Effect of Temperature and Time on Zinc Borate Species Formed from Zinc Oxide and Boric Acid in Aqueous Medium

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The effect of temperature and time of heating of zinc oxide and boric acid in aqueous medium on product type, dehydration behavior, crystal morphology, and structure was investigated for the production of flame retardant and smoke suppressant zinc borate. Two different products dehydrated at 140 and 350 °C were obtained and characterized by thermal gravimetric analysis, X-ray diffraction, energy dispersive spectroscopy, and Fourier transform infrared spectroscopy.

1. Introduction

Plastic materials widely used all throughout our lives release smoke and toxic gases during heating at high temperatures. Zinc borates (ZBs) are widely used flame retardants and smoke suppressants. Zinc borates have been used in flame retarding of paints[1] and EVA.[2] Giudice and Benitez[1] discussed the influence of ZB with molecular formulas containing 3.5 H_2O and 7.5 H_2O on flame resistance of paints. Eight different paint compositions were prepared. Limiting oxygen index (LOI) according to ASTM D 2863 and flame spread index (FSI) tests were carried out to test the flame retardancy. The compositions having both ZBs and having only 7.5 H_2O with antimony trioxide had the maximum LOI values. The increase in the use of synergistic mixture of zinc borate together with aluminum trihydrate has also increased flame retardency. The reason for this usage is that the synergistic mixture of these two compounds promotes a nonhalogen char formation.[1] Bourbigot et al.[2] have studied the recent advances in the use of zinc borate in the flame retardancy of EVA. In their work, zinc borates were used as synergistic agents in ethyl vinyl acetate-aluminum trihydrate (EVA-ATH) and EVA-$Mg(OH)_2$ flame retardant formulations and as smoke suppressants. The flame retardancy of low-density polyethylene (LDPE) treated with complex flame retardant composed of ultrafine zinc borate (UZB) and intumescent flame retardant (IFR) was maximum when the mass ratio of UZB to IFR is 4.2:25.8, and the complex flame retardant mass content was 30% (based on LDPE). Boron orthophosphate (BPO_4) and zinc-containing compounds were formed in the residual char, and these substances may play an important role in stabilizing the intumescent char structure and decreasing the degradation speed substantially when subjected to high temperature.[3] The study about the effects of zinc borate (ZB), aluminum trihydrate (ATH), and their mixture on the flame-retardant and smoke-suppressant properties of poly(vinyl chloride) (PVC) shows that the incorporation of a small amount of ZB, ATH, and their mixture can greatly increase the LOI of PVC and reduce the smoke density of PVC during combustion. The mixture of ZB with ATH has a good synergistic effect on the flame retardance and smoke suppression of PVC. Thermal gravimetric analysis (TGA) and gas chromatography-mass spectroscopy (GC-MS) analysis results show that the incorporation of a small amount of ZB, ATH, and their mixture greatly promotes the char formation of PVC and decreases the amount of hazardous gases such as benzene and toluene released in PVC during combustion. Zinc borate as a flame retardant formulation on some tropical woods reduced drastically their flame propagation rate, after glow time, and flame temperature and increased their residue (char) and LOI. It was observed that zinc borate acidified with HCI functions as a flame retardant (FR) formulation by a complex process that entails the dehydration and condensed phase and vapor phase mechanisms.[5]

A series of different crystal structures of zinc borate (ZB) have been developed and are being used. The most widely used ones are zinc borate with the formula $3ZnO{\cdot}2B_2O_3{\cdot}3.5H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, and anhydrous ZB $2ZnO{\cdot}3B_2O_3$. The heat stability of zinc borate is between 290−300 °C which enables the polymer processibility and the heat stability of anhydrous borate up to 400 °C. Zinc borate $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ is formed when borax is added to aqueous solutions of soluble zinc salts at temperatures below about 70 °C. An X-ray structure determination has indicated that this compound is orthorhombic and has a zinc triborate monohydrate structure $Zn[B_3O_3(OH)_5]{\cdot}H_2O$. Zinc borates $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ release water when heated from 130 to 250 °C.[6]

Zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$) in general is produced with the reaction between zinc oxide and boric acid. Boric acid is dissolved in water between the temperatures 95 and 98 °C, and zinc oxide and seed crystals of $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ is added to this solution at a certain stoichiometric ratio. The reaction continues for a while by mixing, and the zinc borate formed is filtered, dried, and ground. Schubert et al.[7] found out that $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ was actually $Zn[B_3O_4(OH)_3]$ ($ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ written in oxide form). The structure of $Zn[B_3O_4(OH)_3]$ was determined for the first time by single-crystal X-ray diffraction and H magic angle spinning (MAS) NMR, revealing it to be a complex network consisting of infinite polytriborate chains crosslinked by coordination with zinc and further integrated by hydrogen bonding. The boroxyl oxygen involved in zinc coordination lies between the BO_3 and BO_4 polyhedra involved in chain extension. The remaining two zinc coordination sites are occupied by hydroxyl oxygens of the $BO_2(OH)_2$ groups in two separate polyborate chains. In this way, all hydroxyl groups are involved in zinc coordination. $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ hydrolyzes to ZnO and boric acid in aqueous medium if

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10.1021/ie0610243 CCC: $37.00
Published on Web 03/16/2007

Table 1. pH Change after Mixing ZnO and Boric Acid at 60 °C

time (s)	0	10	30	60	120	180	240	360	420
pH	4.30	5.33	5.63	5.68	5.70	5.72	5.72	5.72	5.72

the temperature exceeds 90 °C. Further in the article, the correct formula of $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ will be used as $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$.

Nies et al.[8] developed a method for producing zinc borate with a low hydration number by using sodium borate and zinc salts.

In another patent by Igarashi et al.,[9] zinc borate having a particular crystallite size and containing very little sodium components and a method of preparing the same was studied. The zinc borate had a particular chemical composition, had a crystallite size not smaller than 40 nm as found from diffraction peaks of indexes of planes of (020), (101), and (200) in the X-ray diffraction image (Cu Kα), and contained sodium components in amounts not larger than 100 ppm as measured by the atomic absorption spectroscopy. Igarashi et al.[9] prepared $2ZnO{\cdot}3B_2O_3{\cdot}3.0H_2O$ from boric acid and zinc oxide in two steps. In the first step at 60 °C for 1.5 h, zinc borate crystals form, and in the second step at 90 °C for 4 h, the crystal growth occurs. Schubert et al.[7] indicated that the formation of $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ was initially from ZnO and boric acid and that it is transformed to $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ by slow polymerization of borate ions in the solid state.

In a US patent by Schubert,[10] zinc borate compositions having a $ZnO:B_2O_3$ ratio of 4:1 and anhydrous zinc borate were examined. The patent relates to improved zinc borate compositions and, more particularly, provides a new hydrated zinc borate having a high dehydration temperature which offers significant advantages for compounding with plastics and rubbers at elevated temperatures. The anhydrous form of zinc borate was also provided in this study, offering advantages for compounding at even high temperatures.

Shete et al.[11] have studied the kinetics of the fluid−solid reaction of zinc borate by the reaction between zinc oxide and boric acid. Mixing parameters influencing the final particle size and conversion of zinc oxide were studied for the formation of zinc borate. The formation of zinc borate is via a fluid−solid reaction. The process was kinetically controlled above the minimum speed for particle suspension. The reaction kinetics was developed, and the rate constant was estimated in this study. The reaction was assumed to be a first-order surface reaction with respect to boric acid, and rate constants were found from experimental conversion time data. Shete et al.[11] considered the diffusion of boric acid to ZnO particles but not the rearrangement of borate rings with time to polyborate ions in their kinetic model.

Thousands of metric tons of this material have been manufactured by several companies around the world for more than 35 years using the reaction of zinc oxide with boric acid. Although zinc borate production has long been a widely known and practiced technology, there is no study of the characterization of intermediates formed. Thus, the effects of time and temperature of heating, seed crystals, and refluxing on the type and properties of zinc borate species obtained from zinc oxide and boric acid in aqueous medium were the aim of investigation in this work.

2. Experimental

2.1. Materials. The boric acid supplied by ETİBANK with a molecular weight 61.83 and a molecular formula of $B(OH)_3$ with 99.9% purity and the zinc oxide (99%) from Ege Kimya

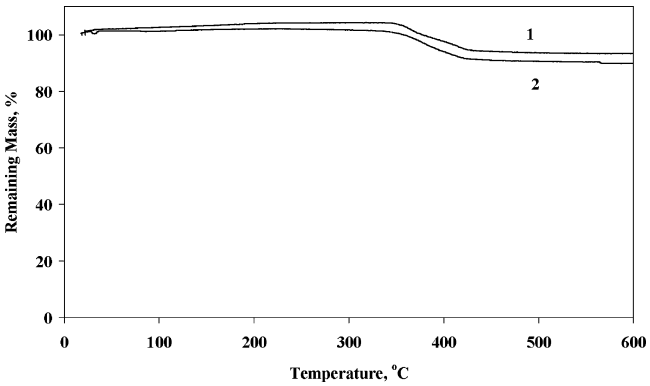

Figure 1. TGA curves of commercial ZB: (1) ZB-2335; (2) Chinese ZB.

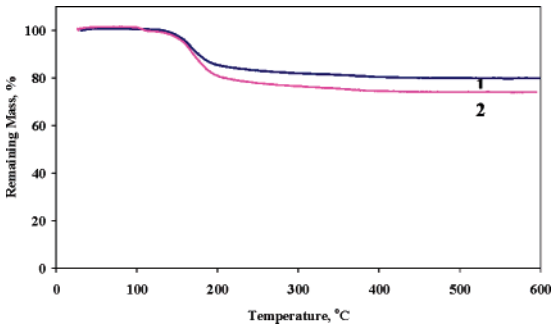

Figure 2. TGA curves of samples prepared at 60 °C for 90 min (1) with seed crystal and (2) without seed crystal.

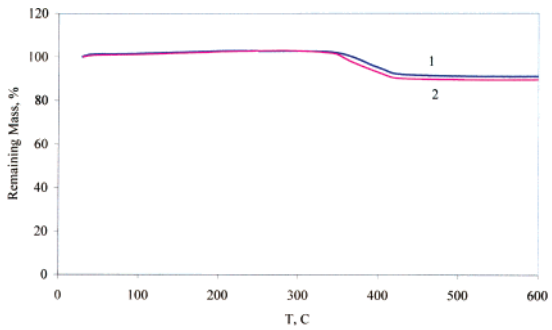

Figure 3. TGA curves of product formed at 90 °C for 4 h (1) with seed crystal and (2) without seed crystal (they were heated at 60 °C for 1.5 h initially).

were used throughout the experiments. Commercial zinc borates called ZB-2335 with 37% ZnO and 47% B_2O_3 and a maximum of 16% water of crystallization and Chinese zinc borate with 37.5% ZnO and 48% B_2O_3 and with ignition loss at 400 °C as a maximum of 14.5% were used in the experiments as reference materials.

2.1. Methods. The synthesis of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ was done according to the overall reaction given in eq 1.

$$2ZnO(s) + 6H_3BO_3(aq) \rightarrow 2ZnO{\cdot}3B_2O_3{\cdot}3H_2O(s) + 6H_2O \quad (1)$$

The experiments were carried out by first dissolving the required amount of boric acid in a separate beaker in pure water. Since the solubility of boric acid at room temperature (20 °C) is 5.04%, the solution of 290 g/dm^3 boric acid in water was prepared by heating the mixture at 60 °C. After boric acid was completely dissolved in water, zinc oxide was added to make the concentration 96 g/dm^3 ZnO in the mixture making the molar molar ratio of B_2O_3 to ZnO be 2. An excess amount of boric acid was used to ensure the formation of $2ZnO{\cdot}3B_2O_3{\cdot}3.0H_2O$.[4]

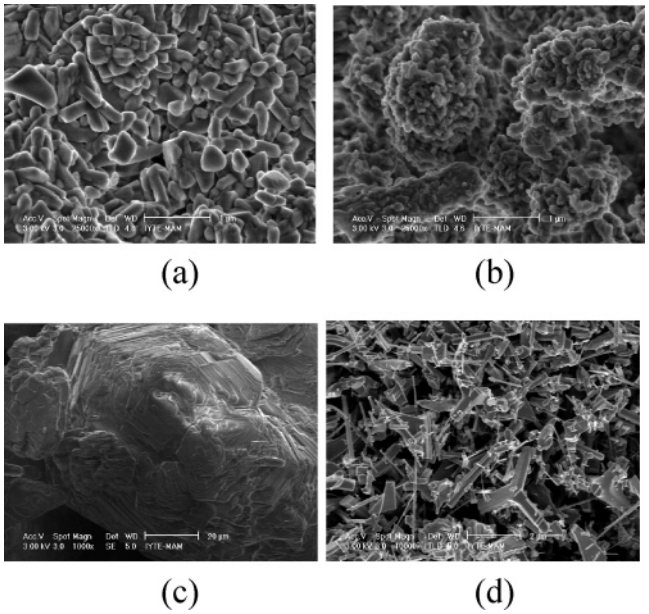

Figure 4. SEM microphotographs of commercial ZB and raw materials (a) ZB-2335 (25 000×), (b) Chinese ZB (25 000×), (c) Boric acid (1000×), and (d) Zinc oxide (25 000×).

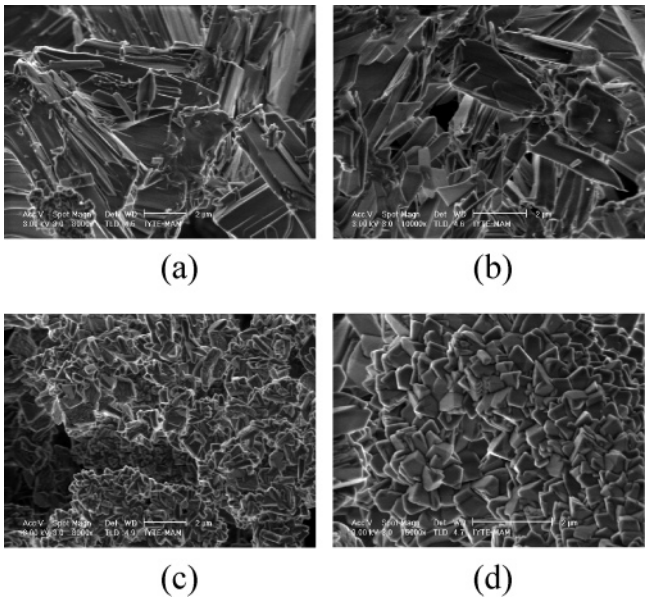

Figure 5. SEM microphotographs of samples prepared at 60 °C for 1.5 h (a) with seed crystals (8000×) and (b) without seed crystals (10 000×) and of samples prepared at 90 °C for 4 h (they were heated at 60 °C for 1.5 h) (c) with seed crystals (8000×) and (d) without seed crystals (15 000×).

A 0.125 g portion of ZB 2335 was added as seed crystal. This mixture in closed Schott bottles was stirred for 1.5 h at this temperature in a constant temperature bath. After a small sample was drawn, the mixture was further stirred and reacted at 90 °C for 4 h. Mixing was achieved by shaking the bottles in a temperature controlled water bath at a rate of 170 rpm. The pH of the mixture was measured by a Methrom pH meter with a glass electrode from time to time. A second experiment under the same conditions but without any seed crystal was also done. The samples were filtered using a Buchner funnel and dried at 105 °C for 2 h in an air circulating oven.

2.2. Characterizations. Each sample was characterized by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and thermal gravimetric analysis (TGA). Microstructural characterization of the samples was done by scanning electron microscopy using a Philips XL-305 FEG SEM instrument. The elemental composition of the samples were determined by conducting energy dispersive X-ray (EDX) analysis in the same instrument.

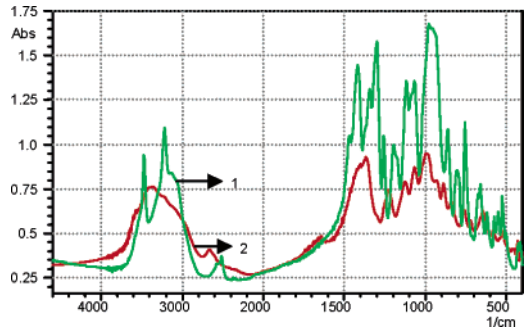

Figure 6. FTIR spectra of (1) ZB-2335 and (2) sample prepared at 60 °C for 1.5 h without seed crystal.

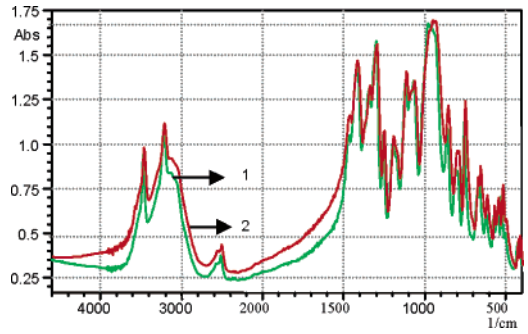

Figure 7. FTIR spectra of (1) ZB-2335 and (2) sample heated at 90 °C for 4 h (initially, it was heated at 60 °C for 1.5 h).

Table 2. Properties of Reference Materials and Products Determined by TGA and EDX

sample	H_2O loss at 600 °C (%)	dehydr onset T (°C)	B_2O_3/ZnO (molar ratio)
60 °C for 1.5 h with seed crystal	21	130	1.49
60 °C for 1.5 h and 90 °C for 4 h with seed crystal	10	350	1.40
60 °C for 1.5 h without seed crystal	27	131	1.78
60 °C for 1.5 h and 90 °C for 4 h without seed crystal	12	340	1.68

All of the samples were characterized by X-ray diffractometer (Philips Xpert-Pro) to analyze the crystal structures of the ZB with Cu Kα radiation at 45 kV and 40 mA. The registrations were performed in the 5°−60° 2θ range.

Thermal gravimetric analyses (TGAs) were done with a Shimadzu TGA-51. ZB samples (10−15 mg) were loaded into an alumina pan and heated from 30 to 600 °C at 10 °C/min under N_2 flow (40 mL/min).

To determine which functional groups are present in the samples, a Shimadzu FTIR 8601 was used. The KBr disc method was used by mixing 4.0 mg of ZB and 196 mg of KBr. A pellet was obtained by pressing the powder mixture under 8 tons of pressure.

3. Results and Discussion

3.1. Reactions. The following reactions are expected to occur in zinc borate preparation. Solid boric acid dissolution (eq 2), hydration of ZnO in water (eq 3), formation of $Zn[B_3O_3(OH)_5]\cdot H_2O$(s) at 60 °C (eq 4), and formation of $Zn[B_3O_4(OH)_3]$(s) at 90 °C (eq 5).

$$B(OH)_3(s) \rightarrow B(OH)_3(aq) \quad (2)$$

$$ZnO(s) + H_2O \rightarrow Zn(OH)_2(s) \quad (3)$$

$$Zn(OH)_2(s) + 3B(OH)_3(aq) \rightarrow Zn[B_3O_3(OH)_5]\cdot H_2O(s) + 2H_2O \quad (4)$$

$$Zn[B_3O_3(OH)_5]\cdot H_2O(s) \rightarrow Zn[B_3O_4(OH)_3](s) + 2H_2O \quad (5)$$

Since an excess of boric acid was used, the solution pH is expected to be acidic. In the experimental run to follow pH change during reaction, it was found that the pH of the boric acid solution was 4.3 and there was a step change to 5.33 in 10 s after ZnO was added as reported in Table 1. The pH was stabilized at 5.72 after 180 s, and it did not change with time any more. Thus, during preparation of ZB, the pH was lower than a pH of 7 and the reaction medium was acidic as expected. This showed that the neutralization occurred instantly after the addition of ZnO to boric acid as there was a step change to pH 5.33 in 10 s. The formed product was not the desired crystal modification of ZB with 3 mol water, but it was a form with a higher amount of crystal water. The further mixing of ZnO and boric acid at 90 °C for 4 h[4,6,7] under reflux would result in a ZB formation which has the desired chemical formula, $2ZnO\cdot 3B_2O_3\cdot 3H_2O$, and thus the desired dehydration temperature.

3.2. Mixing Problems. The volume of the solid products in the reaction mixture increases with time, and mixing problems occur due to an increase in viscosity. The specific gravities of ZnO and $2ZnO\cdot 3B_2O_3\cdot 3H_2O$ are 5.3 and 2.77 g/cm^3, respectively. In the patent by Igarashi et al.,[9] 1 L of water contained 290 g of boric acid and 96 g of ZnO while boric acid is present in dissolved form and ZnO is a solid. The B_2O_3/ZnO ratio was 2.0 in the reactant mixture, but in the product, it was 1.5. The mass of the solid fraction increases 2.66 times and corresponds to a volume fraction increase of 5.11 times considering the densities. This causes a 4.36-fold increase in the viscosity of the mixture during the beginning and end of the reaction as found using eq 6.

$$\eta = \eta_s(1 + k_E\phi) \quad (6)$$

where η is viscosity of the suspension, η_s is the viscosity of the solvent, k_E is 2.5 for spherical particles, and ϕ is the volume fraction of the dispersed solid phase.

Thus, a mechanical mixer which will stir the mixture even when the viscosity is high should be used for this reaction. In the present study, a temperature controlled water bath was used since a small amount of reactants was in consideration. By using a closed container, water loss by evaporation was prevented. In large scale production, a reactor under reflux and with a very powerful mechanical mixer should be used.

3.3. Characterizations. The physicochemical properties of each sample as well as the reference ZBs were determined by thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and X-ray diffraction.

The upward slope of the TGA curves in Figures 1−3 during the initial periods of heating was due to a small drift in the baseline of the instrument. TGA curves of commercial zinc borates in Figure 1 indicated that they were very stable up to 350 °C and they lost 8% and 6% of their mass for ZB 2355 and China ZB, respectively, up to 600 °C. The $2ZnO\cdot 3B_2O_3\cdot 3H_2O$ has been reported to be thermally stable up to 290 °C by Schubert at al.[7] The dynamic heating program of the TGA analysis should have caused to a shift to higher temperatures in observation of the thermal stability temperature. TGA curves of samples prepared at 60 °C for 1.5 h without and with seed crystals are given in Figure 2. For samples prepared at 60 °C for 1.5 h with seed crystals, ZB starts to lose its hydration water at 130 °C with a mass loss of 21% until 600 °C, and for samples prepared at 60 °C for 1.5 h without seed crystals, ZB starts to lose its mass at 131 °C with a mass loss of 26% until 600 °C. When these two samples are compared, it is observed that the one with seed crystals has less mass loss due to dehydration than that without seed crystals. For samples heated further at 90 °C for 4 h, the mass losses started at 350 and 340 °C and amounts to 12% and 10% at 600 °C for the samples with and without seed crystals, respectively, as seen in Figure 3. These samples had dehydration temperatures and mass losses very

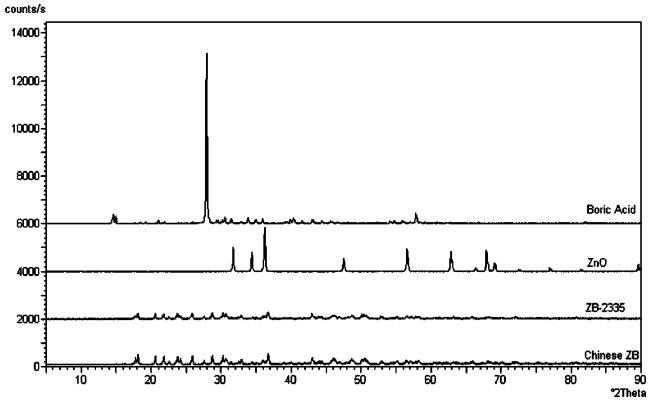

Figure 8. X-ray diffraction diagrams of reference ZB materials and raw materials.

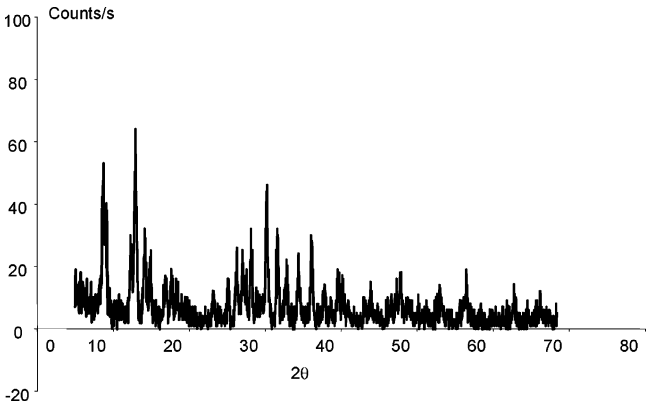

Figure 9. X-ray diffraction diagram of sample prepared at 60 °C for 1.5 h without seed crystal.

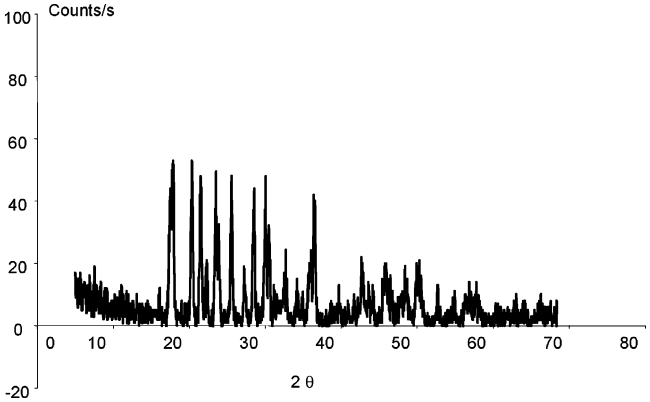

Figure 10. X-ray diffraction diagrams of sample heated at 90 °C for 4 h without seed crystal (initially, it was heated at 60 °C for 1.5 h).

Table 3. X-ray Diffraction Peaks of the Samples

60 °C, 1.5 h		90 °C, 4 h	
with seed crystals	without seed crystals	with seed crystals	without seed crystals
2θ	2θ	2θ	2θ
8.0	8.0		
17.5	17.6	17.7	17.9
20.8	20.4	20.3	20.3
23.0	22.8	21.4	21.6
23.5	23.3	23.4	23.5
27.4	24.0	25.5	25.5
28.7	27.0	27.2	27.2
	28.1	28.4	28.5

close to commercial ones. On the other hand, if $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ were obtained, mass loss should have been 14.9%. The sample prepared without seed crystals at 90 °C had as a closer mass loss (12%) to that of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$. The mass loss values at 600 °C are reported in Table 2.

The SEM micrograph of zinc oxide particles in Figure 4 shows that they were in needle shape and were a maximum of 2 μm long. Two commercial ZBs had similar morphologies as seen in Figure 4. SEM microphotographs of samples prepared at 60 °C for 1.5 h with and without seed crystals were very similar to each other as seen in Figure 5. There were no unreacted ZnO crystals with needle shape. The samples further heated at 90 °C for 4 h had a similar morphology to those which are used as reference products as seen in Figures 4 and 5.

The FTIR spectrum of the sample prepared at 60 °C for 1.5 h was different than the FTIR spectrum of commercial ZB 2335 as seen in Figure 6. While the characteristic peak at 3227 cm^{-1} of $ZnO{\cdot}B_2O_3$ crystal structure[2] is not observed in the sample's spectrum, ZB 2335 had two sharp peaks at 3250 and 3500 cm^{-1} belonging to vibrations of isolated OH groups.[9] In Figure 7, it is seen that the sample prepared by heating at 90 °C for 4 h had the same FTIR spectrum as commercial ZB 2335. The peaks between 900 and 1300 cm^{-1} are all present in the spectra which were reported to be other characteristic peaks of borates.[12] The characteristic peaks of tetrahedral (BO_4) and trihedral (BO_3) borate groups are clearly seen between 1100 and 800 cm^{-1} and between 1450 and 1200 cm^{-1}.

The chemical compositions of the samples were determined by EDX analysis as reported in Table 2. While the theoretical B_2O_3/ZnO ratio was 1.50 for $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, it was 1.40 for samples prepared with seed crystals and it increased to 1.78 and 1.68 for samples prepared without seed crystals. The presence of seed crystals caused the formation of products closer to the B_2O_3/ZnO ratio in $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$.

X-ray diffraction diagrams of raw materials and commercial ZBs are seen in Figure 8. Boric acid and ZnO had X-ray diffraction diagrams of pure materials as indicated by the X-pert pro software. Commercial ZBs had the same X-ray diffraction diagram of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ reported by Igarashi et al.[9] and Nies et al.[8] The X-ray diffraction diagrams of the samples prepared at 60 °C with and without seed crystals were the same. In Figure 9, the X-ray diffraction diagram of a sample prepared at 60 °C is shown and it has no similarity to the ZB X-ray diffraction diagram reported by Igarashi et al.[9] A strong diffraction peak at a 2θ value of 8° corresponding to 1.11 nm present in the sample prepared at 60 °C was not present in the X-ray diffraction diagram of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ samples prepared at 90 °C for 4 h. The X-ray diffraction diagrams of the samples prepared at 90 °C in Figure 10 were identical to each other and to that of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ reported by Igarishi et al.[9] X-ray diffraction peak intensities of the samples prepared at 60 and 90 °C are as shown in Table 3.

4. Conclusions

Using a powerful mixer and good temperature control and keeping the volume constant by using reflux to prevent water evaporation are important requirements in obtaining the desired zinc borate species, since the viscosity of the medium increases to a great extent during reaction.

Two different zinc borates dehydrating at around 130 °C with 21−27% mass loss and at around 350 °C with 10−12% mass loss were obtained at 60 °C and further heating at 90 °C, respectively, from zinc oxide and boric acid in water. They should be $Zn[B_3O_3(OH)_5]{\cdot}H_2O$ or $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $Zn[B_3O_4(OH)_3]$ or $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$. The X-ray diffraction diagrams of the samples prepared at 90 °C with and without seed crystals were identical to that of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ reported by Igarishi et al.,[9] but their B_2O_3/ZnO ratios were different than that of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$. Their TGA curves and FTIR spectra were the same as the two commercial zinc borates which are claimed to be $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ by their producers.

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Received for review August 4, 2006
Revised manuscript received February 2, 2007
Accepted February 7, 2007

IE0610243