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Preparation of ultra-fine dispersions of zinc oxide by simple ball-milling: Optimization of process parameters

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ABSTRACT

Ultra-fine aqueous dispersions of zinc oxide were prepared by a combination of wet ball-milling and ultrasonication in the presence of various concentrations of a process control agent (PCA). The particles in the dispersions were characterized by dynamic light scattering (DLS) and zeta potential measurements. Six hours of ball-milling of the zinc oxide dispersion containing 3 wt.% PCA followed by ultrasonication resulted in the formation of particles having size below 500 nm.

1. Introduction

Stable colloidal dispersions of zinc oxide are in great demand for a broad range of products such as paints, dyes, cosmetics, pharmaceuticals, ceramics and micro-electronics. The annual worldwide demand of zinc oxide is about 1,200,000 metric tons [1]. Incorporation of fine particles of zinc oxide in rubber latex based formulations improves the strength of the product as a result of the improved homogeneity, solubility, and reactivity of the additive [2]. Addition of a suitable dispersant (process control agent — PCA) is one of the methods to improve the dispersability and stability of aqueous dispersions [3].

Wet ball-milling is one of the most economic and efficient techniques for the preparation of fine and ultra-fine dispersions of particulate materials. This technique is also used for the applications such as blending of materials [4,5]. Finely divided materials undergo spontaneous aggregation, adsorption and recrystallization in an activated system during grinding or after the grinding has been completed [6]. Homogenization, dispersion and stability are very difficult goals at submicron and nano-scales where the particles have a strong tendency to agglomerate and form larger structures [7]. Ultrasonication is commonly used for the de-agglomeration of particle assemblies. A combination of ball-milling and ultrasonication may lead to an effective particle size reduction.

Stabilizations of colloidal dispersions of many metal oxide nano powders by electrostatic and steric methods have been reported [8,9]. In electrostatic stabilization, charges generated at the surface of particles prevent the re-agglomeration of fine particles. Steric stabilization occurs when large molecules adsorb on to the surface of particles thereby providing a physical barrier between them. A combination of these two may stabilize the fine dispersions.

One of the objectives of the work reported in this paper was to assess the stability of zinc oxide dispersions by zeta potential measurements. Zeta potential (ζ) is a function of surface charge of the particles. A highly negative or positive ζ potential value (more than 30 mV or less than -30 mV) shows dispersions with reasonable stability [10].

Dry processes are the popular methods for the production of nanoparticles of materials. These dry particles agglomerate during the preparation of aqueous dispersions. To the best of the knowledge of the authors, no research reports are available regarding the production of ultra-fine dispersions of zinc oxide by simple wet ball-milling. The pioneering efforts to prepare and characterize the stable ultra-fine dispersions of zinc oxide by a combination of wet ball-milling and ultrasonication in the presence of a process control agent are discussed in this paper.

2. Experimental

Zinc oxide used in this study was white seal grade supplied by SUMIT chemicals Pvt. Ltd., Kanpur, India. Details of the zinc oxide used are given in Table 1. Ball-milling (wet grinding) was performed in a stainless steel vessel having a capacity of 2.5 l (20.5 cm diameter × 15.5 cm height).

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Table 1
Details of zinc oxide.

Product name	Physical form	Solubility in water (%)	Bulk density (g/cc)
Zinc oxide active	Fine powder	Up to 1	0.5–0.6

Porcelain balls of 18–20 mm diameter were used as grinding media and the powder to ball weight ratio was maintained as 1:5. The mixture (formulations shown in Table 2) was ball milled at 35 rpm so as to ensure the cascading action of the slurry inside the jar. In one batch, 500 g ZnO was milled. Withdrawing of dispersion was carried out at regular intervals of time (say 6, 12, 18, 24 and 30 h) and around 1–2 g samples were withdrawn at these intervals for particle size analysis. Disodium methylene *bis*-naphthalene sulfonate (Dispersol F) was used as the process control agent (PCA). The PCA was added along with the powder before starting the milling process. Particle size, size distributions and specific surface area of the zinc oxide dispersion were measured using a particle size analyzer (Mastersizer 3000, Malvern, UK) by dynamic light scattering (DLS) technique. Size distribution was determined as the average of three replicates. Aggregation of particles has been avoided by subjecting the samples to ultrasonication performed in a Vibra Cell ultrasonics (model VCX-750) at a frequency of 20 kHz having a power rate of 750 W. The amplitude of vibration, time of ultrasonication and pulsation rate were 45%, 15 min and 10 s respectively. Ultrasonication of the particle dispersions was carried out in a water bath maintained at a constant temperature (28 °C).The stability of wet ball-milled zinc oxide dispersion was measured using a Zetasizer (Nano Z, Malvern UK) at 25 °C.

The polydispersity index or width of particle size distribution of the dispersion was expressed by span.

$$Span = \frac{[D(v,90) - D(v,10)]}{D(v,50)}$$

Where $D\,(v,90)$, $D\,(v,10)$ and $D\,(v,50)$ are the equivalent volume diameters at 90%, 10% and 50% cumulative volume respectively. A small span indicates a narrow size distribution [11].

3. Results and discussion

3.1. Effect of milling time on volume weighed mean at various concentrations of process control agent

Volume weighed mean, D [4,3] is also known as the De Broucker Mean. D [4,3] is very relevant for many samples as it reflects the size of those particles which constitute the bulk of the sample volume. It is most sensitive to the presence of large particulates in the size distribution. The effect of concentration of PCA on D [4,3] of ball-milled zinc oxide at various intervals of wet ball-milling is shown in Fig. 1. As evident from the figure irrespective of the concentration of the PCA, zinc oxide particles are larger in all the formulations. The particle size of zinc oxide decreases considerably in all the formulations after 6 h of wet ball-milling. The particle size remained almost unchanged as the ball-milling was continued up to 18 h. The zinc oxide dispersions containing 3 and 4 wt.% of PCA showed a gradual increase in D [4,3] after 18 h of wet ball-milling. On the other hand, a sharp rise in D [4,3] was observed in the case of the zinc oxide dispersion stabilized with 2 wt.% PCA after 24 h of wet ball-milling. The sharp increase in particle size after 24 h of wet ball-milling is apparently due to the re-agglomeration of the broken zinc oxide particles as the low PCA concentration (2 wt.%), is inadequate to prevent the interaction among the particles.

Table 2
Formulations used for preparing zinc oxide dispersions.

Ingredients	Parts by weight (%)		
	A	B	C
Zinc oxide	100	100	100
Dispersol F (PCA[a])	2	3	4
Water (distilled)	198	197	196

[a] PCA = process control agent.

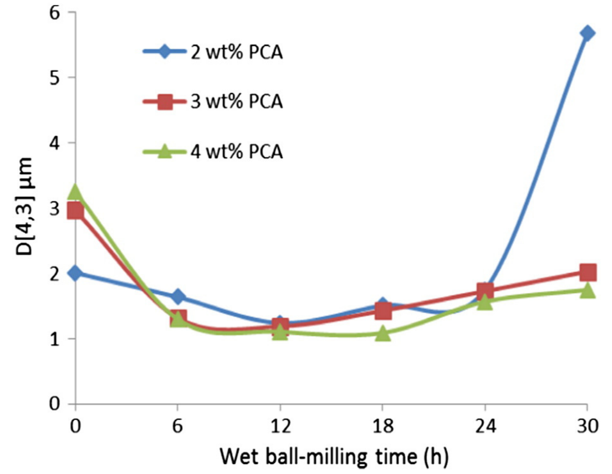

Fig. 1. Effect of wet ball-milling time on the volume weighed mean (D [4,3]) of zinc oxide aqueous dispersions containing various concentrations of PCA.

3.2. Effect of process control agent on the specific surface area of zinc oxide

The specific surface area (SSA) of wet ball-milled zinc oxide dispersion with various concentrations of PCA as a function of milling time is shown in Fig. 2. For the first 12 h of ball-milling, SSA of zinc oxide stabilized with 2 and 3 wt.% of PCA remains almost steady at 7377 and 7156 m^2/kg respectively. After 12 h of ball-milling, there has been a marginal decline in SSA of zinc oxide irrespective of the concentration of PCA. An interesting observation is that the SSA of zinc oxide stabilized with 2, 3 and 4 wt.% PCA coincides after 24 h of ball-milling. The decrease in SSA after prolonged ball-milling indicates that the ultra-fine particles produced during extended period of milling leads to the aggregation of the particles. The size of the ultra-fine particles with high surface energies quickly increases to micro-scale range in water due to

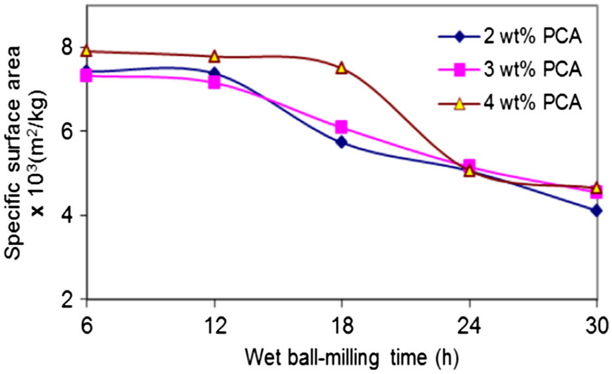

Fig. 2. Variation of specific surface area of zinc oxide aqueous dispersions with wet ball-milling time.

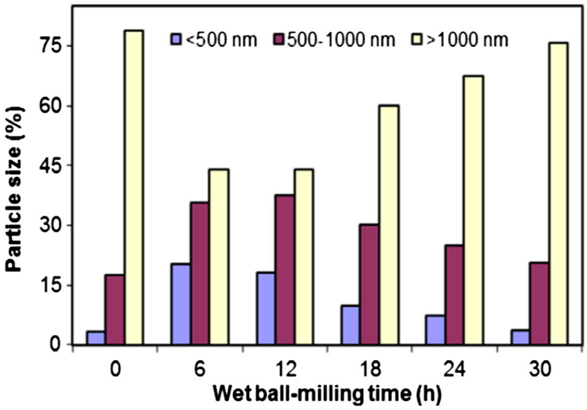

Fig. 3. Effect of wet ball-milling time on the size (%) of zinc oxide particles in aqueous dispersions containing 2 wt.% PCA.

rapid particle collision, *Van der Waals* attraction, water bridging and high surface energy [12].

3.3. Effect of the concentration of the process control agent on the size (%) of zinc oxide particles

The effects of wet ball-milling time (6, 12, 18, 24 and 30 h) on the particle size of zinc oxide in the dispersions containing various concentrations (2, 3 and 4 wt.%) of the PCA are shown in Figs. 3, 4 and 5.

The particle size distributions in each case are grouped into three discrete categories and designated as sizes below 500 nm (ultra-fine), sizes between 500 and 1000 nm (fine), and sizes above 1000 nm (coarse). For convenience they can be designated as ultra-fine, fine and coarse particles.

In the case of the zinc oxide dispersion containing 2 wt.% PCA (Fig. 3), 20% of the particles were in the ultra-fine range and 44% of the particles were in the coarser range after 6 h of wet ball-milling. After 30 h of ball-milling the quantity of ultra-fine particles decreased to 3.5% whereas the quantity of coarser particles increased to 74%.

After 6 h of wet ball-milling, 19% of the particles were in the ultra-fine range and 45% of the particles were in the coarser range in the case of the zinc oxide dispersion containing 3 wt.% PCA (Fig. 4). After 30 h of ball-milling the quantity of ultra-fine particles decreased to 6% whereas the quantity of coarser particles increased to 74%.

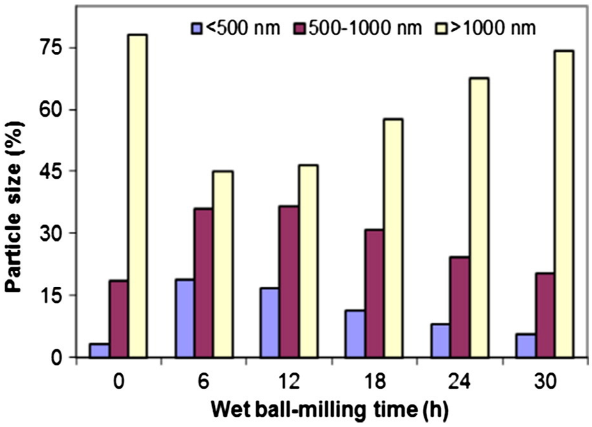

Fig. 4. Effect of wet ball-milling time on the size (%) of zinc oxide particles in aqueous dispersions containing 3 wt.% PCA.

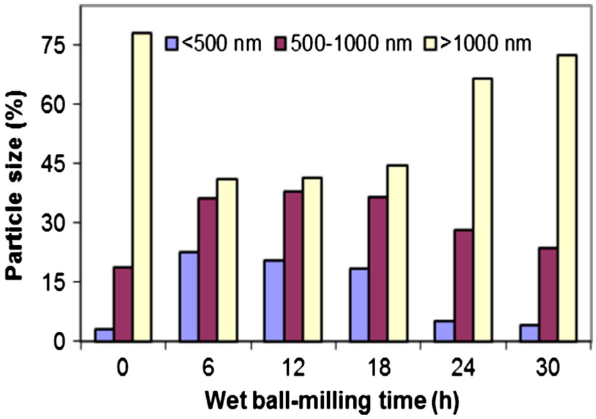

Fig. 5. Effect of wet ball-milling time on the size (%) of zinc oxide particles in aqueous dispersions containing 4 wt.% PCA.

In the case of the zinc oxide dispersion containing 4 wt.% PCA (Fig. 5), the share of ultra-fine particles after 6, 12 and 18 h of wet ball-milling was 22%, 20% and 18%. As the milling time was increased to 24 and 30 h the share of the ultra-fine particles decreased to 5% and 4%. The share of coarser particles after 6 h and 12 h of milling is 41% only and it increased to 44%, 67%, and 72% respectively after 18, 24 and 30 h of milling.

The results cited above show that the portion of lower sized particles decreases as the milling time increases, irrespective of the concentration of the process control agent. Though prolonged milling is expected to decrease the average size of the particles, the reason for the reverse trend might be due to the agglomeration of particles. As the milling time increases apparently the cold welding mechanism (i.e., the smaller particles making bonds between them) predominates over the expected fracturing mechanism. However up to a milling time of 6 h, the share of the lower particle size is maximum at all concentrations of the PCA and thereafter it decreases gradually.

The cumulative particle size curves of unmilled zinc oxide and after 6, 12, 24 h of ball-milling with 4 wt.% of PCA is shown in Fig. 6. A shift in the curve towards left is observed after 6 h of milling indicating sample size reduction. A slight increase in size distribution was observed after 12 h of ball-milling. However, the shift of the curves towards right (increase in particle size) is more pronounced at higher milling time. Thus with the same concentration of the PCA, prolonged ball-milling increases the size of the zinc oxide particles in the dispersion due to agglomeration.

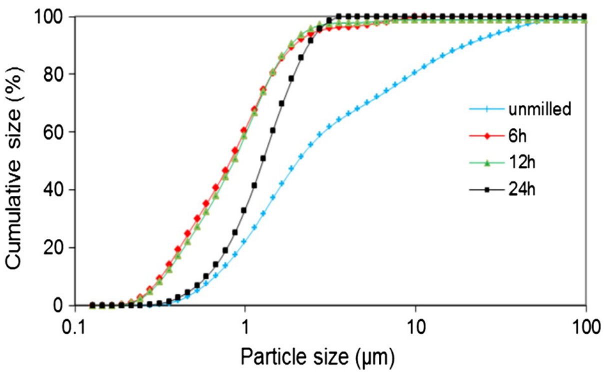

Fig. 6. Cumulative particle size distributions of unmilled ZnO and after 6, 12 and 24 h of wet ball-milling with 4 wt.% PCA.

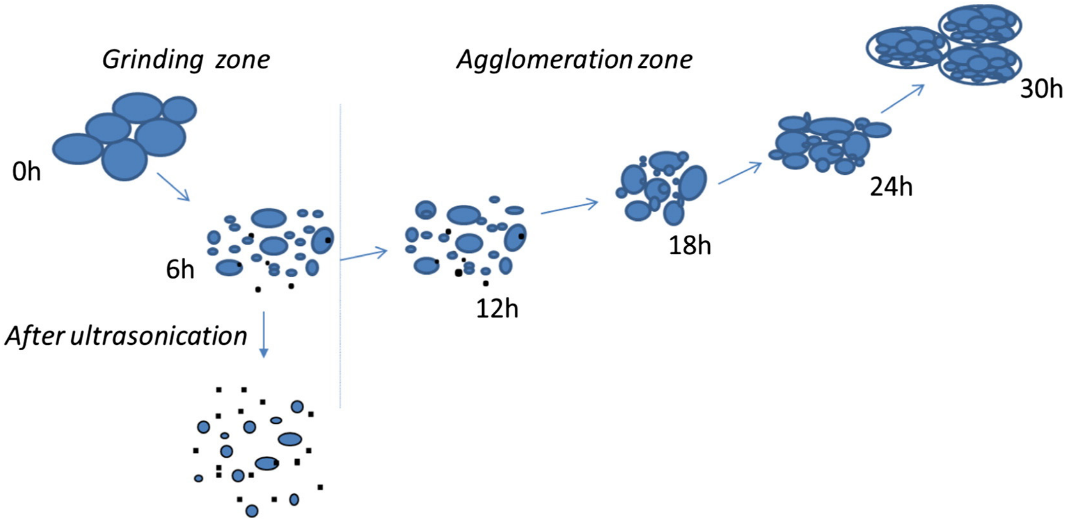

Fig. 7. Schematic diagram showing the formation of agglomerated (coarse) zinc oxide particles in aqueous dispersion upon prolonged wet ball-milling. (To be reproduced as color figure on web.)

A schematic representation of the changes in the particle size of zinc oxide during wet ball-milling is shown in Fig. 7. The reduction in particle size is due to the formation of fresh surfaces during the course of grinding [13]. However, a slight increase in particle size was observed after 12 h of milling. The increase in particle size of zinc oxide after 12 h of ball-milling is expected to be due to the heat generation inside the milling vessel. As milling time increases the heat generated in the milling jar leads to agglomeration causing an increase in the size of the particles [14] as evident from the decrease in specific surface area.

4. Effect of ultrasonication

Ultrasonication is an effective tool for preparing aqueous dispersion of ultra-fine particles. Ultrasonic cavitation is very effective in breaking agglomerates and aggregates. When ultrasound is used for the milling of highly concentrated batches, the liquid jet streams resulting from ultrasonic cavitation make the particles collide with each other at velocities of up to 1000 km/h. This breaks the primary particles and the *Van der Waals* forces in agglomerates. Large particles are subjected to surface erosion (via cavitation collapse in the surrounding liquid) or particle size reduction (due to fission through inter-particle collision or the collapse of cavitation bubbles formed on the surface) [15].

4.1. Effect of ultrasonication on the specific surface area of zinc oxide particles

The effect of ultrasonication on the specific surface area (SSA) of wet milled zinc oxide dispersions with various concentrations of PCA (2, 3 and 4 wt.%) is shown in Fig. 8. The specific surface areas of the particles in the ultrasonicated zinc oxide dispersions after 6 h of ball-milling with 3 and 4 wt.% PCA are almost the same whereas a reduction in SSA is observed with 2 wt.% PCA. The decrease in SSA of the samples sonicated after 12 h milling indicates re-agglomeration of the particles. The extent of agglomerate breakage depends on the nature of inter-particle bonds. Once agglomerates or aggregates are formed in a synthesis process it would be difficult to convert them back to their primary particles [8].

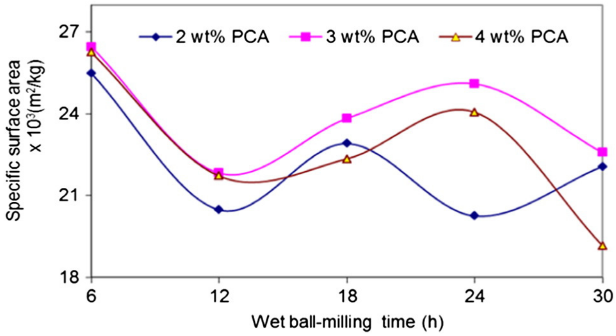

Fig. 8. Specific surface area of zinc oxide particles in aqueous dispersion after wet ball-milling followed by ultrasonication.

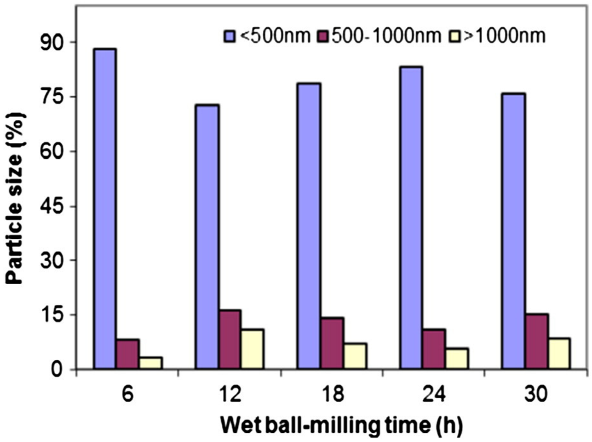

Fig. 9. Size (%) of zinc oxide particles in aqueous dispersions containing 3 wt.% PCA after wet ball-milling for various durations followed by ultrasonication.

Table 3
Span values of aqueous dispersions of zinc oxide containing 2, 3 and 4 wt.% PCA.

Milling time (h)	Span 2 wt.% PCA		Span 3 wt.% PCA		Span 4 wt.% PCA	
	BS[a]	AS[b]	BS	AS	BS	AS
6	2.30	1.72	1.89	1.57	1.90	1.65
12	1.78	3.70	1.59	3.11	1.66	2.99
18	1.69	2.41	1.60	2.35	1.59	2.95
24	1.70	2.43	1.68	1.89	1.40	2.14
30	2.09	2.85	1.61	2.6	1.39	2.91

[a] BS—before ultrasonication.
[b] AS—after ultrasonication.

4.2. Effect of ultrasonication on the size (%) of zinc oxide particles

A higher reduction in the size of the zinc oxide particles has been achieved by wet ball-milling followed by ultrasonication. Effect of ultrasonication on wet ball-milled zinc oxide dispersion containing 3 wt.% PCA is shown in Fig. 9. Ultrasonication after 6 h ball-milling gave 88% of the particles in the ultra-fine size range. However on ultrasonication after 30 h of wet ball-milling, the share of ultra-fine size zinc oxide particles in the dispersion decreased to 76%.

5. Effect of milling and ultrasonication on polydispersity

The polydispersity indices (span) of ball milled zinc oxide stabilized with 2, 3 and 4 wt.% PCA before and after ultrasonication are shown in Table 3. A lower span value of 1.57 was observed for zinc oxide dispersion containing 3 wt.% PCA after 6 h of ball-milling followed by sonication. This indicates that 6 h of ball-milling followed by sonication at the PCA concentration of 3 wt.% is the ideal condition for the preparation of monodispersed zinc oxide suspensions. A broad span indicates highly polydispersed particles. Polydispersity index greater than 2 is not desirable.

6. Variation of zeta potential with PCA concentration

The colloidal stability and the evaluation of optimal dispersing conditions of zinc oxide dispersion after various wet ball-milling intervals were measured using zeta potential analysis. The criterion for surface stability is identified to be $|\zeta| > 30$. Fig. 10 shows the change in zeta potential with PCA concentration at various milling intervals. In all the cases, higher negative zeta potential values were observed for samples stabilized with 4 wt.% of PCA. As the concentration of PCA decreases, the zeta value also decreases. Lowest zeta potential value of −28.4 mV was obtained after 24 h wet ball-milling with 2 wt.% of PCA. The schematic representation shown at the top of the figure indicates the effect of concentration of PCA on the particle–particle interaction. As the concentration of PCA increases; particle–particle interaction decreases resulting in a stable dispersion. Thus, irrespective of the milling time, greater negative surface charges on zinc oxide particles in the aqueous dispersion can be achieved with 3–4 wt.% PCA, which imparts better stability to the dispersion.

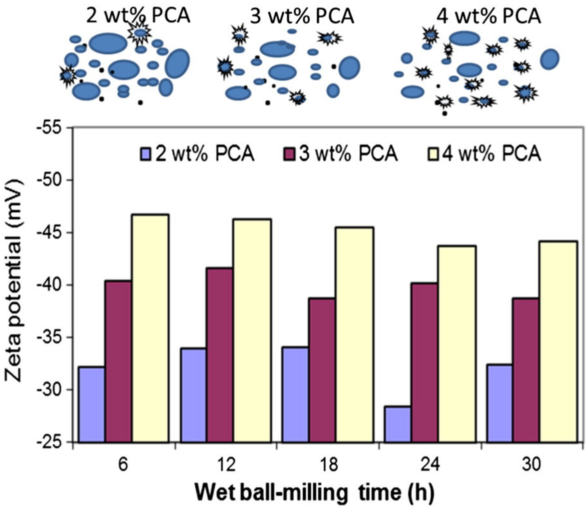

Fig. 10. Variation of the magnitude of zeta potential with PCA concentration after various ball-milling intervals. (Proposed schematic representation is shown at the top.)

7. Conclusion

The particle size of zinc oxide in aqueous dispersions containing various concentrations of process control agent decreases considerably after 6 h of wet ball-milling. The decrease in specific surface area after prolonged ball-milling indicates that the ultra-fine particles produced during extended period of ball-milling lead to the aggregation of the particles. As the milling time increases apparently the cold welding mechanism predominates over the expected fracturing mechanism. A higher reduction in the size of the zinc oxide particles has been achieved by wet ball-milling followed by ultrasonication. The zeta potential value decreases as the concentration of the process control agent in the aqueous dispersion decreases.

Acknowledgments

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References

[1] J. Walter, Tire Technology International, March 2009. 18.
[2] M. Asif Inam, Soualo Ouattara, Christine Frances, Effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process, Powder Technol. 208 (2011) 329–336.
[3] K. Gharanjig, F. Sadr Dadras, M. Sadeghi-Kiakhani, S. Tafaghodi, Stability of dye dispersions in the presence of various surface active agents and additives, J. Dispers. Sci. Technol. 34 (2013) 381–388.
[4] H.B. Fadhel, C. Frances, A. Mamourian, Investigations on ultra-fine grinding of titanium dioxide in a stirred media mill, Powder Technol. 105 (1999) 362–373.
[5] Vladimir Monov, Blagoy Sokolov, Stefan Stoenchev, Grinding in ball mills: modelling and process control, Cybern. Inf. Technol. 12 (2) (2012) 51–68.
[6] M.K. Beyer, H. Clausen-Schaumann, Mechanochemistry: the mechanical activation of covalent bonds, Chem. Rev. 105 (8) (2005) 2921–2948.
[7] C. Saltiel, Q. Chen, S. Manickavasagam, L.S. Schadler, R.W. Siegel, M.P. Menguc, Identification of the dispersion behavior of surface treated nanoscale powders, J. Nanoparticle Res. 6 (2004) 35–46.
[8] N. Mandzy, E. Grulke, T. Druffel, Breakage of TiO_2 agglomerates in electrostatically stabilized aqueous dispersions, Powder Technol. 160 (2005) 121–126.
[9] S.G.J. Heijman, H.N. Stein, Electrostatic and steric stabilization of TiO_2 dispersions, Langmuir 11 (2) (1995) 422–427.
[10] www.malvern.co.uk (lecture Dispersion Stability and Zeta Potential).
[11] O.Y. Toraman, Use of wet grinding and aging to produce narrow particle size distribution, Part. Sci. Technol. 29 (2011) 475–480.
[12] Chih-ping Tso, Cheng-min Zhung, Yang-hsin Shih, Young-Ming Tseng, Shian-chee Wu, Ruey-an Doong, Stability of metal oxide nano particles in aqueous solutions, Water Sci. Technol. 61 (1) (2010) 127–133.
[13] Gaoxiang Du, Qiang Xue, Hao Ding, Zhaohui Li, Mechanochemical effect of brucite powder in a wet ultra-fine grinding process, Indian J. Eng. Mater. Sci. 20 (2013) 7–13.
[14] M. Ramezani, T. Neitzert, Mechanical milling of aluminum powder using planetary ball milling process, J. Achiev. Mater. Manuf. Eng. 55 (2) (2012) 790–798.
[15] T. Hielscher, Ultrasonic production of nano-size dispersions and emulsions ENS'05, Paris, France, December 2005.

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