Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 34 (2008) 523–529

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

I: Dispersibility of robust alumina particles in non-aqueous solution

Amit Mukherjee [a,*], R. Khan [a], B. Bera [b], H.S. Maiti [c]

[a] Department of Basic Sciences & Humanities, College of Engineering & Management, Kolaghat, Kolaghat 721171, India
[b] R & D Division, Berger Paints India Limited, Shibpur, Howrah 711103, India
[c] Central Glass & Ceramic Research Institute, Calcutta 700032, India

Received 2 February 2006; received in revised form 23 June 2006; accepted 26 November 2006
Available online 22 December 2006

Abstract

This article presents the preparation of well dispersed alumina slurries containing relatively large alumina particles that can withstand accelerated weather conditions. Besides using conventional dispersants such as phosphate esters and menhaden fish oil, dispersants widely used in the surface coatings industries such as Disperbyk 110 and Triton X 100 have also been employed. However, sedimentation tests, sediment density, viscosity and gloss measurements indicate the failure of the anionic dispersants as well as menhaden fish oil to disperse the alumina particles in non-aqueous medium. Instead the binder polyvinyl butyral itself acts as the best dispersant. The well dispersed alumina slurry is stabilized in the presence of a commercially available rheology modifier, Bentone SD2 for a period of 144 h at 60 °C. The rheological behavior of the aged sample was studied under various conditions. Although a rise in viscosity of the suspension was observed when the slurry was exposed to accelerated weather conditions, a lower shear thinning index and higher gloss values indicate a better dispersion state with aging.

Keywords: A. Suspensions; C. Lifetime; Alumina

1. Introduction

The paint, ceramic, electronic, mechanical industries, etc. utilize well dispersed suspensions of particles in liquids as stock materials for the production of various end products. Advances in processing of powders through the colloidal route have shown that a proper dispersion of powders by this technique allows the end-user to get rid of many of the inherent drawbacks of conventional processing of powders [1–6]. The typical steps involved in the preparation of suspensions are well documented in the literature [7–10] and usually takes a considerable time in the tune of 24–48 h. In many cases, stocks of the well dispersed particle suspensions are stored without agitation and the particles either due to their density mismatch with the suspending fluids (water or organic) or due to colloidal forces that exist between the particles, form agglomerates. This renders the suspension useless. Previous attempts to stabilize well dispersed suspensions have been made in several directions such as by imparting thixotropy [11], using polyelectrolytes [12], heat treatment of powders [13], doping the metal oxides [14,15] adsorption of hydroxylated benzoic acid [16], increasing the pH [17], and by using a polymeric thickener [18].

The present investigation aims at preparing robust alumina suspensions which have a long shelf life so that these suspensions can be readily used with minimum processing times such as a few hours of ball milling even after storage. To realize such an objective an organic derivative of montmorillonite clay is used in low quantities in the overall formulation and the effects of such addition to the shelf life of alumina suspensions prepared is studied under accelerated weather conditions.

1.1. Experimental

Coarse alumina powder Tabular Alumina; T Al (ACC-Almatis), was used for the present study (Table 1). The binder used was poly vinyl butyral (PVB) of grade Maripol B30 (Table 2). The plasticizers used were butyl benzyl phthalate [2-$(CH_3(CH_2)_3O_2C)C_6H_4CO_2CH_2\ C_6H_5$] BBP (SD Fine Chemicals) and poly ethylene glycol 400 [$HO(C_2H_4O)_nH$ where $n = 380–400$]; PEG (Merck). The solvent used was an

---

* Corresponding author. Tel.: +91 3228 249 444x1153.
E-mail address: amitmukherjee100@yahoo.co.in (A. Mukherjee).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.11.009

Table 1
Composition of the alumina slurry and formulation particulars

Components	wt%	Vol.%
Polyethylene glycol 400 (PEG)	5.30	6.73
Butyl benzyl phthalate (BBP)	1.28	1.62
Solvent[a]	34.54	61.73
Alumina[b]	51.74	21.12
Poly vinyl butyral (PVB)	6.11	7.90
SD2	1.03	0.90

Applied for protection in India (File No.: 0035NF 2006/IN).

[a] Solvent is an azeotropic mixture of 66 wt% methyl ethyl ketone and 34 wt% ethanol. *Inorganic to organic ratio*, i.e. wt of Al_2O_3/(wt of Al_2O_3 + binder + plasticizer + SD2) × 100 = 79%. *Loading*, i.e. wt of Al_2O_3/(wt of Al_2O_3 + binder + plasticizer + solvent + SD2) × 100 = 51.74. Weight percent of the binder with respect to wt of the powder is 11.80%. The wt ratio of BBP: binder was kept at 0.21 whereas the wt ratio of PEG: binder was maintained at 0.86. The dispersants were added with respect to powder weight; for TX 100 the variations were 0.5–5 wt%, for PE 0.25–2 wt%, for D 110 0.5–4 wt%, for MFO 0.5–4 wt%, respectively and was added in the mixture before powder addition.

[b] The composition of the alumina powder according to the manufacturer's information is typically Al_2O_3 >99.5%, ≤0.4% Na_2O and 0.01–0.05% SiO_2, Fe_2O_3 and CaO combined. The powders had a low surface area (1.06 m^2/gm). The particle size distribution as analyzed by Malvern Mastersizer 2000 was found to have a wide particle size distribution; d_{10} = 3.235 μm d_{50} = 17.632 μm, d_{90} = 43.200 μm.

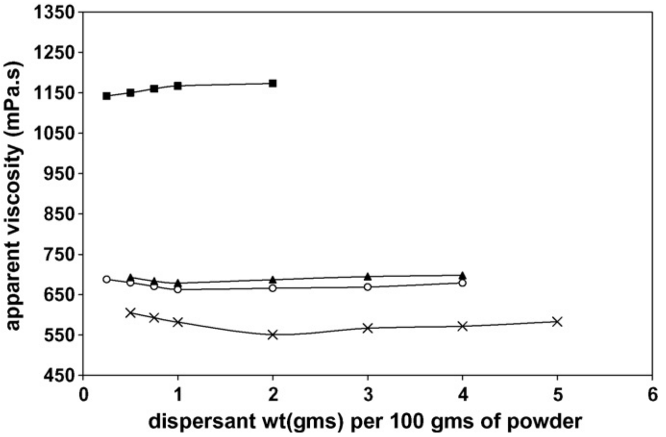

Fig. 1. Plot of apparent viscosity vs. various dispersant concentration: (X) T Al–TX 100; (■-) T Al–PE; (▲) T Al–D 110 and (○) T Al–MFO at 7 s^{-1}.

azeotropic mixture of 66% (w/w) methyl ethyl ketone; MEK (Merck) and 34% (w/w) of 99.9% ethanol; EtOH (Jiangyin Huaxi, China). Each of the individual solvents had a moisture content of 0.1% and were used as supplied. The various dispersants used in the present work along with their salient features have been presented in Table 2. The antisettler used was bentone SD2; SD2 (NL Chemicals). The following procedure for slurry preparation was adopted. The powders were heated at 100 °C for 6 h in air prior to using them. This ensures a negligible moisture content of the powders [19]. In the first stage, to a portion (37%) of the total azeotropic solvent mixture utilized in the formulation (Table 2), 5.30%, w/w of PEG, 1.28%, w/w BBP and 1.03%, w/w of SD2 was added. When dispersants were utilized for stabilizing the suspensions, different concentrations of dispersants were utilized (Table 1 and Fig. 1). The resultant mixture was stirred in a magnetic stirrer for half an hour. The 51.75%, w/w of the heat treated powder was then weighed and poured into the above mixture containing solvent, plasticizers, dispersants and SD2 (when used), respectively. The resultant slurry was subsequently ball milled for 24 h with alumina balls as the grinding medium. In the second stage 6.11% w/w of (PVB) was added along with the remaining 63 wt% of the azeotropic solvent. The slurry was further ball milled for 20–24 h. The alumina suspension thus formed was poured into a container and was de-aired under vacuum conditions (400 mm Hg) till no more bubbles were seen to form. The de-aired slurry was stored under ambient conditions in an air tight plastic container. Since the solvents had negligible moisture content and the powders heated prior to their use, the overall moisture content of the slurry can be safely assumed to be negligible.

Sedimentation tests, sedimentation bulk volume and sedimentation density were carried out as described by Sacks et al. [20]. Viscosity measurements were carried out with a programmable Brookfield rotatory viscometer DV II + by

Table 2
Details of the dispersants

Name	Chemical formula/generic family	Abbreviation used	Make	Description[a]
Triton X 100	Octyl phenol ethoxylate	TX 100	Dow chemicals	Non-ionic surfactant; steric stbilization
Phosphate ester surfonic 1168	Alkyl aryl ether phosphates	PE	Huntsman	Anionic dispersant; electrosteric stabilization; acid value = 103 mgKOH/g
Manhaden fish oil	Mixture of large variety of fatty acid esters	MFO	Sigma Chemical Co.	Non-ionic surfactant; steric stabilization contains 20 or more different types of fatty acids ranging from linoleic to palmitic to myristic to stearic
Disperbyk 110	Solution of copolymer with particle affinic groups	D 110	BYK Chemie	Anionic surfactant; steric stabilization; acid value=53 mgKOH/g
Poly vinyl butyral[b]; grade: Maripol B-30	Poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate)	PVB	Parekh Chemicals	Binder; polyvinyl acetal: 76-81%; polyvinyl acetate: 1-3%; polyvinyl alcohol: 18-21%

[a] Datasheet information.

[b] The molecular weight distribution as measured with GPC (Waters, Model 510 attached with Waters 410 Differential Refractometer using polystyragel column and THF as the solvent), was found to be M_n = 45,723; M_w = 85,919 and M_w/M_n = 1.879, respectively.

utilizing a small sample adaptor (SSA) and the spindle SC 34. The temperature of measurements was kept constant at 25 °C. The viscosities of the slurries containing various dispersants with variable dispersant concentration were monitored at 7 s^{-1} (25 rpm) while for measuring the change of viscosity with shear, depending upon the suspension viscosity and the limitations of the viscometer, the viscometer was programmed to measure the viscosity at the shear rates in the range of 0.84 s^{-1} (3 rpm) to 25.2 s^{-1} (90 rpm), respectively. The shear thinning index [21] of the slurries were measured by dividing the apparent viscosity at a low rotational speed (12 rpm, 3.36 s^{-1}) by the viscosity at a higher speed (50 rpm, 14 s^{-1}). The thixotropic behavior of alumina slurries was investigated by slightly modifying the ASTM standard [21]. The degree of thixotropy was estimated as the ratio of the lowest speed viscosity before and after the rest period. The higher the ratio the greater is the thixotropy. Aging studies were performed with the de-aired sample by exposing them to accelerated weather conditions of 60 °C for 72 h. Aging under such conditions generally correspond to an industrial standard of approximately 60 days of shelf life under ambient conditions. The resultant heat treated slurry was subsequently ball milled for 3 h before viscosity and gloss measurements were undertaken for the aged suspensions. The pH and conductivity measurements were carried out with microprocessor based pH meter (Systronics 361) and a microprocessor based conductivity measurement unit (Systronics 306). Gloss measurements were undertaken with a Glossometer (Sheen Instruments, Model No. 160). The samples for gloss measurements were prepared by spreading the slurries on black and white paper with the help of a bar coater (No. 7). The specular angle for gloss measurement was kept at 85°.

2. Results and discussion

2.1. Dispersion studies

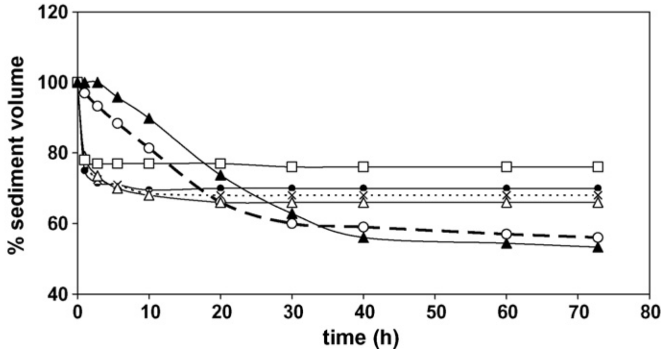

Fig. 2. Percentage sediment volume with time for various dispersants: (▲) T Al–PVB (2%); (○) T Al–TX 100 (2%); (□) T Al; (●) T Al–PE (0.25%); (X) T Al–D 110 (1%); (Δ) T Al–MFO (1%). The percentages are with respect to the powder weight.

In order to find out the optimum concentration of the dispersants necessary to stabilize the T Al suspensions, measurements of the apparent viscosity versus various weight percent of dispersant employed per 100 gm of powder were undertaken (Fig. 1). Since the particles used were coarse, and suffered rapid sedimentation, binder in the prescribed weight percent according to Table 1 was included in the slurries for achieving reproducible viscosity measurements. The concentrations of minimum viscosities for the slurries (Fig. 1) containing D 110, TX 100 and MFO were found to be 1, 2 and 1%, w/w per 100 gms of powder, respectively. However, in the case of using PE as the dispersant a continuous increase in viscosity was observed. These results show that the above mentioned concentration of D 110, TX 100 and MFO is able to keep the smaller agglomerates or primary particles (formed as a result of ball milling of suspension), separated to some extent from each other [2]. Sedimentation tests (Fig. 2) and sediment density measurements (Fig. 3) also reflect similar results. In addition to all the dispersants used in their optimum concentration a 2% (w/w) PVB was also used to ascertain the role of PVB in dispersing Tab Alumina. It was observed (Fig. 2) that the initial fall (3 h) in sediment height followed the order; T Al (without any dispersant) > T Al–PE ~ T Al–D 110 >T Al–MFO >T Al–TX 100 > T Al–PVB, respectively. Furthermore, only T Al–TX 100 and T Al–PVB systems showed hard sediments with the maximum sediment density (Fig. 3). These observations reflect that apart from the suspensions containing PVB and TX 100 none of the dispersants utilized are effective in dispersing T Al [22]. Surprisingly two of the most effective dispersants for alumina powders, i.e. MFO and PE [1,23] showed no significant dispersing ability in the present case.

Attempts for measuring the electrophoretic mobility of the alumina particles failed as the particles being large had a tendency of sedimentation in the capillary of the electrophoretic cell. However, it was noticed that the alumina particles were moving towards the cathode implying a positive charge on the surface of the particles. Therefore, the reason for such failure of both the anionic dispersants may lie in the fact that Tab Alumina being prepared by the Bayer's process contains excess amount of caustic soda (0.40% w/w) [24] compared to the different grades of alumina utilized in previous investigations (0.05–0.08% w/w) [26–30]. The positive Na$^+$ ions thus liberated from Tabular Alumina may form ion pair with the anionic functional head of the dispersants thereby restricting

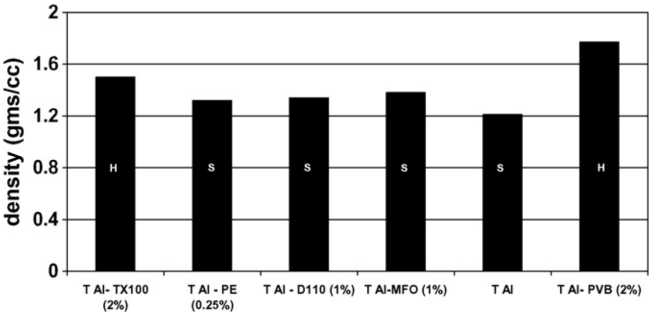

Fig. 3. Sediment density of the various alumina slurries with aging at 60 °C for 72h: (from left) T Al–TX 100 (2%); T Al–PE (0.25%); T Al–D 110 (1%); T Al–MFO (1%), T Al, T Al–PVB (2%). "H" corresponds to hard sediments and "S" corresponds to soft sediments. The percentages are with respect to the powder weight.

Table 3
pH and conductivity changes for different slurries upon addition of various components

Serial no.	System description	pH	Conductivity (μS cm^{-1})
1	PEG + BBP + solvent	5.33	14.7
2	PEG + BBP + solvent + PVB	4.78	12.40
T Al–PVB system			
3	PEG + BBP + solvent + alumina (after ball milling)	7.64	72.6
4	PEG + BBP + solvent + alumina + binder (after ball milling)	7.18	38.1
T Al–D 110 (2%)–PVB system			
5	D 110 + PEG + BBP + solvent	1.64	12.6
6	D 110 + PEG + BBP + solvent + alumina (after ball milling)	5.83	49.5
7	D 110 + PEG + BBP + solvent + alumina + binder (after ball milling)	5.28	43.6
T Al–MFO (1%)–PVB system			
8	MFO + PEG + BBP + solvent	5.04	9.21
9	MFO + PEG + BBP + solvent + alumina (after ball milling)	6.7	60
10	MFO + PEG + BBP + solvent + alumina + binder (after ball milling)	6.46	45
T Al–PE (0.25%)–PVB system			
11	PE + PEG + BBP + solvent	1.37	13.3
12	PE + PEG + BBP + solvent + alumina (after ball milling)	5.12	51.8
13	PE + PEG + BBP + solvent + alumina + binder (after ball milling)	4.91	39.52
T Al–TX 100 (2%)–PVB system			
14	TX 100 + PEG + BBP + solvent	5.12	8.9
15	TX 100 + PEG + BBP + solvent + alumina (after ball milling)	8.82	27.6
16	TX 100 + PEG + BBP + solvent + alumina + binder (after ball milling)	8.13	21.2

their attachment to the powder surface. The lower dielectric constant of the medium may also restrict the ion pairs to dissociate effectively thereby inhibiting the dispersing ability of these anionic dispersants. The fall in pH (Table 3) upon addition of ionic dispersants (PE and D 110) to the mixture containing solvent and plasticizers and the subsequent increase in pH of the slurry with addition of powder and ball milled for 24 h do point to such a contention especially when NaOH is known to be soluble in ethanol [25]. On the other hand, a survey of the literature shows that the binder molecules such as PVB [31–33] can act as a more effective dispersant than conventional dispersants. This is precisely what is observed in the present case (Figs. 1–3). The other non-ionic dispersant utilized for this study, TX 100 (octyl phenol ethoxylate), is known for its chemical stability in most acidic and alkaline solutions [34]. The failure of MFO, another widely used non-ionic dispersant is surprising [35] and it may be due to the hydrolysis [26] of the ester moieties during its initial exposure to the alkaline conditions just after the addition of powder in the system. The results of conductivity measurements (Table 3) during step wise addition of the ingredients were in expected lines. On addition of PE and D 110 to the solvent plasticizer combination, no significant decrease in the conductivity of the solution was observed due to lower mobility of the bulky anions of the dispersants coupled with the increase in viscosity of the medium. The fall in conductivity after binder addition in all the cases is due to viscosity increase of the medium. The gloss [36] of the dried films were also in expected lines with the better dispersions, e.g., T Al–PVB and T Al–PVB–TX 100 (Table 3) give higher gloss values compared to agglomerated dispersions. Furthermore, viscosity studies reveal all the slurries to be pseudoplastic in nature (Fig. 4). It is well established that the shear thinning of the slurry is dependent on the degree of flocculation of the slurry [37,38] and the capability of the particles to align them with increasing shear rates [39]. Therefore, it is expected that the shear thinning effect will be low with lower particle flocculation. The order of the shear thinning (Table 4) is in conformity with the results obtained previously from sedimentation tests and gloss measurements which showed the ionic dispersants do not work effectively with the Tabular Alumina system while the non-ionic dispersants are much more effective.

2.2. Aging studies

In order to stabilize the well dispersed suspension of T Al–PVB, optimization studies involving various concentration (w/w) of SD2 were undertaken, e.g., 0.25% (BB1), 0.50% (BB2),

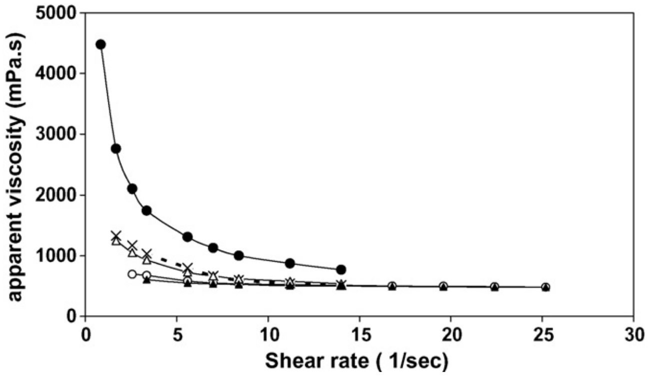

Fig. 4. Variation of apparent viscosity under different shear rates for suspensions; (▲) T Al–PVB; (○) T Al–TX 100 (2%)–PVB; (●) T Al–PE (0.25%)–PVB; (X) T Al–D 110 (1%)–PVB and (Δ) T Al–MFO (1%)–PVB.

Table 4
Shear thinning index, thixotropic index and gloss of various slurries

Serial no.	Slurry composition	Shear thinning index[a]	Thixotropic index[b]	Gloss[c]
1	T Al–PVB	1.2	1.01	2.1
2	T Al–PVB–TX 100	1.3	1.01	2
3	T Al–PVB-MFO	1.7	1.02	1.8
4	T Al–PVB–D 110	2.0	0.99	1.5
5	T Al–PVB–PE	2.2	0.99	1.3
6	T Al–PVB–SD2 (0.25%), (BB1), fresh	1.2	–	–
7	T Al–PVB–SD2 (0.25%), (BB1), heat treated (60 °C, 72 h)	1.4	–	–
8	T Al–PVB–SD2 (0.50%), (BB2), fresh	1.2	–	–
8	T Al–PVB–SD2 (0.50%), (BB2), heat treated (60 °C, 72 h	1.4	–	–
9	T Al–PVB–SD2 (1%), (BB3) fresh	1.2	1.03	2.8
10	T Al–PVB–SD2 (1.0%), (BB2), ambient, 14 days	1.1	1.04	3.0
11	T Al–PVB–SD2 (1.0%), (BB3), heat treated (60 °C, 72 h)	1.1	1.05	3.3
12	T Al–PVB–SD2 (0.50%), (BB2), heat treated (60 °C, 144 h)	1.0	1.07	3.3

[a] The shear thinning index was measured by taking the ratio (viscosity at 3.36 s^{-1})/(viscosity at 14 s^{-1}).

[b] The lowest shear rate in the shear ramp experiments was 3.36 s^{-1} and the rest period was 4 min.

[c] Gloss measurements were undertaken at a specular angle of 85°.

1% (BB3), respectively. Fig. 5 shows the variation of viscosity with shear for the freshly prepared suspensions containing SD2 in the concentrations of 0.25, 0.50 and 1.0%, respectively. As expected that with increase in SD2 concentration, the viscosity of the slurry increases. This is because SD2, consisting of stacks of agglomerated platelets [40,41] can form a gel structure by edge-to-edge hydrogen bonding between hydroxyl groups on the organoclay platelet edges. Therefore, with increase in concentration of SD2 in the composition, more hydrogen bonds are formed resulting in higher viscosities of the suspensions. Moreover, it was also noticed that in the case of BB3 suspension (1% SD2 concentration) no sediments were formed even after aging in contrast to BB1 (0.25% SD2) and BB2 (0.5% SD2) suspensions. Such an observation points that with a concentration of SD2 in the tune of 1% in the overall formulation, sedimentation of the T Al–PVB slurry can be totally retarded in the time frame measured in this investigation. Detailed viscosity measurements of the T Al–PVB suspension containing a SD2 concentration of 1%, w/w were therefore undertaken under various conditions of aging. These conditions were (i) freshly prepared BB3 (SD2,1%) slurries; (ii) BB3 slurries kept under ambient conditions for a period of 14 days, (iii) heating of the ambient aged BB3 slurry at 60 °C for 72 h and ball milled for 3 h and (iv) heating the slurry at 60 °C for 144 h and ball milling for 3 h, respectively.

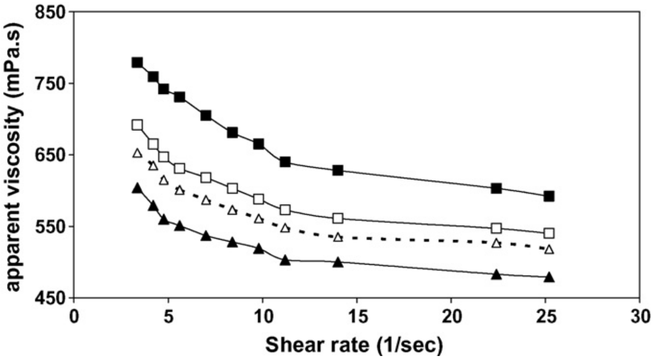

Fig. 5. Variation of apparent viscosity under different shear rates for the alumina suspensions containing different concentrations of SD2. (Δ) BB1 (SD2: 0.25%); (□) BB2 (SD2: 0.50%) and (■-) BB3 (SD2: 1.0%).

As is observed (Fig. 6) the viscosity of the freshly prepared suspension with BB3 (SD2 1%) is almost 28% greater than the T Al–PVB system. The shear thinning index of this slurry is also comparable with the base slurry of T Al–PVB. (Table 3). However, with aging (ambient conditions 14 days) the viscosity of the slurry falls down considerably. Keeping the suspension under ambient conditions even for a period of 21 days do not show any significant decrease in viscosity. Such observation reflects that the viscosity loss has reached its saturation and the system has stabilized. Such cases of viscosity loss without the slurry undergoing any sedimentation during storage is not uncommon for high loading suspensions such as paints and is commonly attributed to incomplete deflocculation of powders during the ball milling stage. Heating the aged sample (14 days ambient conditions) at 60 °C for 72 h, and for 144 h at the same temperature resulted in an increase in viscosity of the samples compared to the aged sample (14 days ambient conditions). However, lowering of the shear thinning index of these slurries do indicate a better dispersion state of powders with aging. The higher gloss value of the aged suspensions (Table 4) also point to the above contention of progressive better dispersion of alumina with aging. Therefore, the increase in viscosity of the aged suspension can be thought as the result of more effective hydrogen bonding imparted to the system by well separated

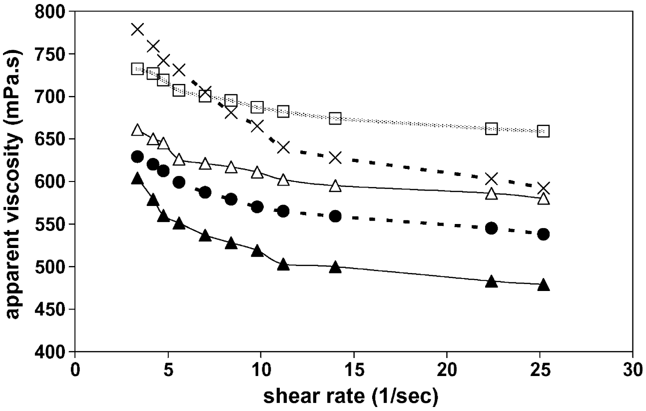

Fig. 6. Variation of apparent viscosity under different shear rates for the BB3 suspension. (▲) T Al–PVB, (X) BB3 (freshly prepared); (●) BB3 (ambient conditions, 14d); (Δ) BB3 heat treated for 72 h at 60 °C and (□) BB3 heat treated for 144 h at 60 °C.

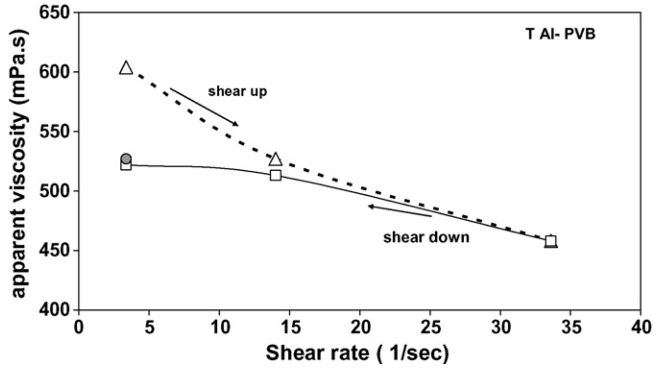

Fig. 7. Thixotropic curve of T Al–PVB suspension; (Δ) represents the shear up curve, (□) represents the shear down curve and (●) represents the viscosity after rest period of 4 min.

platelets of SD2 capable of forming a higher concentration of hydrogen bonds and not due to agglomeration. Thixotropic measurements of T Al–PVB, and T Al–PVB–SD2 (1%) at the various conditions of its aging was also undertaken. All the slurries showed typical thixotropic behavior as that of T Al–PVB (Fig. 7) albeit with different viscosity values. However, the progressive increase in thixotropic index (Table 4) with aging points out to the fact that the aged samples show greater efficiency of viscosity buildup thereby preventing sedimentation.

2.3. Conclusion

The present study investigates the dispersing ability of some anionic and non-ionic dispersants utilized for dispersing coarse alumina particles in non-aqueous medium. It has been observed that even though alumina powders have positive surface charge none of the anionic dispersants are efficient in dispersing the suspension. This has been pointed by higher sedimentation rate, low sediment density, soft sediment nature, inferior gloss values and a higher viscosity with greater shear thinning index. The cause of such failure of the anionic dispersants may be due to the presence of ion pair formation between Na^+ with the anionic head of the dispersant. The study also indicates that the binder PVB is the most effective dispersant and in the present case the binder serves the dual function of binding the particles as well as acting as the most effective steric dispersant. Aging studies under accelerated weather conditions carried out with the well dispersed alumina in presence of a commercially available organoclay in the concentration range of 1% shows no sign of sedimentation, but a progressive increase in viscosity with aging time was observed. However, the lower shear thinning index and higher gloss value of aged suspensions compared to the freshly prepared suspensions do carry the signature of a better dispersed suspension with aging. It is likely that with aging the organoclay particles are becoming better dispersed and as a result a more effective network structure formed by hydrogen bonds is able to arrest sedimentation. Thixotropic measurements carried out with suspensions also show a higher viscosity buildup with aging thus points to such a possibility.

Acknowledgements

This work was supported by the Department of Science & Technology, Government of India under the Young Scientist Scheme to the corresponding author vide order no. SR/FTP/CS-95/2001. The corresponding author would also like to thank Prof. B. Pal, College of Engineering & Management, Kolaghat & Prof. M.M. Maiti, I.I.T, Kharagpur for their suggestions at various stages of this work.

References

[1] W.H. Rhodes, et al., Agglomeration of Particle Size affects sintering of Y_2O_3 stabilized zirconia, J. Am. Ceram. Soc. 64 (1981) 19–22.
[2] A. Mukherjee, B. Maiti, A. Das Sharma, R.N. Basu, H.S. Maiti, Correlation between slurry rheology, green density and sintered density of tape cast yttria stabilized zirconia, Ceram. Int. 27 (2001) 731–739.
[3] H.K. Bowen, et al., Basic needs in high temperature ceramics, J. Mater. Sci. Eng. 44 (1980) 1–5.
[4] F.F. Lange, Processing related fracture origins, J. Am. Ceram. Soc. 65 (1983) 396–408.
[5] I.A. Aksay, F.F. Lange, B.I. Davis, Uniformity of alumina-zirconia composites by colloidal filtration, J. Am. Ceram. Soc. 66 (1984) 190–192.
[6] G.Y. Onada, Ceramics Processing Before Firing, John Wiley & Sons, NY, 1978.
[7] G.D. Parfitt, in: G.D. Parfitt (Ed.), Dispersion of Powders in Liquids, Elsevier Publishing Company Limited, 1969, pp. 81–83.
[8] J.S. Reed, Principles of Ceramic Processing, John Wiley & Sons, NY, 1995, p. 280.
[9] A. Aksay, Microstructure Control through Colloidal Consolidation, in: Forming of Ceramics, in: J.A. Mangels, G.L. Messing (Eds.), Advances in Ceramics, vol. 9, Am. Ceram. Soc., Westerville, OH, 1984 pp. 94–103.
[10] F.F. Lange, Powder processing science and technology for increased reliability, J. Am. Ceram. Soc. 72 (1) (1989) 3–15.
[11] T.J. Garino, Thixotropic particles suspensions and method for their formulation, US Patent No.: 5,639,296, June 17 (1997).
[12] B.E. Novich, M.A. Ochionero, R.L. Pober, Highly loaded pourable suspension of Particulate Materials, US Patent No.: 4,904,411, Feburary 27 (1990).
[13] M. Yasrebi, K.M. Traft, D.H. Sturgis, M. Gerald, M.E. Springate, D.G. Nikolas, Methods for Processing Casting Materials to Increase Slurry Lifetime, US Patent No.: 6,920,913,B2, June 26 (2005).
[14] M. Yasrebi, W.W. Kemp, D.H. Sturgis, D.G. Nikolas, G.L. Wright, T. Kelly, J. Thomas, M.E. Springate, T.R. Crego, Yttria-Zirconia slurries & Mould facecoats for casting reactive metals, US Patent 5,407,001, April 18 (1995).
[15] M. Yasrebi, M.E. Springate, N.M. Edwin, G.D. Nikolas, W.W. Kemp, D.H. Sturgis, R. Van Ginhoven, Method for stabilizing ceramic suspensions, US Patent 5,643,844, July 1 (1997).
[16] M. Yasrebi, W.W. Kemp, D.H. Sturgis, I.A. Aksay, H. Nakagawa, Method for Stabilizing Ceramic Suspensions, US Patent, 5,624,604, April 29 (1997).
[17] R.A. Horton, Method for Casting a Reactive Metal Against a Surface Formed from an Improved Slurry Contaning Yttria, US Patent, 4,947,927, August 14 (1990).
[18] C.C. Payne, Concentrated Lapping Slurries, US Patent No.: 4,752,628, June 21 (1988).
[19] R.E. Mistler, E.R. Twiname, Tape-Casting Theory and Practice, American Chemical Society, 2000, pp. 64–65.
[20] M.D. Sacks, C.S. Khadilkar, J. Am. Ceram. Soc. 66 (7) (1983) 488–494.
[21] Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) viscometer, Designation D 2196-99, ASTM International, 1999, pp. 221–224.
[22] S.H. Bell, V.T. Crowl, in: G.D. Parfitt (Ed.), Assessment of Dispersion in Dispersion of Powders in Liquids, Elsevier Publishing Company Limited, 1969, pp. 186–190.
[23] R. Moreno, The role of slip additives in tape-casting technology. Part: II binders & plasticizers, Ceram. Bull. 71 (11) (1992) 1647–1657.

[24] H.H. Pohland, Aluminum Oxide, in: Production Properties & Applications, Alcoa Chemie GmbH, 1999, pp. 4–17.

[25] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 81st ed., CRC Press, 2000, pp. 4–88.

[26] W. Black, in: G.D. Parfitt (Ed.), Surface Active Compounds Dispersion of Powders in Liquids, Elsevier Publishing Company Limited, 1969, p. 205.

[27] T. Chartier, E. Streicher, P. Boch, Phosphate esters as dispersants for tape casting of alumina, Ceram. Bull. 66 (11) (1987) 1653–1655.

[28] K.P. Plucknett, C.H. Caceres, C. Huges, D.S. Wilkinson, Processing of tape-cast laminates prepared from fine alumina/zirconia powders, J. Am. Ceram. Soc. 77 (8) (1994) 2145–2153.

[29] K.P. Plucknett, C.H. Caceres, D.S. Wilkinson, Tape casting of fine alumina/zirconia powders for composite fabrication, J. Am. Ceram. Soc. 77 (8) (1994) 2137–2144.

[30] W.C.J. Wei, S.J. Lu, B.K. Yu, Characterization of submicron alumina dispersion with poly(methacrylic acid)polyelectrolyte, J. Eur. Ceram. Soc. 15 (1995) 155–164.

[31] T. Hayashi, Surface Chemistry of Ceramic Shaping Process in FC Annual Report for Overseas Readers Japan Fine Ceramic Association, September 1991.

[32] K.R. Mikesha, W.R. Cannon, Dispersants for tape casting pure barium titanate, in: Forming of Ceramics, in: J.A. Mangels, G.L. Messing (Eds.), Advances in Ceramics, vol. 9, Am. Ceram. Soc., Westerville OH, 1984, pp. 164–183.

[33] H. Goldschmidt, B. Streitberger, BASF Handbook on Basics of Coating Technology, 2003, pp. 352–356.

[34] Product, Information DOW Surfactants, Form No.: 119-01882.

[35] R.E. Mistler, D.J. Shanefield, R.B. Runk, Tape casting of ceramics, in: G.Y. Onada, Jr., L.L. Hench (Eds.), Ceramics Processing Before Firing, John Wiley & Sons, NY, 1978, pp. 41–47.

[36] J. Hocken, The additive for high gloss top coats, in: Technical Publications, Sachtleben Chemie GmbH, Germany, 2005, pp. 1–12.

[37] M. Wu, G.L. Messing, Fabrication of oriented SiC whisker-reinforced mullite matrix composite by tape-casting, J. Am. Ceram. Soc. 77 (1994) 2586–2592.

[38] M.D. Sacks, Rheological science in ceramic processing, in: L.L. Hench, D.R. Ulrich (Eds.), Science of Ceramic Chemical Processing, Wiley, New York, 1986, pp. 522–538.

[39] M.D. Sacks, C.S. Khadilkar, G.W. Scheiffele, A.V. Shanoy, J.H. Dow, R.S. Dow, Dispersion and rheology in ceramic processing, in: G.L. Messing, K.S. Mazdiyasni, J.W. Cauley, R.A. Haber (Eds.), Ceramic Powder Science: Advances in Ceramics, vol. 21, Am. Cer. Soc., Westerville, 1987.

[40] P. Maiti, Influence of miscibility on viscoelasticity, structure and intercalation of oligo-poly(caprolactone)/layered silicate nano composities, Langmuir 19 (2003) 5502–5510.

[41] J. Dau, G. Lagaly, Surface modification of bentonites, II modification of montmorillonite with cationic poly(ethylene oxides), Croat. Chem. Acta 71 (4) (1998) 983–1004.