Gazi University Journal of Science
GU J Sci
27(3):987-991 (2014)

Solid Phase Synthesis of Anhydrous Zinc Borate from Zinc and Boron Oxide and Utilization as a Flame Retardant in Dye and Textile

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Received:30/01/2014 Revised: 01/04/2014 Accepted:17/04/2014

ABSTRACT

Durability of materials against flame and stability at high temperatures are very important in order to increase the field of use. Non-flammability is not the only requirement; these materials should not have toxic gas products during the burning, also. Anhydrous zinc borate was chosen as flame retardant due to its advantages, such as; light weight, high melting point, low thermal expansion, and intrinsic smoke suppression and corrosion resistance properties. For the synthesis, metallic zinc and anhydrous boron oxide powders were mixed in the attritor working at 600 rpm. Powder product was sintered under atmospheric conditions according to the phase change temperature that was determined by TGA-DSC analyses. Synthesized zinc borate was grinned up to nanometer size by Spex type grinder. Zinc borate was introduced in binder to decrease the flammability. The properties of the produced materials were determined and compared by LOI, TGA-DSC, SEM and oven according to the zinc borate ingredients.

Key Words: *Zinc borate, Pigment, Flame retardant, Flame resistant dye*

1. INTRODUCTION

Dyes are widespread used in our lives as a coating material to resist corrosion [1]. However, they are inflammable materials and release smoke and toxic compounds in case of fire and at high temperatures. Addition of flame retarder into the combustible materials related to dyes, varnishes, plastics and furniture etc. are getting importance by new restrictions of law and rules. Therefore, it is necessary to develop new materials, which gives acceptable changes at high temperatures. In many cases, alumina, magnesium hydroxide, antimony trioxide, phosphorus, boron, chlorine and bromine compounds are used as a flame retardant. Antimony trioxide and the halogenated compounds of the former have been banned because of their toxic gas releases during the fire. Many applications results some hazards presented from the toxicity, smoke and corrosiveness of halogenated compounds [2]. The ban of halogenated compounds has increased the usage of synergistic

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compounds. Thus the usage of zinc borates for this purpose has become attractive [3].

Anhydrous and hydrated zinc borate forms are both available in industry. Hydrated zinc borate was obtained from zinc oxide and boric acid at 823 K by wet method and produced pigment can be used in dye as flame retardant alike other borates such as calcium borate [4]. The removal of hydration water was recorded at 430 K, 523 K and 614 K in three endothermic peaks by DSC instrument. As a result of dehydration, micro porosities were formed at dye coatings during the elevation of temperatures [5]. Giudice and Benitez discussed the influence of zinc borates with molecular formulas of 3.5 H_2O and 7.5 H_2O on the performance of chlorinated alkyd flame retardant coatings. Results of laboratory tests indicate that coatings with chlorine resin that was used as the film forming material, zinc borates can act as a flame retardant [6]. In a distinct study seven compositions of anticorrosion pigments of zinc-strontium borophosphates were prepared and then characterized by XRD analysis. The pigments were dispersed in an alkyd resin formulation, used in paints, and their anticorrosive properties were determined [7]. In the similar study, zinc borates are used as synergistic agents in EVA-ATH and EVAMg$(OH)_2$ flame retardant formulations and as smoke suppressants [8]. Furthermore, several methods were examined to prepare functionalized zinc borates and their coupling reaction with allylic compounds [9, 10]. The influence of various combinations of aluminum trihydroxide and zinc borate as flame retardant fillers on the flammability for wire and cable applications was also explored [11]. An effective flame retardant system for polyamide-4,6 was found based on inorganic iron compounds with polyphenylene oxide and zinc borate [12]. Flammability of polypropylene, sawdust/rice husk filled polypropylene composites and flame-retarding effect of magnesium hydroxide for these composites was investigated by horizontal burning rate and oxygen index tests. In addition, effect of flame-retardants such as boric acid or zinc borate in combination with magnesium hydroxide was also studied [13]. Inoculating effect of some tropical woods with zinc borate and their thermal characteristics was studied [14]. Synthesis and characterization of two new bulky tris (mercaptoimidazolyl)borate ligands and their zinc and cadmium complexes were investigated [15]. Zinc borate compounds were used for their flame retardant and corrosion resistance properties [7, 16].

The usage of pigments extensively depends on their performance features, selection of cheap raw materials and economy of the production method. Since, zinc has relatively low melting point, low specific gravity and high resistance to atmospheric corrosion, and boron oxide has durability against flame and it is stable at high temperatures, the synthesis and usage of zinc borates are gaining importance. Substances that constitute the dyes should not result toxic gases during fire as much as they show resistance against fire. Contrary to that, the chlorine ingredients lead to form toxic gases such as phosgene with carbon monoxide. For this reason, chlorine compounds were not used in this study.

The aim of the present investigation is to synthesis anhydrous zinc borate from zinc and anhydrous boron oxide by solid phase reaction as a novel method and in dye and textile structures, determining its performance against flame and at high temperatures.

2. EXPERIMENTAL

2.1. Instruments

In order to provide uniform grinding and mixing of zinc and boron oxide, the powders were mechanically milled in an attritor (Szegvari 01- HD). Thermal behavior of the mixture was examined in 100 µL alumina crucible that was exerted at 10 K/min temperature increase by TGA-DSC instrument (Setaram Set-Sys 1750) and reaction temperature was specified according to the exothermic peak. The mixture of powders was pressed under 500 MPa without using binder and kept in an oven at 700 ± 10 K for 3 h. After reaction, pigment material was milled by Spex type grinder (Serti Prep 8000M). The mean particle size was determined by Malvern Mastersizer particle analyzer. Chemical analysis of pigment was accomplished by XRD (Rigaku D/Max-2200 ULTIMAN+/PC) instrument. Application of the dye was performed by dispenser (Sheen Disper Master 2027). LOI (limit oxygen index) instrument (Dynisco) was utilized for flammability tests. Surface characteristics of the dye were determined by SEM (JEOL JSM-6360 LV equipped with EDS).

2.2. Reagents and chemicals

Zinc borate pigment was synthesized by the mechanical reaction of Zn and anhydrous boron oxide in attritor working with stainless steel balls and under air at 600 rpm for 4 h. Pigment and talc were dispersed in HK 46 silicon based binder by means of dispenser. Applicability of dye was increased by xylene. Dye was coated on the standard metal plate by means of applicator, in addition, on the piece of wood by means of brush. Painted materials were dried in the atmosphere for 24 h. Coated plate was dried in drying oven at 473 K for 1 h. Stability of dye at high temperatures was tested by TGA-DSC instrument and oven. Non-flammability tests of coated wooden pieces were carried out according to ASTM D 2863 standard by LOI instrument and compared with LOI value of original wood. Scanning electron microscopy was used to characterize the microstructure of the dye that exerted high temperature. Qualitative X-ray element analysis and mapping of Zn and B elements was carried out using the energy dispersive spectrometer (EDS) analyzer.

Also, polyester was doped with zinc borate pigment. Durability of polyester with zinc borate to flame was compared with original polyester by means of LOI instrument. Furthermore, pieces of woven were treated with zinc borate solution by the P-Selecta Unitronic OR instrument. Durability of woven treated with zinc borate to flame was also compared with original woven by using of LOI instrument again.

3. RESULTS AND DISCUSSION

3.1. Mechano-chemical reactions

Melting-related phase change temperature of the mixture was recorded as 678-693 K (405- 420 ºC) by the

endothermic peaks of a previously performed study. In the same study oxidation reaction was detected with exothermic peak, which appears at 913 K (640 ºC) [17]. Therefore, solid phase reaction temperature for this mixture was specified above the exothermic peak temperature as 973 ±10 K.

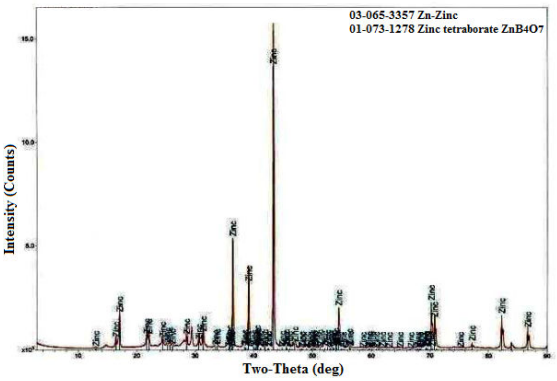

Figure 1. XRD patterns of zinc borate pigment at 0.8 molar ratio of Zn/B_2O_3.

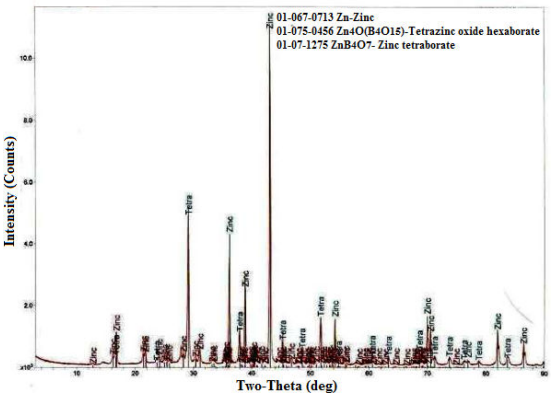

Figure 2. XRD patterns of zinc borate pigment at 1.0 molar ratio of Zn/B_2O_3.

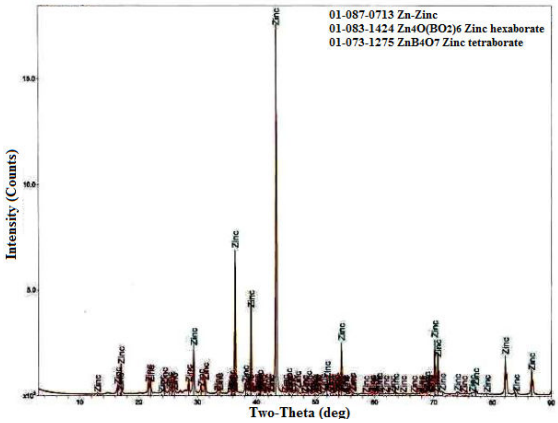

Figure 3. XRD patterns of zinc borate pigment at 1.2 molar ratio of Zn/B_2O_3.

Performed experiments at three different reactant ratios showed that the optimum yield can be obtained when the ratio is kept as 1. The mean particle size of zinc borate pigment was determined as 780 nm by means of particle analyzer. Various amounts of zinc borate from 2% (wt) to 15% (wt) were dispersed in the binder. Economically the best covering dye composition was found out as 10% pigment, 15% talc and 15% xylene according to the total mass.

3.2. Thermal analysis

After hard drying at 473 K in an oven, dye deposit was scraped from plate surface and examined by TGA-DSC. As can be seen from Fig. 4, observed endothermic or exothermic peaks are not sharp till 1473 K on DSC pattern of anhydrous zinc borate pigment. Under air only 3% weight loss was observed up to that temperature. Non-endothermic peak proves that zinc borate pigment has no hygroscopic water. However, hydrated zinc borate pigment results in three endothermic peaks at 430 K, 523 K and 614 K [5]. On the other hand, when the $2ZnO.3B_2O_3.3.5H_2O$ and the $2ZnO.3B_2O_3.7.5H_2O$ pigments were examined under argon atmosphere by TGA, the total weight loss at 1073 K were 14.5% and 26.6%, respectively [6]. It was reported that zinc borate in the presence of hydrogen chloride effectively works as a flame retardant for all the woods [14] even though; there is a risk of toxic phosgene compound formation during fire. It was detected by TGA-DSC graph, that the dye based anhydrous zinc borate and silicon binder can be recommended to use at high temperatures up to 1473 K (1200 ºC) safely.

Molar ratio of Zn/B_2O_3 was changed from 0.8 to 1.2, other conditions were fixed. After the mechanical grinding, zinc borate peaks do not appeared at the XRD patterns due to the amorphous structure of the mixture. However, zinc borate compounds were detected after solid phase reaction at 973 ±10 K for 3 h. As can be seen from Fig. 1, poor zinc tetraborate (ZnB_4O_7) peaks were obtained at 0.8 molar ratio of Zn/B2O3. Furthermore, in Fig. 2 and 3, zinc hexaborate $Zn_4O(BO_2)_6$ and zinc tetraborate (ZnB_4O_7) peaks were observed strongly at 1 and 1.2 molar ratio of Zn/B_2O_3.

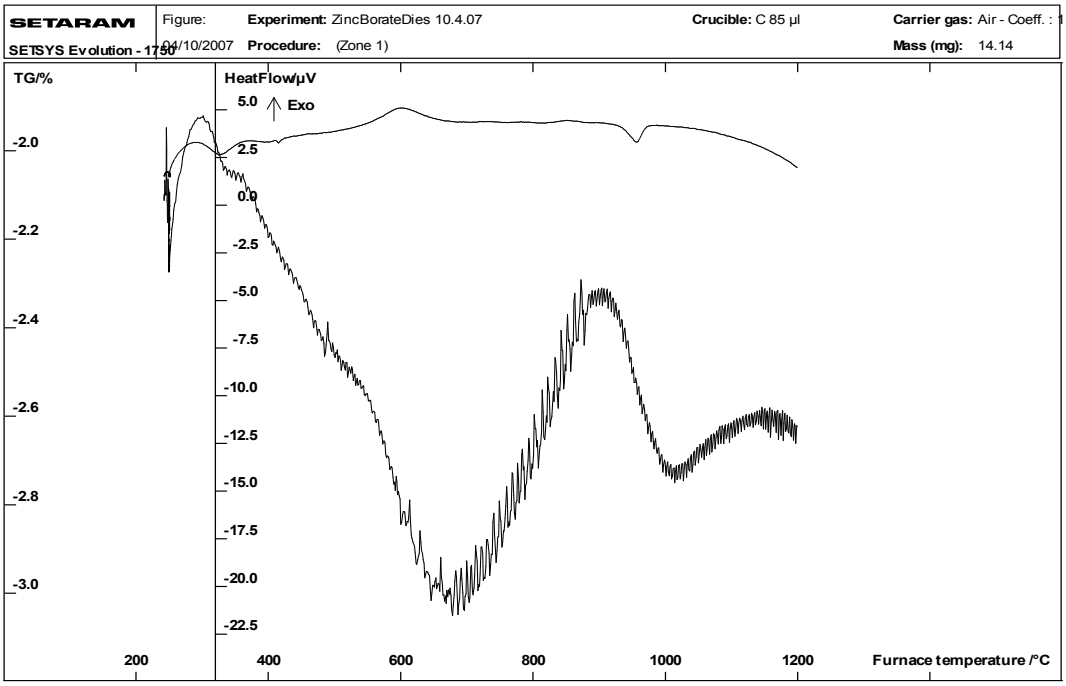

Figure 4. TGA-DSC pattern of hard dried dye at 473 K (200 ºC) temperature for 1h.

3.3. Deformation search over the dye coating

Produced dye was applied on metal plates and they were heated up to 1473 K for 2 hours. Plates were cooled naturally down to 573 K in the oven and taken out to room temperature. Any cracks, flakes, porosities, bubbles, inclusions and darkness as a result of ignition could not be observed on coated plate surface. It was concluded that this behavior must be one of the positive effect of the low expansion coefficient of the produced dye [17]. Uniformity of ignited dye surface on the SEM micrograph and EDS mappings were illustrated in Fig. 5.

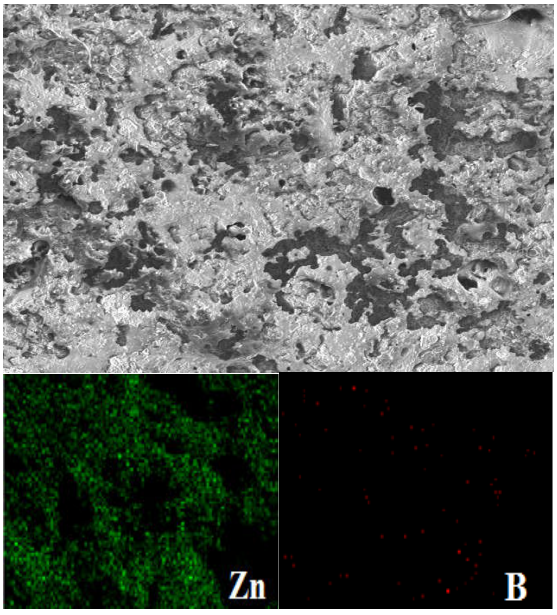

Figure 5. SEM microstructure and EDS analysis of ignited dye surface of pate.

3.4. LOI tests

The limiting oxygen chamber instrument determines the minimum oxygen requirement to burn the samples. Burning of material was achieved under equilibrium conditions of candle like flame. The LOI value of original wooden sample was determined as 23%. Since this LOI value is lower than 28%, which qualify a sample as self-extinguishing, the original wood is called as combustible. However, dyed and dried wood could not be burned up to 55% LOI value. This is the maximum oxygen amount that can be provided by limiting oxygen chamber instrument. It was concluded that, combustible wood was converted to non-combustible form by applying dye that produced with anhydrous zinc borate and silicon binder.

Furthermore, LOI value of original cotton woven was determined as 19.39%. This value was also increased to 42.43% oxygen content by the treatment of cotton wool with zinc borate based dye.

4. CONCLUSIONS AND RECOMMENDATIONS

The present study was conducted to produce a dye that is; economically favorable, easy processed, strong coverage on surface, flame retardant, high temperature resistant, with low temperature expansion and high corrosion resistance dye. The appropriate producing conditions of zinc borate pigment are recommended as solid phase reaction by ball milling and sintering at 973 K. Besides, it was found out that if the reactants ratio of Zn/B_2O_3 was kept as 1, optimum yield could be achieved. The advisable content of dye is 10 (wt)% powder anhydrous zinc borate pigment, 15 (wt)% talc, 15 (wt)% xylene and the rest is silicon binder. The thermal and fire resistance of metallic, wooden and woven materials were improved by means of anhydrous zinc borate pigment. This dye can be used to increase the materials resistance against

extreme temperature, corrosion and to provide dimensional stability in industrial applications.

ACKNOWLEDGEMENTS

This work has been supported by DPT (The State Planning Organization of Turkey) under project number 2001K120590 and by BOREN (the National Boron Research Institute) under project number BOREN 2006-17-Ç16-11. The authors are grateful to the DPT and BOREN for financial support and Gazi University for the provision of laboratory facilities.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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