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Effects of Span 60 template and freeze drying on zinc borate produced from zinc nitrate hexahydrate and borax decahydrate

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ABSTRACT
Zinc borate is an important additive to polymers and lubricants. The process variables such as reactant concentration, presence of template in precipitating medium and drying method determine the composition and particle size of zinc borates. In the present study, zinc borate precipitate obtained by mixing aqueous zinc nitrate and borax decahydrate solutions was dried either by conventional method or by freeze drying. The products were well characterized by advanced methods. Zinc borate from 1 mol dm$^{-3}$ reactants had $(2.1 \pm 0.5) \times (2.5 \pm 0.5) \times (1.3 \pm 0.2) \, \mu m$ and $(0.5 \pm 0.1) \times (1.3 \pm 0.1) \times (0.028 \pm 0.001) \, \mu m$ dimensions by conventional and freeze drying respectively. Individual particles smaller in size is obtained since the particles are not agglomerated due to absence of surface tension of liquid water for case of freeze drying. Planar particles agglomerated into 20 to 60 \( \mu m \) crystals in the presence of template Span 60 in 1 mol dm$^{-3}$ reactants for conventional drying. Nano zinc borate particles with primary particle size of $(46 \pm 9) \, nm$ were obtained by decreasing the reactant concentration to 0.1 mol dm$^{-3}$. The primary particle size was decreased to $(40 \pm 3) \, nm$ by addition of Span 60 to dilute solutions. However, zinc borate nanoparticles obtained from dilute solutions adhered to each other forming agglomerates during conventional drying. Their freeze drying would allow formation of a freely flowing nano powder.

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Zinc borate; micro particles; nanoparticles; template; Span 60; freeze drying

Introduction
Zinc borates are industrially important chemicals which are used as flame retardant additives in polymers, and additives in lubricants. Zinc borates can be produced either by the heterogeneous reaction of zinc oxide and boric acid or from the homogeneous reaction of borax and water soluble zinc salts. Eltepe et al.\cite{1} investigated the effect of reaction time and temperature for zinc borate synthesis from boric acid and zinc oxide. Gönen et al.\cite{2,3} applied both supercritical carbon dioxide drying and supercritical ethanol drying techniques for the production of nano zinc borates. Carbonates form during supercritical carbon dioxide drying and zinc borate decomposed to zinc oxide and boric acid in supercritical ethanol drying. Acarali et al.\cite{4,5} and Akgül et al.\cite{6} investigated the synthesis of zinc borates from zinc oxide and boric acid. Acarali et al.\cite{4} used palm oil to make hydrophobic zinc borates. Acarali et al.\cite{4,5} and Schubert\cite{7} reviewed industrially important zinc borate hydrates.

The use of borax as a boron source for the nano-sized metal borate synthesis has increased recently.\cite{8,9} The transfer of the structure from a variety of organic templates (e.g., PEG, PVP, CTAB, etc.) to the inorganic product allowed the formation of otherwise unattainable inorganic structures. 2D and 3D nano/microstructures of 4ZnO-B$_2$O$_3$-H$_2$O with different morphologies have been successfully synthesized by a hydrothermal route in the presence of surfactant polyethylene glycol-300 (PEG-300) from Na$_2$B$_4$O$_7$•10H$_2$O and ZnSO$_4$\cite{10}. Savrik et al.\cite{11} synthesized zinc borate from borax and zinc nitrate by inverse emulsion technique for lubrication. Nano-sized zinc borate particles were obtained by homogeneous precipitation technique developed by Ting et al.\cite{12}. Ammonia was added to the mixture of dilute zinc nitrate and borate solution in this method. The precipitation reaction of metal ions and precipitator can reach molecular level, which ensures the sedimentation of desired nanomaterials yielding and separating out homogeneously from the solution. The precipitation mechanism is based on
the formation of \( \text{Zn(NH}_3\text{)}_4^{2+}\text{(aq)} \) complex, therefore a few \( \text{Zn}^{2+} \) ions present in the solution which inhibits the enlargement of the zinc borate crystals and provides formation of nano-sized particles. Nano zinc borate as a lubricant additive was produced from 0.1 mol dm\(^{-3}\) borax and zinc nitrate by Savrik et al.\cite{13} The gelatinous zinc borate precipitates were dried under vacuum at 10 kPa for 18 hours at 25°C to obtain nanoparticles. The average particle sizes of zinc borates were determined as 35.3 nm and 234 nm for without any template and with Span 60, respectively. When the zinc borate nanoparticles were added to light neutral oil, the wear scar diameter and friction coefficient was lowered by 50% and 20% respectively.\cite{13}

The dispersibility of the zinc borate particles in polymers and lubricating oils is required in industrial applications of zinc borates. Since drying of zinc borates by conventional methods causes agglomeration, an alternative method such as freeze drying could be used to obtain a freely flowing powder. Freeze drying or lyophilization is a technique in which water is sublimated from the frozen material under vacuum. In recent years, ultrafine nano particles were obtained by the freeze drying method. There are two fundamental necessities in the freeze drying: the first one is to prevention of the particles’ agglomeration or keeping of the three dimensional network e.g., silica aerogel. The latter one is the removal of water from the materials which are temperature sensitive such as proteins. Abdelwahed et al.,\cite{14} Chen and Wang\cite{15} and Mi et al.\cite{16} reviewed freeze drying of nanoparticles. There are many examples for the application of freeze drying to produce nano particles. Silver nanopowders with regular shape and uniform diameter were prepared in four steps: preparing the precursor solution, freezing the solution, drying the congealed sample, and calcining the drying product. The starting raw materials were silver nitrate and caustic soda, whereas the precursor was silver diammine solution. The products of freeze drying are pure amorphous silver nanopowders without hard agglomerations. Silver cubic nanocrystals are subsequently obtained by calcination.\cite{17} Nano copper particles were obtained by washing with distilled water, collecting centrifugally, adding to the mixed solution of distilled water and ethanol (25% by vol.), as well as completing by freeze drying.\cite{18} Tachiwaki et al.\cite{19} produced the fine powders for the YBCO superconductor by freeze-drying of the suspensions synthesized by co-precipitation of carbonates. Zeng et al. used \( \text{AlCl}_3\text{-6H}_2\text{O} \) and ammonia as precursor materials to precipitate boehmite (\( \gamma\text{-ALO(OH)} \)) in aqueous solution, peptized boehmite to a transparent sol with nitric acid and then freeze dried the sol. \( \text{Al}_2\text{O}_3 \) particles with an average diameter of 42 nm were obtained by calcining the freeze dried boehmite at 1100°C.\cite{20} Tallon et al. synthesized of \( \gamma\text{-Al}_2\text{O}_3 \) nanopowders by a freeze-drying method.\cite{21} Aqueous solutions of \( \text{Al}_2\text{(SO}_4\text{)}_3\cdot18\text{H}_2\text{O} \) were freeze dried to get homogeneous spherical granules of amorphous aluminum sulfate with diameters ranging from 1 to 100 μm. These porous granules formed by soft agglomerates of nanoparticles with primary particle size lower than 20 nm. Freeze dried amorphous aluminum sulfate powder heated to decompose at 825°C to form \( \gamma\text{-Al}_2\text{O}_3 \). Bovone et al. investigated the large scale production of doped Nano sized boron powder. Dissolved precursor (\( \text{B}_2\text{O}_3 \)) and doping agent (Si) was cryogenically frozen in liquid nitrogen and finally lyophilized. The nano structured boron precursor obtained in freeze drying was further processed by magnesiothermic reaction in which it was reduced by magnesium metal.\cite{22} Freeze drying is usually utilized to get a well distributed precursor which is further processed by calcination or other techniques e.g., reduction to get nano particles. Polycaprolactone (PCL) nanoparticles prepared by the emulsification-diffusion method and then freeze dried at different rates.\cite{23} The freezing process can break the nanoparticles and cause the leakage of their contents during the freeze-drying step.

The particle size of zinc borates is an important property in its applications. While micron sized particles are sufficiently used in flame retarding applications, nano sized particles are essential as lubricant additives. Present study aims at the synthesis of micron sized and nano sized zinc borate particles by controlling the process variables. Thus the effects of concentration, use of template Span 60 (sorbitan mono stearate), conventional and freeze drying methods on zinc borate produced from zinc nitrate and borax were investigated. The wet zinc borate cakes were dried by conventional and freeze drying methods and the products were characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction, Scanning Electron Microscopy (SEM), thermal gravimetric (TG) analysis and particle size analysis.

**Materials and methods**

**Materials**

Borax decahydrate (99.9%) obtained from Eti Maden Inc. and zinc nitrate hexahydrate (99.9%) from Fluka,
Span 60 from Sigma Aldrich, ethanol (99.8%) from Riedel were used in the experiments. De-ionized water was used in all experiments.

**Production of zinc borate and zinc borate with Span 60 from borax decahydrate and zinc nitrate hexahydrate by conventional drying**

Zinc borate was produced by mixing 50 cm$^3$ of 1.0 mol dm$^{-3}$ borax decahydrate and 50 cm$^3$ of 1.0 mol dm$^{-3}$ zinc nitrate hexahydrate at 70°C for 4 hours in a Haake temperature controlled stainless steel reactor by mixing at 900 rpm rate. Zinc borate with Span 60 was obtained by adding 1 g Span 60 to the mixture of 50 cm$^3$, 1.0 mol dm$^{-3}$ borax decahydrate and 50 cm$^3$, 1.0 mol dm$^{-3}$ zinc nitrate hexahydrate at 70°C for 2 hours in a glass reactor by mixing at 900 rpm rate. In order to remove the unreacted zinc nitrate and sodium borate decahydrate, the prepared precipitates were washed using de-ionized water. Subsequently, zinc borates were washed three times by ethanol to replace water. Conventional drying was achieved in an air circulating oven at 110°C till constant weight was obtained.

**Production of nano zinc borate and nano zinc borate with Span 60 by conventional drying**

50 cm$^3$ of 0.1 mol dm$^{-3}$ sodium borate solution was added instantly to 50 cm$^3$ of 0.1 mol dm$^{-3}$ zinc nitrate solution to obtain a hydrosol and mixed at 600 rpm for 2 hours at ambient temperature of 25°C. The experiments were repeated by adding 1 cm$^3$ of 0.002 mol dm$^{-3}$ (corresponding to 0.0086 g) Span 60 to the mixture. Since the particles formed passed through the filter paper due to their small size, they were separated from the aqueous phase by centrifugation using Rotofix 32 centrifuge (Andreas Hettich GmbH, Tutlingen Germany) at 2000 rpm for 10 minutes, washed with ethanol and centrifuged again at 2000 rpm for 10 minutes. The obtained gelatinous precipitates were dried conventionally under vacuum at 10 kPa for 18 hours at 25°C to get nanoparticles. Because the nanoparticles were in an agglomerated state they were ground in a porcelain mortar and pestle before the characterization.

**Freeze drying of zinc borate**

Zinc borate from 1 mol dm$^{-3}$ solutions were freeze dried using Labconco Free Zone-4.5 freeze drier (Labconco Corporation, Kansas City, USA). Before freeze drying, 15 g of wet zinc borate sample was mixed with 50 ml of ethanol and then filtered. Partially dried zinc borate sample by ethanol placed in a vial of the equipment and it was frozen at −18°C in a deep freeze. The frozen sample was placed in freeze drier and it was dried at −51°C under vacuum at 0.020 mbar pressure for 14 hours. The codes and preparation conditions of the zinc borates are as shown in Table 1.

**Characterization of the samples**

Diboron trioxide (B$_2$O$_3$) and zinc oxide (ZnO) contents of zinc borate samples were determined by analytical titration using 0.1 N NaOH and 0.1 mol dm$^{-3}$ EDTA, respectively. Erichrome Black T indicator for Zn titration by EDTA, methyl red for HCl titration and phenolphthalein for B(OH)$_3$ by NaOH were used as indicators.[24] Elemental analysis of zinc borate with Span 60 was performed by CHNS elemental analysis (Leco Corporation, St. Joseph MI, USA).

SEM images were taken with Philips XL30 SFEG (Philips XL30 SFEG, FEI Company, Oregon, USA) to examine the morphology of zinc borate particles. Conductive double sided tape was used to fix the particles to the specimen holder before sputtering them with a thin layer of gold. EDX analysis with the same instrument was made for nano zinc borate particles with and without Span 60.

X-Ray diffraction pattern was obtained using Philips Xpert-Pro X-ray diffractometer (Panalytical, Almelo, Netherlands). The incident CuK$_α$ radiation at 45 kV and 40 mA with 0.154 nm wavelength was used in the analysis. The dried powders were examined using a 0.5-mm thick glass sample holder.

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**Table 1.** Experimental conditions of reaction between 50 cm$^3$ borax decahydrate solution and 50 cm$^3$ zinc nitrate hexahydrate solution and the sample codes of the products.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Drying method</th>
<th>Preparation</th>
<th>Drying</th>
<th>Mixing time (hr)</th>
<th>Mixing rate (rpm)</th>
<th>Concentration (mol dm$^{-3}$)</th>
<th>Temperature (°C)</th>
<th>Mixing</th>
<th>Mixing rate (rpm)</th>
<th>Span 60 (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc borate</td>
<td>Conventional</td>
<td>70</td>
<td>110</td>
<td>4</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Zinc borate with Span 60</td>
<td>Conventional</td>
<td>70</td>
<td>110</td>
<td>2</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Freeze dried zinc borate</td>
<td>Freeze drying</td>
<td>70</td>
<td>−51</td>
<td>4</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nano zinc borate</td>
<td>Conventional</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>600</td>
<td>0.1</td>
<td>0.1</td>
<td>0.086</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano zinc borate with Span 60</td>
<td>Conventional</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>600</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0086</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. ZnO, B_{2}O_{3}, and H_{2}O contents of conventional and freeze dried zinc borates.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>ZnO (%)</th>
<th>B_{2}O_{3} (%)</th>
<th>B_{2}O_{3}/ZnO molar ratio</th>
<th>H_{2}O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Borate</td>
<td>40.14</td>
<td>42.93</td>
<td>1.25</td>
<td>18.7</td>
</tr>
<tr>
<td>Zinc borate with Span 60</td>
<td>30.14</td>
<td>46.6</td>
<td>1.92</td>
<td>23.2</td>
</tr>
<tr>
<td>Freeze dried Zinc borate</td>
<td>38.8</td>
<td>41.5</td>
<td>1.25</td>
<td>19.7</td>
</tr>
<tr>
<td>Nano zinc borate</td>
<td>56.7</td>
<td>26.3</td>
<td>0.54</td>
<td>–</td>
</tr>
<tr>
<td>Nano zinc borate with Span 60</td>
<td>60.6</td>
<td>22.4</td>
<td>0.43</td>
<td>–</td>
</tr>
</tbody>
</table>

Results and discussion

The following reactions occur during zinc borate synthesis. Borax dissolves in aqueous phase according to Eq. (1) to form tetra borate anion $\left[B_{4}O_{5}(OH)_{4}\right]^{-2}$ and sodium cation $70^\circ C$ and sodium cation $70^\circ C$. In Eq. (2), zinc nitrate dissolves to produce zinc cations and nitrate anions. These are expected reactions based on literature data of borate and polyborate anions.\(^{25,26}\) The formed polyborate anions and zinc cations precipitate when mixed together as shown in Eq. (3). There are various types of zinc borate species which can be produced by changing reaction parameters or molar ratio of reactants. After the precipitation, formed building blocks, $\left(Zn[B_{3}O_{3}(OH)_{5}]\right)\cdot H_{2}O$ or $Zn[B_{3}O_{3}(OH)_{5}]$ as depicted in Eqs. (4) and (5), respectively. Further polymerization of these units results in sheets and networks of three dimensional structures.

$$\begin{align*}
Na_{2}B_{4}O_{5}(OH)_{4} \cdot 8H_{2}O(s) & \rightleftharpoons 2Na^{+}(aq) \\
+ & B_{4}O_{5}(OH)_{4}^{2-}(aq) + 8H_{2}O \\
Zn(\text{NO}_{3})_{2} \cdot 6H_{2}O(s) & \rightleftharpoons Zn^{2+}(aq) + 2NO_{3}^{-}(aq) \\
+ & 6H_{2}O(l)
\end{align*}$$

$$
B_{4}O_{5}(OH)_{4}^{2-}(aq) + Zn^{2+}(aq) + H_{2}O(l) \\
\rightarrow Zn\left[B_{4}O_{5}(OH)_{4}\right] \cdot H_{2}O(s)
$$

Other possible parallel reactions taking place in the reaction medium are shown in Eqs. (6)–(8).

$$\begin{align*}
Zn^{2+}(aq) + 3OH^{-}(aq) + NO_{3}^{-}(aq) \\
\rightarrow Zn_{2}(OH)_{3}(NO_{3})\,(s)
\end{align*}$$

$$Zn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Zn(OH)_{2}(s)$$

$$Zn^{2+}(aq) + B_{4}O_{5}(OH)_{4}^{2-}(aq) + NO_{3}^{-}(aq) \\
\rightarrow Zn\left[B_{4}O_{5}(OH)_{4}\right]_{1/2}(NO_{3})\,(s)
$$

As soon as borax and zinc nitrate solutions were mixed, a white precipitate was formed from borate anion and zinc cation in the mixture. Since zinc borate species is sparingly soluble in aqueous phase, supersaturation is exceeded immediately after mixing. In this reactive crystallization, nucleation, crystal growth on formed nuclei, and interaction of those formed crystals take place. Borax-zinc nitrate system includes also other dissolved ions, such as Na$^{+}$ and NO$3$$^{-}$ ions. The presence of those ions in equilibrium with crystals formed in the medium affects crystallization process. The crystals dissolve, reform, and transform to the different zinc borate species during long reaction periods.

The properties of zinc borates

The samples were analyzed by titration method and their compositions are shown in Table 2. The conventional and freeze dried zinc borate samples had $B_{2}O_{3}/ZnO$ ratio of 1.25 and the sample with Span 60 had this ratio as 1.99. On the other hand, EDX analysis showed that nano zinc borate and nano zinc borate with Span 60 had $B_{2}O_{3}/ZnO$ ratio as 0.54 and 0.43 respectively.
The conventional dried zinc borate had 18.08% water as indicated by the material balance of chemical analysis. The elemental analysis (CHNS) of conventional dried zinc borate with Span 60 showed that both carbon (1.91%) and hydrogen (2.89%) elements were present in the product. Neither N nor S element existed in the sample. The presence of carbon element for the sample arises from the Span 60 and the 1.91% C demonstrates that this sample contains 2.85% Span 60 since 1 gram of this surfactant includes 66.9% C, 10.6% H and 22% O elements by weight. H element introduced by Span 60 should be 0.31% and 2.58% H should be present in zinc borate as water. This corresponds 23.2% H2O in zinc borate fraction.

While TG analysis is a dynamic method, elemental analysis is based on the analysis of combustion products of the sample that was burned at 900 °C. For this reason TG analysis indicated lower water content than elemental analysis for all samples.

Characterization of zinc borates

FTIR

The FTIR spectrum of conventionally dried zinc borate is shown in Figure 1. The peaks observed between 1450–1300 cm\(^{-1}\) and 1200–1000 cm\(^{-1}\) are related to asymmetric stretching vibrations of trihedral borate (B\(_{3}\)-O), and tetrahedral borate (B\(_{4}\)-O) groups, respectively. The other peaks between 960–740 cm\(^{-1}\) belong to symmetric stretching vibrations of (B\(_{3}\)-O) and(B\(_{4}\)-O) groups. Moreover, the peaks between 3200–3600 cm\(^{-1}\) and the at 2590 cm\(^{-1}\) belong to stretching vibrations of OH groups and stretching vibrations due to hydrogen bonding in the structure of zinc borate. This product includes interstitial water in its structure since there is H-O-H bending vibration at 1650 cm\(^{-1}\) wavenumber.

The FTIR spectrum of zinc borate prepared via precipitation technique in the presence of Span 60 is shown in Figure 2 and it exhibits both the specific peaks of the surfactant and the zinc borate having seven moles of crystal water (2ZnO·3B\(_2\)O\(_3\)·7H\(_2\)O). The characteristic peaks of zinc borate are assigned referring the literature. The band at 1047 cm\(^{-1}\) is the stretching of B\(_{4}\)-O, and the peaks between 745–658 cm\(^{-1}\) are belonging to out of plane bending mode of B\(_{3}\)-O. The presence of CH\(_2\) stretching peaks of Span 60 at 2850, 2920 cm\(^{-1}\) reveals that small amount of Span 60 was present in the sample.

Zinc borate, which was produced from borax and zinc nitrate in stainless steel reactor using 900 rpm stirring rate, was dried by freeze drying to observe the drying effects. Figure 3 shows the FTIR spectrum of freeze dried zinc borate produced from borax and zinc nitrate. The characteristic peaks defined previously in Figure 1 were aligned with FTIR spectrum of freeze dried sample. Those characteristic peaks reveal the presence of zinc borate type of ZnO·B\(_2\)O\(_3\)·2H\(_2\)O.

The FTIR spectra of the nano zinc borate and nano zinc borate with Span 60 are very similar to each other as seen in Figure 4. There is a broad peak at 3358 cm\(^{-1}\) due to hydrogen-bonded O-H group vibrations. Asymmetric B\(_{3}\)-O vibrations were observed at 1383 cm\(^{-1}\) and at 1350 cm\(^{-1}\). H-O-H bending vibration was detected at 1624 cm\(^{-1}\). At 1014 cm\(^{-1}\) a peak for symmetric B\(_{3}\)-O vibration was present. Besides it, out of plane bending vibration of B\(_{3}\)-O gave a small peak at 694 cm\(^{-1}\).
X-ray diffraction. The presence of peaks with high intensity in x-ray diffraction diagram of conventional dried zinc borate in Figure 5 shows that the product has a crystalline structure. The major peaks in XRD patterns of zinc borate at 10.22°, 20.75°, 28.20°, and 33.18° 2θ values are different than the well-known zinc borates, such as 2ZnO·3B₂O₃·7H₂O, 2ZnO·3B₂O₃·3H₂O⁶ and 4ZnO·B₂O₃·3H₂O⁷. These peaks coincided with the x-ray diffraction diagram of ZnO·B₂O₃·2H₂O which was reported first time by Gönen.⁸

Figure 6 shows the XRD pattern of the zinc borate produced via precipitation technique with Span 60 in aqueous medium. The presence of peaks with high intensity shows that product has a crystalline structure. The major peaks in XRD pattern of zinc borate are observed at 13.07°, 17.58°, 19.66°, 25.54°, 26.38°, 27.04°, 29.42° and 36.97° 2θ values. When these values were compared to those in the JPDS database, it was implied that the specific peaks were consistent with those of Zn(B₃O₃(OH)₅)·H₂O. In literature this type of zinc borate was also defined as 2ZnO·3B₂O₃·7H₂O⁹. Moreover, no other crystalline phases can be detected, which is indicative of pure 2ZnO·3B₂O₃·7H₂O obtained under the current conditions.

Figure 2. FTIR spectrum of zinc borate with Span 60.

Figure 3. FTIR spectrum of freeze dried zinc borate.
synthetic conditions. All the diffraction peaks can be perfectly indexed to $2ZnO\cdot3B_2O_3\cdot7H_2O$ with JCPDS PDF File Number 721789.

Only a broad peak is observed at 2$\theta$ value of 28° in X-ray diffraction diagram of the nano zinc borate and nano zinc borate with Span 60 samples in Figure 7. The small size of the crystals formed caused broadening of the diffraction lines.

**Thermal gravimetric analysis.** TG curves of conventionally dried zinc borate, zinc borate with Span 60 and freeze dried zinc borate are shown in Figure 8. Conventionally dried zinc borate decomposed in one step between 160–400°C temperature ranges. The total mass loss occurred as 18.0% due to removal of water. It corresponds to the H$_2$O content of ZnO-B$_2$O$_3$·2H$_2$O and could be compared to the calculated water content value of 19.25%. It can be inferred the zinc borate sample has the structure of ZnO-B$_2$O$_3$·2H$_2$O based on H$_2$O content.

TG curve of zinc borate with Span 60 in Figure 8 indicates that mass loss of the sample is 22.08% due to the removal of water of crystallization.

Figure 8 also represents TG curve of the zinc borate produced by freeze drying. The total mass loss occurred as 17.7% when the sample was heated from ambient temperature to 600°C. Zinc borate sample started to lose mass at around 180°C and very
little mass loss was observed between 400°C and 600°C. The mass loss of 17.7% is due to the condensation of hydroxyl groups in that temperature range corresponds to water content of ZnO·B₂O₃·2H₂O and can be compared to the calculated water content value of 19.25%. B₂O₃/ZnO molar ratio for zinc borate was calculated as 1.2 from analytical titration results as given in Table 2. This result supported the zinc borate structure of ZnO·B₂O₃·2H₂O.

The water content of the samples in this study is reported in Table 2. Conventional and freeze dried zinc borates had nearly the same water content (18.7%, and 19.7% respectively) as indicated by TG analysis. However, zinc borate with Span 60 had higher water content (22.8%).

The important points in the TG curves of the samples are shown in Table 3. The dehydration onset temperature (100°C) of zinc borate with Span 60 was lower than that (180°C and 200°C) of the conventionally and freeze dried zinc borates respectively.

TG curves of nano zinc borate and nano zinc borate with Span 60 are almost identical as shown in
The temperature of onset of mass loss was 90°C and 100°C since they were conventionally dried at 25°C. The presence of gel water in wet nano zinc borates required higher temperatures than 25°C that was used in conventional drying. The total mass loss up to 600°C was 17.7% and 16.7% for nano zinc borate and nano zinc borate with Span 60 which corresponded to the water content of the samples.

Alp et al. showed that Zn[B_3O_3(OH)_5]·H_2O and Zn[B_3O_4(OH)_3] dehydrated with 24% and 12% mass losses due to evaporation of the water initially present and formed by the condensation of B-OH groups mainly at around 129°C and 320°C, respectively. Parallel to dehydration, a negligible amount of boric acid was sublimed from both zinc borates on heating up to 250°C. In the present study, the onset temperature of the mass loss and the total mass loss % were different than either of the Zn[B_3O_3(OH)_5]·H_2O and Zn[B_3O_4(OH)_3] as shown in Table 3. That set out the formation of different zinc borates other than Zn[B_3O_3(OH)_5]·H_2O and Zn[B_3O_4(OH)_3]]. The mass loss around 19.0% of the zinc borate, freeze dried zinc borate, nano zinc borate and nano zinc borate due to the removal of water corresponds to the H_2O content of ZnO·B_2O_3·2H_2O and could be compared to its calculated water content value of 19.25%. It can be inferred that the four zinc borate samples have the structure of ZnO·B_2O_3·2H_2O based on their H_2O content.

Zinc borate, zinc borate with Span 60 and freeze dried were thermally more stable than nano zinc borate and nano zinc borate with Span 60 since they had 10% mass loss at 230–260°C and 158–172°C respectively.

**Particle morphology.** The particles are in the form flakes having average dimensions of \((2.1 \pm 0.5) \times (2.5 \pm 0.5) \times (1.3 \pm 0.2) \ \mu m\) as seen in SEM micrograph of conventionally dried zinc borate in Figure 10.

SEM micrographs of the crystals obtained by using Span 60 are shown in Figure 11. Micron sized prismatic crystals as well as lamellar-like crystals are observed in the microphotographs. Closer inspection reveals that the lamellar-like crystals in 20–60 \(\mu m\) size are the conglomeration of planar particles with \((11 \pm 1) \times (3.5 \pm 0.1) \times (0.5 \pm 0.1) \ \mu m\) dimensions.

SEM images of freeze dried zinc borate at different magnifications are shown in Figure 12. Particles have a plate-like morphology with \((0.5 \pm 0.1) \times (1.3 \pm 0.1) \times (0.028 \pm 0.01) \ \mu m\) dimensions. Since the water is frozen in the bulk of product, particles are enforced to orient in certain place (layer by layer). After the removal of water

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**Table 3.** The important points from TG curves of the samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Dehydration onset (98% mass) temperature (°C)</th>
<th>Temperature (°C) at 90% mass</th>
<th>Mass (%) at 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc borate</td>
<td>180</td>
<td>265</td>
<td>82.3</td>
</tr>
<tr>
<td>Zinc borate with Span 60</td>
<td>100</td>
<td>230</td>
<td>77.7</td>
</tr>
<tr>
<td>Freezed dried zinc borate</td>
<td>200</td>
<td>260</td>
<td>82.3</td>
</tr>
<tr>
<td>Nano zinc borate</td>
<td>90</td>
<td>158</td>
<td>82.3</td>
</tr>
<tr>
<td>Nano zinc borate with Span 60</td>
<td>100</td>
<td>172</td>
<td>83.3</td>
</tr>
</tbody>
</table>

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**Figure 9.** The temperature of onset of mass loss was 90°C and 100°C since they were conventionally dried at 25°C. The presence of gel water in wet nano zinc borates required higher temperatures than 25°C that was used in conventional drying. The total mass loss up to 600°C was 17.7% and 16.7% for nano zinc borate and nano zinc borate with Span 60 which corresponded to the water content of the samples.

**Figure 8.** TGA curve of conventionally dried zinc borate, zinc borate with Span 60 and freeze dried zinc borate.
from solid to gas phase by sublimation, particles are obtained as single flakes with $(28 \pm 10)$ nm thickness.

The SEM micrographs of the dried nano zinc borate samples are shown in Figure 13. The dried powders consisted of agglomerates of primary particles of $(46 \pm 9)$ nm and $(40 \pm 3)$ nm for nano zinc borate and nano zinc borate with Span 60. The particles were attracted to each other due to capillary forces during drying. Water in the wet samples was replaced with ethanol which had a lower surface tension to decrease the attractive forces between the particles due to capillarity. However they were also agglomerated even by the drying of the ethanol washed hydrogel.\footnote{13}

**Figure 9.** TG curves of nano zinc borate and nano zinc borate with Span 60.

**Figure 10.** SEM microphotograph of conventionally dried zinc borate at $6500 \times$ magnification.

**Figure 11.** SEM images of zinc borate produced in the presence of Span 60 (a) $1500 \times$, (b) $5000 \times$ magnifications.
Particle size distribution. Particle size distribution of zinc borate sample has a bimodal distribution as shown in Figure 14. Zinc borate produced at the end of 4 h reaction time has particles in two ranges; the first group has an average particle size of 460 nm whereas second group has mean particle size of 1.9 \( \mu \)m.

Particle size distribution of zinc borate produced in the presence of Span 60 determined by Mastersizer 2000 is indicated in Figure 15. The distribution had two small intensity peak being maximum 0.5 \( \mu \)m and 3 \( \mu \)m and one high intensity peak at 27 \( \mu \)m. The mastersizer assumes particles are spherical and report the results accordingly. The three peaks could be due to three different dimensions of the particles. Each dimension is assumed as spheres by the instrument.

Nano zinc borates particle size distribution is shown in Figure 16. 6.6\% of the particles had size of \((33 \pm 5)\) nm, 11\% of the particles had mean size of \((31 \pm 15)\) nm and 82\% of the particles had size of \((336 \pm 132)\) nm. Nano zinc borate with Span 60 was mono disperse. 100\% of the particles had size of \((236 \pm 20)\) nm.

![Figure 12. SEM microphotograph of freeze dried zinc borate (a) 12,000×, (b) 50,000× magnification.](image)

![Figure 13. SEM micrographs of nano zinc borate and nano zinc borate with Span 60.](image)

![Figure 14. Particle size distribution of conventional dried zinc borate (Malvern Zetasizer 3000 HSA).](image)
The size of the particles obtained from SEM micrographs and zetasizer is tabulated in Table 4 to show that the particles were present as agglomerates in the aqueous phase. Both nano zinc borate particles and nano zinc borate particles with Span 60 were agglomerated when they were dispersed in aqueous solutions with a broad size distribution. While SEM micrographs showed that they had primary particles of \((46 \pm 9)\) nm and \((40 \pm 3)\) for nano zinc borate and Nano zinc borate with Span 60, their particle size in water was higher and had a broad range of distribution.

Zinc borates were obtained by precipitation method in the present study. Nucleation and growth are two consecutive processes in obtaining crystals by precipitation. Nano particles form by nucleation and they grow by subsequent addition of reactants from solution to their surfaces. In concentrated solutions the reactants are abundant to make the particles grow to large sizes. However in dilute solutions the growth stops due to scarcity of the reactants.

The shape of the crystals obtained by precipitation can be controlled by adding templates. In the case of zinc borate prepared in the presence of Span 60, selected surfaces of the particles were covered by Span 60 allowing them to grow in the surfaces not covered with Span 60. Thus the morphology of the particles,
the boric acid to zinc oxide ratio and the crystal structure of the zinc borate were different compared to the case without Span 60. The particle size of the sample was larger for zinc borate with Span 60 indicating the sticking of primary particles during conventional drying.

The crystals obtained are not very stable in size after precipitation. They undergo changes in particle size during drying. Particles were attracted and adhere to each other when water was removed by conventional drying due to surface tension of water (72 mN m⁻¹ at 25°C). Water was attempted to be replaced by ethanol which had a lower surface tension (22 mN m⁻¹ at 25°C) in the present study. However the total removal of water was only possible by conventional drying at 110°C. Thus the adhesion of the particles to each other causing agglomeration was observed in conventional drying since liquid water with high surface tension pulled the particles together during evaporation process. The zinc borate was freeze dried to avoid the sticking of the particles. During evaporation process the ethanol phase was completely removed by evaporation of the liquid phase since the temperature of the freeze drying (−51°C) was much higher than the freezing point of ethanol (−113°C). On the other hand, water was in ice form and it sublimed directly to vapor phase avoiding the pulling of the particles due to surface tension. Thus single particles were obtained since they did not stick to each other. Lamellar crystals having thickness (28 ± 10) nm and which did not stick to each other were obtained by freeze drying of zinc borates obtained from 1 mol dm⁻³ solutions. TG analysis of conventionally dried and freeze dried samples indicated nearly the same dehydration onset temperature (100°C for conventionally dried sample, it was 200°C for freeze dried sample).

Particle size of the zinc borates formed when dilute solutions with 0.1 mol dm⁻³ concentration were used. The nano particles that were obtained in aqueous phase were attracted to each other due to capillary forces during drying. Water in the wet samples was attempted to be replaced with ethanol which has a lower surface tension to decrease the attractive forces between the particles due to capillarity. However nano particles also agglomerated even drying of the ethanol washed hydrogel. Since silver,[17] copper,[18] alumina,[21] B₂O₃ precursor[22] and polycaprolactone[23] nanoparticles were obtained successfully by freeze drying, freeze drying of the zinc borate nano particles would allow drying without agglomeration of nano zinc borate particles.

Even if the same equilibrium state is obtained in conventional and freeze drying, the rate of drying is very slow in freeze drying since the vapor pressure of ice is very low compared to liquid water. Thus, even if the slow drying is a disadvantage of freeze drying, it’s worth to use it in drying zinc borate crystals. The formation of independent particles is only possible by this method.

### Table 4. Particle size of the zinc borates.

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<th>Zetasizer</th>
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**Conclusion**

Composition, crystal structure and particle morphology of zinc borate produced from zinc nitrate and borax decahydrate could be controlled by solution concentration, template addition and drying by conventional and freeze drying. The B₂O₃/ZnO ratio was 1.25 for conventional and freeze dried zinc borate and they had nearly the same water content (18.7%, and 19.7% respectively) as indicated by TG analysis. While dehydration onset temperature was 180°C for conventionally dried sample, it was 200°C for freeze dried sample.

Zinc borate with Span 60 had a different B₂O₃/ZnO ratio 1.92 and its water content was 23.2 and 22.8% by chemical analysis and TG analysis respectively. Its dehydration onset temperature (100°C) was also lower. Nano zinc borate and nano zinc borate

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with Span 60 from dilute solutions had lower $\text{B}_2\text{O}_3/\text{ZnO}$ ratio 0.54 and 0.43 than that of zinc borate from concentrated solutions. They contained 17.7% and 16.7% water, respectively, and their dehydration onset temperature were 90°C and 100°C since they were dried at 25°C under vacuum.

$\text{ZnO-B}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ and $2\text{ZnO-B}_3\text{O}_3\cdot 7\text{H}_2\text{O}$ were presented respectively in conventionally dried zinc borate and in conventionally dried zinc borate with Span 60. Nano zinc borate and nano zinc borate with Span 60 samples were not crystalline as indicated by their x-ray diffraction diagrams.

The use of higher solution concentration (1 mol dm$^{-3}$) leads to the growth of the particles and thus micron sized agglomerated particles were obtained if conventional drying was applied. Lamellar crystals having thickness ($28\pm10$) nm which did not stick to each other were obtained by freeze drying of zinc borates form 1 mol dm$^{-3}$ concentrated solutions. The synthesis of Nano sized primary particles with $(46\pm9)$ nm and $(40\pm3)$ nm for cases with and without Span 60 was achieved using the dilute initial solution of 0.1 mol dm$^{-3}$. However, the nanoparticles of zinc borate adhered to each other during conventional drying process. When they were dispersed in water they were present as agglomerates with broad size distribution. A freely flowing nano powder could only be obtained by freeze drying of zinc borates from dilute solutions.

The equilibrium and kinetics of freeze drying of the micro and nano particles of zinc borates will be studied in future work.

**Disclosure of interest statement**

There is no conflict of interest with anyone about this paper.

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[2] Gönen, M.; Balköse, D.; Ülkü, S. Supercritical Ethanol Drying of Zinc Borates of $2\text{ZnO-3B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ and $\text{ZnO-B}_2\text{O}_3\cdot 2\text{H}_2\text{O}$. *The Journal of Supercritical Fluids* 2011, 59, 43–52. DOI: 10.1016/j.supflu.2011.08.004.


