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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

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.

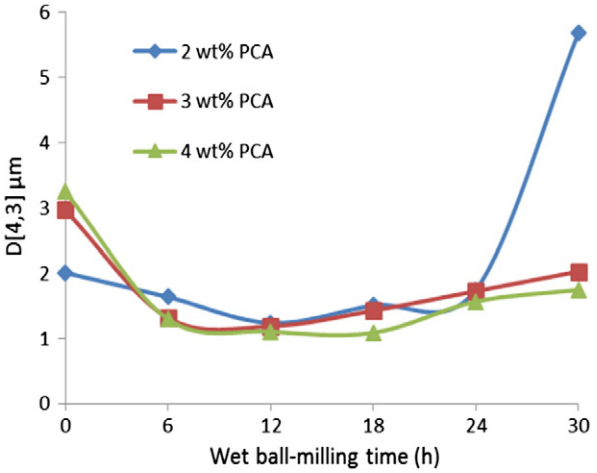

Fig. 1. Effect of wet ball-milling time on the volume weighed mean (D [4,3]) of zinc oxide aqueous dispersions containing various concentrations of PCA.

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.

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

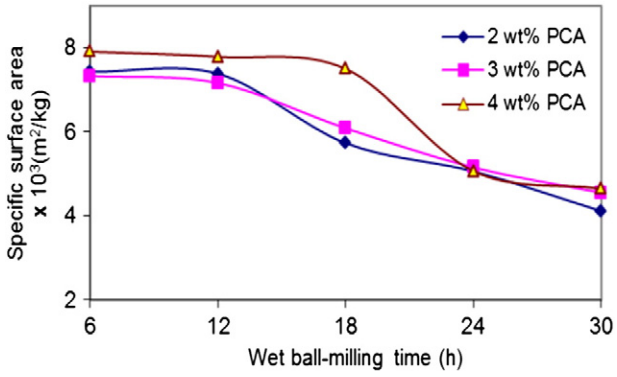

Fig. 2. Variation of specific surface area of zinc oxide aqueous dispersions with wet ball-milling time.