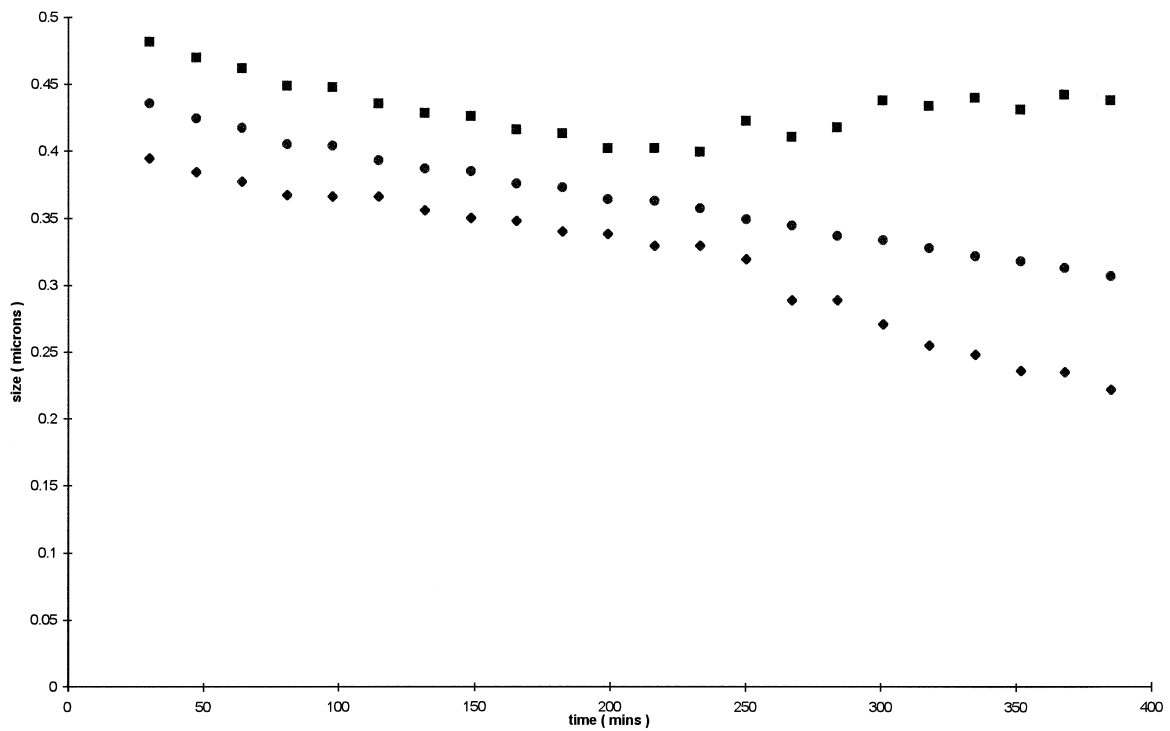


Fig. 3. Effect of time on the particle size distribution of a suspension prepared from the Tosoh zirconia powder: d_{10} , diamonds; d_{50} , circles; d_{90} , squares.

after that it widened out. The yttria could be dissolving out of the powder forming Y^{3+} and Y^{4+} ions in solution which then behaved like a buffer solution keeping the pH approximately the same. The yttrium ions could then precipitate on the powder surface such that the amount of positive charge builds up with time. This would also explain why there is no large increase in the conductivity as the ions are not free in solution. This increase in

zeta potential with time corresponds to an increase in stability, hence the particle size decreases as the aggregates break down into smaller units.

To confirm that it is yttria dissolving out of the powder, an experiment was established in which suspensions of the same volume fraction, 0.05, were prepared from fresh zirconia powder. After intervals of 2, 4, 6 and 8 h contact with the water the suspensions were centrifuged down (Baird and

Tatlock Autobench Centrifuge Mark IV, 20 min at 5000 r.p.m.). The supernatants were then carefully removed by pipette and analysed by ICP OES (Inductively Coupled Plasma Optical Emission spectroscopy, Thermounicam ICAP 61E) at CERAM for the following elements; calcium, aluminium, yttrium, sodium, zirconium and magnesium. It was not possible to analyse for the hafnium. The results are presented in Table 4. It was not possible to present results for zero contact time as it takes a finite time for the powder to come to equilibrium with the water and then a finite time to centrifuge the sample down.

It can be seen that there are large amounts of sodium and yttrium ions present in the supernatant. The concentration of sodium ions was constant, whereas the amount of yttrium ions increased slightly with time. The other elements studied were present in minute quantities. This confirms that the yttria was dissolving out of the powder under the slightly acidic conditions and causing the increase in zeta potential with time. There does not, however, seem to be a noticeable evolution in concentration of the yttrium ions with time, which suggests they dissolve out of the powder fairly readily.

The iso electric point of the Mandoval zirconia powder was identified as occurring at pH 5.4 (see Fig. 4). There was some hysteresis which could possibly be due to some dissolution of the yttria at

the low pH values or alternatively it could be due to the inability of the stirrer to break up the flocculated structure of the suspension as the particles were restabilised. An alternative explanation for the hysteresis could be due to the changes in ionic strength with the addition of the acid and base. As the yttria dissolves out of the Tosoh powder fairly readily it was deemed pointless to record its i.e.p accurately. However, as the zeta potential was +15 mV at a pH of 6.1 an estimate of about pH 7–7.5 could be made for the i.e.p. This is in reasonable agreement with other observations for the i.e.p of a 3 mole% yttria stabilised zirconia.^{17,18}

3.3 Zeta potential of titania suspensions against amount of dispersant added

The suspensions prepared from the Tioxide titania powder consistently produced initial zeta potentials of $+15.0 \pm 1.7$ mV at a pH of 7.10 ± 0.07 . Once again this was insufficient to stabilise the particles against van der Waals attractive force and the particles were flocculated. A typical adsorption isotherm of Darvan 7 is shown in Fig. 5. Addition of a small amount of dispersant reduces the magnitude of the zeta potential to near zero, further addition leads to a small negative zeta potential as the surface characteristics of the powder are now dominated by that of the polyelectrolyte. Further addition of dispersant increases the magnitude of the negative zeta potential until a point is reached where no more dispersant adsorbs and the powder surface is covered with dispersant. This optimum amount can be seen to be 0.12 mg m^{-2} . As before the optimum amounts and final value of the plateau zeta potential are listed in Table 5. From which the following dispersants can be recommended for the Tioxide titania powder; polyacrylic acid 5100, Dispex A40, Darvan 821A, Darvan 7, tetrasodium pyrophosphate and sodium hexaphosphate.

Suspensions prepared from the Rhone Poulenc titania had a similar pH of 7.24 ± 0.04 to that of

Table 4. Results of ICP analysis of the supernatant after different contact times with the Tosoh zirconia powder

Element	2 h contact (mg l^{-1})	4 h contact (mg l^{-1})	6 h contact (mg l^{-1})	8 h contact (mg l^{-1})
Calcium	4	5	4	5
Aluminium	<1	<1	<1	<1
Yttrium	20	20	20	25
Sodium	25	25	25	25
Zirconium	0.6	0.6	0.6	0.7
Magnesium	<1	<1	<1	<1

Table 5. Adsorption isotherm summary for Tioxide titania

Dispersants	pH initial	pH final	Zeta initial (mV)	Zeta final (mV)	Optimum amount (mg m^{-2})
Darvan 7	7.01	7.97	+14	-86	0.12
Darvan 821A	7.04	8.05	+15	-94	0.15
Polyacrylic acid 2100	7.08	8.35	+16	-106	0.15
Polyacrylic acid 5100	7.10	8.29	+18	-117	0.15
Triammonium citrate	7.17	7.98	+13	-55	0.12
Tetrasodium pyrophosphate	7.17	9.37	+18	-103	0.25
Tiron	7.07	6.65	+17	-71	0.22
Hercules 3021	7.05	7.75	+15	-81	0.24
Dolapix CA	7.06	8.05	+16	-81	0.11
Dolapix PC21	7.05	8.45	+12	-71	0.14
Dolapix PC33	7.08	8.25	+15	-77	0.11
Sodium hexaphosphate	7.04	8.55	+14	-96	0.21
Dispex A40	7.28	8.13	+15	-95	0.13
Daxad 19 LA	7.18	8.06	+15	-80	0.20

the suspensions prepared with the Tioxide powder, however the zeta potential at this natural pH was negative; -10.5 ± 0.5 mV, implying that the surface chemistry of the two powders is extremely different. From Fig. 4 the i.e.p of the Rhone Poulenc titania can be identified at pH 6.1, whilst that of the Tioxide powder can be identified at pH 7.5. This shift in the i.e.p is due to the large amount of alumina present (which itself has an i.e.p in the pH

region 8–9¹⁹). As this alumina is a coating on the titania particles, it alters the surface chemistry, hence the i.e.p is closer to that recorded for pure alumina suspensions. The Tioxide powder also shows very little hysteresis compared to the Rhone Poulenc powder, again possibly indicative of the later powders ability to form strong flocs from the small particles, which are difficult to break down with the stirrer.

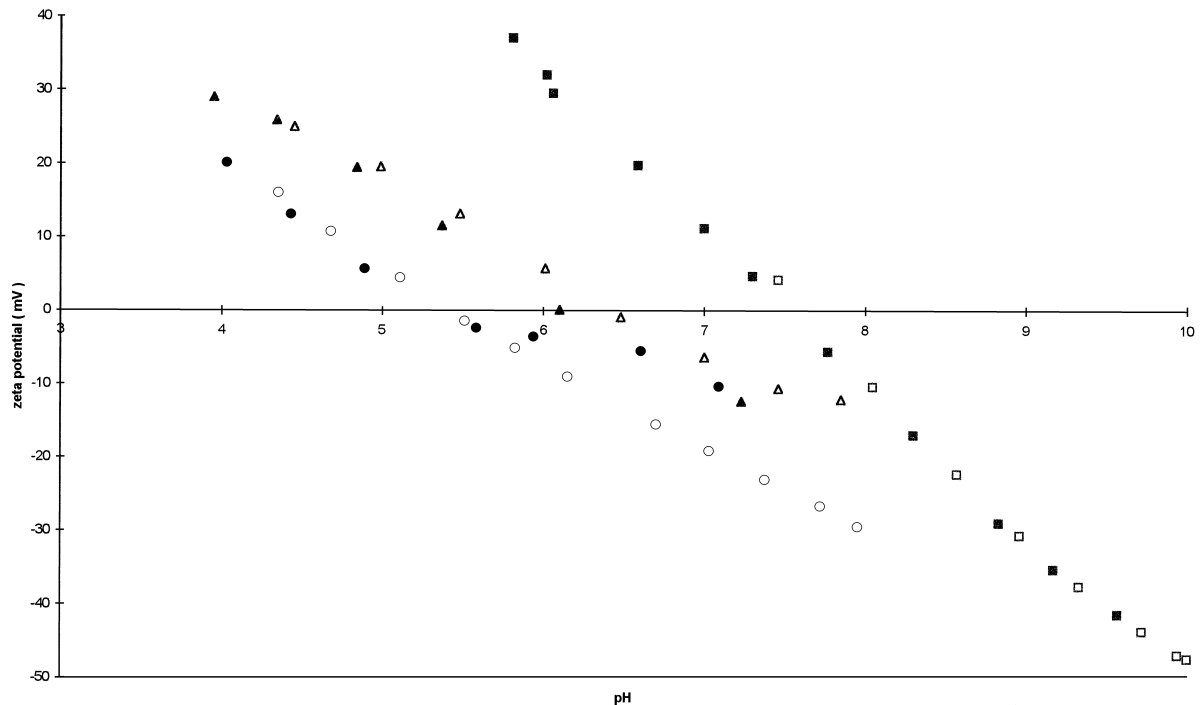


Fig. 4. Zeta potential against pH for the Tioxide titania powder (squares), Rhone Poulenc titania powder (triangles) and Mandalval zirconia powder (circles). Open symbols depict an increase in pH whilst closed symbols indicate decreasing pH.

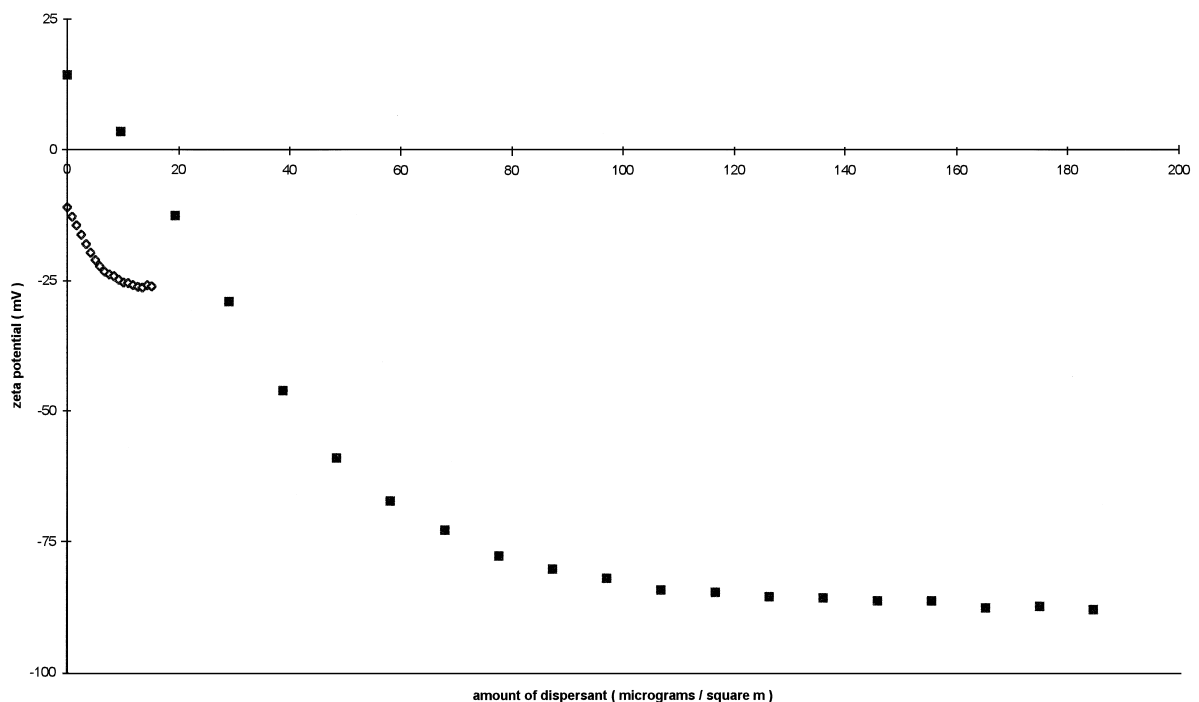


Fig. 5. Zeta potential against amount of dispersant added to suspensions prepared from the two titania powders. Open diamonds indicate adsorption of polyacrylic acid 5100 on to Rhone Poulenc powder. Squares indicate adsorption of Darvan 7 on to the Tioxide powder.

Another typical plot of zeta potential against amount of dispersant is shown in Fig. 5, polyacrylic acid 5100 on the Rhone Poulenc titania. Once again the same trends as before are seen. However, the final plateau values of the zeta potentials are very low (about -25 mV) and the amount of dispersant required to give the maximum zeta potential was extremely low with concentrations expressed in micro grams of dispersant per unit surface area, as opposed to milligrams, (see Table 6). This is due to the organic coating on the powder that prevents effective adsorption of the dispersants. With all the surface sites occupied by the organic coating there are very few sites available for the dispersant to bind onto, hence very little is adsorbed. Additionally on adsorption of the dispersants the pH of the suspensions did

not increase, so the dispersants are not fully dissociated and can not impart stability to the powder effectively. So none of dispersants tried were suitable for dispersing this powder (as supplied) as the zeta potentials were too low to lead to effective stabilisation.

However, the experiment was then repeated with a batch of calcined powder (700°C for 2 h and then sieved through a 45 micron mesh to remove the larger aggregates). The weight loss on calcination was about 15%, which is much greater than suggested by the XRF data, but in accordance with the manufacturers values. The surface area of this calcined powder was measured at $36.9\text{ m}^2\text{g}^{-1}$, which is much smaller than before due to some of the finer particles sintering together. Particle size analysis of this powder before sieving gave the

Table 6. Adsorption summary for Rhone Poulenc titania

Dispersants	pH initial	pH final	Zeta initial (mV)	Zeta final (mV)	Optimum amount ($\mu\text{g m}^{-2}$)
Darvan 7	7.30	7.37	-10	-22	8
Darvan 821 A	7.22	7.29	-10	-23	8
Polyacrylic acid 2100	7.21	7.39	-11	-25	16
Polyacrylic acid 5100	7.21	7.38	-11	-26	14
Triammonium citrate	7.22	7.39	-11	-17	27
Tetrasodium pyrophosphate	7.24	7.79	-11	-2	35
Tiron	7.29	7.23	-11	-15	10
Hercules 3021	7.22	7.30	-11	-24	27
Dolapix CA	7.23	7.31	-11	-26	7
Dolapix PC21	7.23	7.30	-10	-24	10
Dolapix PC33	7.34	7.36	-11	-22	8
Sodium hexaphosphate	7.22	7.42	-11	-22	15
Dispex A40	7.21	7.35	-10	-24	10
Daxad 19 LA	7.25	7.27	-10	-18	13

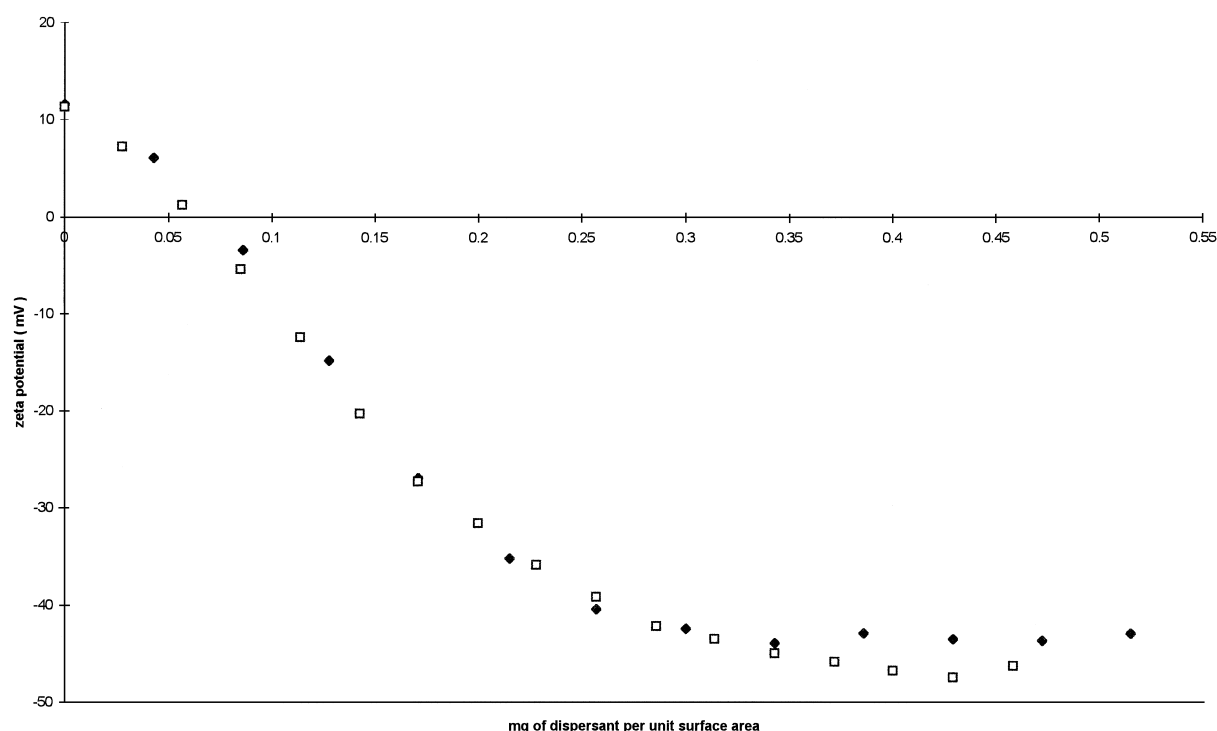


Fig. 6. Zeta potential against the amount of dispersant added to suspensions prepared from the calcined Rhone Poulenc titania powder. Diamonds indicate polyacrylic acid 5100. Open squares indicate Darvan 821A.

following size distribution; $d_{10}=0.54$ microns, $d_{50}=1.45$ microns and $d_{90}=3.23$ microns. After sieving this became $d_{10}=0.56$ microns, $d_{50}=1.35$ microns and $d_{90}=2.54$ microns. In both cases a small amount of polyacrylic acid was used to aid dispersion.

Suspensions were prepared using the same procedure as before and at the same volume fraction. Only this time just two dispersants were tried; Darvan 821A and polyacrylic acid 5100. The natural pH of the suspension was now much lower than before (pH 3.40 compared to \sim pH 7.2) and the initial zeta potential was $\sim +11.5$ mV. The two plots of zeta potential against amount of added dispersant are now shown in Fig. 6. Note that this again is expressed in terms of mg of dispersant per unit surface area of the calcined powder. It can be seen that the optimum adsorbed amount is now much greater, (0.31 mg m^{-2} for polyacrylic acid and 0.37 mg m^{-2} for Darvan 821A) than previously measured and that the final zeta potentials are much greater (~ -45 mV compared to ~ -25 mV). Hence, it is the presence of this organic coating that prevents the effective adsorption of the dispersants.

4 Conclusions

Acoustophoresis is an ideal tool for studying the adsorption of dispersants onto aqueous suspensions of ceramic powders as the method is quick, robust and reliable. It also allows numerous dispersants to be tested quickly to select those which will impart the greatest stability to ceramic suspensions.

Several suitable dispersants were identified for the Tioxide titania powder whilst none could be recommended for the Rhone Poulenc titania powder as the resulting zeta potentials of the suspensions were low and adsorbed amounts minuscule. The i.e.p of the two powders were also widely different, occurring at pH 7.5 for Tioxide powder and pH 6.1 for the Rhone Poulenc powder. This was due to the different coatings on the powders; alumina and an organic coating respectively. By removing the organic coating on the Rhone Poulenc titania it was then possible to adsorb much more dispersant and achieve greater zeta potentials.

It was also possible to identify dispersants that would lead to stable suspensions of the Mandoval zirconia powders. However, the yttria leached out of the Tosoh zirconia powder under the slightly acidic natural pH of the suspension, generating yttrium ions which then re adsorbed onto the powder surface. This increased the amount of positive charge on the particle surface, increasing the zeta potential. The i.e.p of the Mandoval

powder was identified as occurring at pH 5.4 and an estimate of 7–7.5 was made for the Tosoh powder.

Acknowledgements

CERAM (Stoke on Trent, UK) are thanked for the BET surface areas, XRF and ICP Atomic Absorption spectroscopy measurements and for access to the Acoustosizer.

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