



## **NANO ZINC BORATE AS A LUBRICANT ADDITIVE**

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*(This article first appeared in PPM2017 and was accepted as a non-peer-reviewed manuscript to be published in JOTCSA)*

**Abstract:** Lubricants consist of base oils and chemical additives such as dispersants, surfactants, oxidation inhibitors, and antiwear agents. Organic and inorganic boron-based additives increase wear resistance and decreases friction. Hexagonal boron nitride and metal borates are used for this purpose. Zinc borate is a synthetic hydrated metal borate. The production techniques of zinc borate generally include the reaction between zinc source materials (zinc oxide, zinc salts, zinc hydroxide) and the boron source materials (boric acid and borax). The nano zinc borate particles were prepared from zinc nitrate and borax in the present study by using low initial zinc and borate concentrations and low temperature to prevent particle growth. The templates span 60 and PEG 4000 were used to control the particle size. The particles were separated from mother liquor by centrifugation, washed with ethanol, dried and ground and used as additive to base oil. The particles have H<sub>2</sub>O and B(3)-O vibrations in their FTIR spectra. The empirical formula of the nanoparticles was approximately 3ZnO.2B<sub>2</sub>O<sub>3</sub>.4H<sub>2</sub>O from EDX and TGA analysis. X-ray diffraction diagram indicated the particles were in amorphous state. When the nanoparticles were added to light neutral oil the wear scar diameter and friction coefficient was lowered 50% and 20% respectively.

**Keywords:** Base oil, nano zinc borate, lubricant additive.

**Cite this:** Atakul Savrik S, Alp B, Ustun F, Balkose D. NANO ZINC BORATE AS A LUBRICANT ADDITIVE. JOTCSA. 2017;5(sp. is. 1):45–52.

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## **INTRODUCTION**

Numerous studies have been carried out in recent years on the effects of various metal borate particles as lubricating oil additives on wear and friction [Hu and Dong, 1998; Hu et al., 2000]. Their effectiveness can be related to the formation of a borate glass as a tribochemical film or the deposition of particles on the rubbing surface [Varlot et al., 2001]. The friction reduction and anti-wear behaviors are dependent on the characteristics of nanoparticles, such as size, shape, and concentration.

Zinc borate is a synthetic hydrated metal borate. There are various kinds of crystalline hydrated zinc borate. In these products,  $B_2O_3/ZnO$  mole ratios change from 0.25 to 5 and it determines the characteristics of product. The production techniques of zinc borate generally include the reaction between zinc source materials (zinc oxide, zinc salts, zinc hydroxide) and the boron source materials (boric acid and borax) [Eltepe et al., 2007].

Nanoparticles of zinc borate are a requirement for their use as a lubricant additive. Synthesis of nano particles of zinc borate in inverse emulsions in lubricating oil was possible [Savrik et al, 2011]. Nanoparticle formation by supercritical carbon dioxide ( $CO_2$ ) drying of zinc borate species was investigated to evaluate possible chemical modifications in the product during the drying [Gonen et al, 2010]. Nanometer crystal zinc borate with a particle size of 20–50 nm was prepared using the ethanol supercritical fluid drying technique [Dong and Hu, 1998]. Supercritical ethanol drying of zinc borate species to obtain nanoparticles was also investigated by Gonen et al [2011]. It was found that from zinc borates, zinc oxide and boric acid were formed [Gonen et al, 2011]. A nano-flake-like zinc borate  $2ZnO.2B_2O_3.3H_2O$  was prepared via coordination of homogeneous precipitation method using ammonia, zinc nitrate and borax as raw materials [Ting et al, 2009]. The crystal and hydrophobic zinc borate  $Zn_2B_6O_{11}.H_2O$  nanodiscs and nanoplatelets were successfully prepared by a wet method using  $Na_2B_4O_7.10H_2O$  and  $ZnSO_4.7H_2O$  as raw materials *in situ* aqueous solution, and oleic acid as the modifying agent. It had been found that the as-prepared materials displayed nanodisc morphology with average diameters from 100 to 500 nm and the thicknesses about 30 nm [Tian et al, 2006].

The production and characterization of nano particles of hydrated zinc borate for lubrication was aimed at in the present study. Dilute solutions of borax and zinc nitrate were mixed instantly at room temperature to avoid particle growth and hydrosols were formed. The particles were separated by centrifugation and washed with ethanol and dried at 25 °C under vacuum.

## **EXPERIMENTAL**

Anhydrous borax (Sigma Aldrich), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (Sigma-Aldrich), light neutral oil (TUPRAŞ A.Ş), and sorbitan monostearate (Span 60, Sigma-Aldrich), PEG 4000 (Merck) were used in the preparation of hydrated zinc borate nanoparticles and lubricants.

50 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> sodium borate solution was added instantly to 50 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> zinc nitrate solution and mixed at 600 rpm for 2 hours at ambient temperature of 23 °C. Experiments were repeated by adding 1 cm<sup>3</sup> of 0.002 M span 60 and 1 cm<sup>3</sup> of 0.4 g PEG 4000 in 100 cm<sup>3</sup> to the mixtures. While hydrosols have been mixed, their temperature and pH values were recorded. Since the particles passed through the Whatman filter paper, they were separated from the aqueous phase by centrifugation. They were separated by centrifugation using Rotofix 32 centrifuge at 2000 rpm for 10 minutes, washed with ethanol and centrifuged again at 2000 rpm for 10 minutes. The gelatinous precipitates were dried under vacuum at 10 kPa for 18 hours at 25°C to obtain nanoparticles. Since the nanoparticles were in an agglomerated state they were ground in a porcelain mortar and pestle before use.

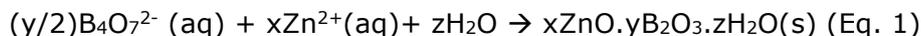
The morphologies of the samples were examined using QUANTA 250F Scanning Electron Microscope (SEM). EDX analysis was carried out using the same instrument. The particle size of the powders were measured by Malvern 2000 zetasizer. X-ray diffraction diagrams were obtained by Phillips x'pert pro X-ray diffractometer employing Ni-filtered Cu K<sub>α</sub> radiation. FTIR spectra of the samples were taken with SHIMADZU FTIR-8400S using KBr disc technique. TG analysis was performed by using SETARAM labsys TGA to determine changes in weight with heating under nitrogen flow at 40 cm<sup>3</sup> min<sup>-1</sup> rate and at a heating rate of 10 °C min<sup>-1</sup> up to 600 °C.

25 cm<sup>3</sup> of light neutral oil, 0.25 g of Span 60 and 0.25 g of the nanoparticles of zinc borate with Span 60 were mixed thoroughly at 600 rpm rate and at 160 °C for one hour on a magnetic hot plate (Ika RH Digital KT/C) and left to cool down to room temperature by continuous stirring. A four ball tester (Ducom) was used to determine the friction coefficient and wear scar diameter. The tests were performed according to ASTM D 4172-94 at 392 N and the test duration was 1 h at 75 °C. The upper ball was rotated at 1200 rpm. Test balls were made from AISI standard steel No. E-52100 and had 12.7 mm diameter. Microphotographs of the wear scars of the three fixed and one rotating test balls were taken by using Olympos BX 60 equipped with Canon Powershot 590IS camera.

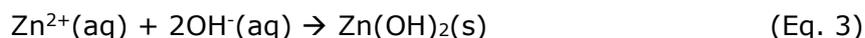
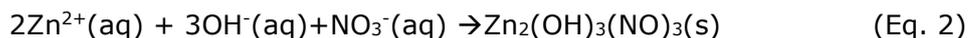
The visible spectrum of base oil separated by centrifugation from base oil was taken by using Perkin Elmer UV-Vis spectrophotometer by using base oil without any additive as thereference.

**RESULTS AND DISCUSSION****Reaction of aqueous borax and zinc nitrate solutions**

The zinc borate precipitation reaction is expected to occur as given in Equation 1

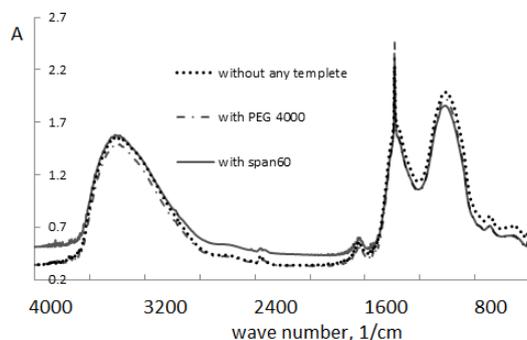


There are other simultaneous reactions in the reaction medium, such as

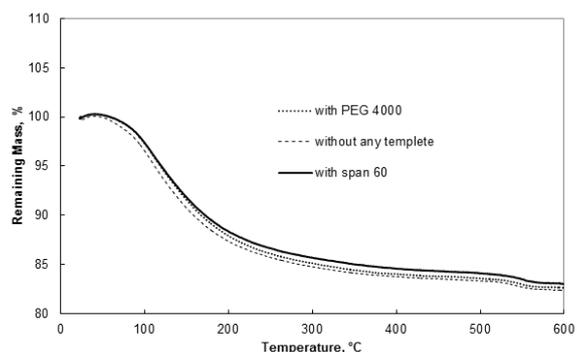
**Functional groups by FTIR spectroscopy and TG analysis**

The FTIR spectra of the samples without any template and with templates span 60 and PEG 4000 are very similar to each other as seen in Figure 1. There is a broad peak at  $3358 \text{ cm}^{-1}$  due to hydrogen-bonded O-H group vibrations. Asymmetric B(3)-O vibrations were observed at  $1383 \text{ cm}^{-1}$  and at  $1350 \text{ cm}^{-1}$ . H-O-H bending vibration was observed at  $1624 \text{ cm}^{-1}$ . At  $1014 \text{ cm}^{-1}$  a peak for symmetric B(3)-O vibration was present. Out of plane bending vibration of B(3)-O gave a small peak at  $694 \text{ cm}^{-1}$ .

TG curves of the samples were very similar to each other as depicted in Figure 2.



**Figure 1:** FTIR spectra of the zinc borates.

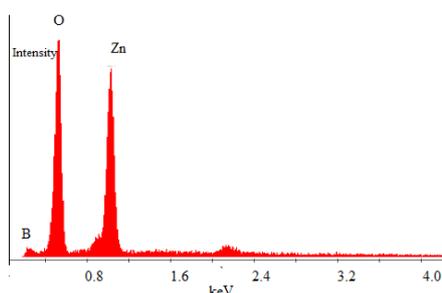


**Figure 2:** TG curves of the zinc borates.

On heating the samples only water is eliminated from the samples. All the samples contained very similar amount of water, around 17 % . The total amount of water was less than the zinc borate samples prepared from at higher initial borax and zinc nitrate concentrations. Savrik [2010] has determined the samples prepared at 70°C from 1 mol dm<sup>-3</sup> initial concentration contained around 20.6 % water with the same FTIR spectra of the samples in the present study.

### **Chemical Analysis by Energy Dispersive X-ray Spectroscopy (EDX)**

The energy dispersive spectroscopy was used to determine the elemental composition of zinc borates. The EDX spectrum of the samples are very similar for each zinc borate. The EDX spectrum of zinc borate with span 60 template is seen in Figure 3.

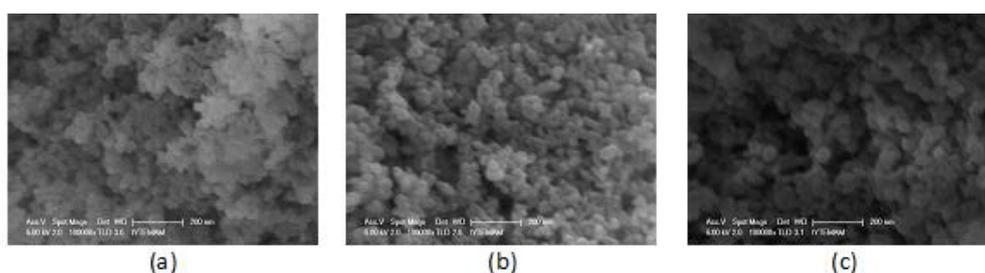


**Figure 3:** EDX spectrum of the zinc borate with span 60.

The chemical composition of the samples are similar to each other. The empirical formula of the nanoparticles was approximately 3ZnO.2B<sub>2</sub>O<sub>3</sub>.4H<sub>2</sub>O from EDX analysis. However it could be a mixture of zinc borate and zinc hydroxide due to parallel reactions.

### **Morphologies of the powders**

The SEM micrographs of the dried samples are shown in Figure 4. The dried powders consisted of agglomerates of primary particles of 40 nm, 50 nm and 80 nm for samples without template, with span 60 and with PEG 4000 respectively. The particles were attracted to each other due to capillary forces during drying. Water in the wet samples was replaced with ethanol which has a lower surface tension to decrease the attractive forces between the particles due to capillarity. However they were also agglomerated even drying of the ethanolic hydrogel.



**Figure 4:** SEM micrograph of the sample a. without template b. with span 60 c. with PEG 4000.

### **Particle Size Distribution of the initially formed hydrated zinc borates in solution**

The size distribution of particles were monodisperse with number average sizes of 35.3 nm and 234 nm respectively for zinc borates without any template and with span 60 respectively. However the particle size distribution of particles with PEG 4000 were bidisperse, the average size was 228.5 nm and 969.7 nm for 94.6% and 5.4 % of the particles. While the primary particles were dispersed in zinc borate without any template, these particles were agglomerated in the presence of surface active agents span 60 and PEG 4000.

### **X-ray Diffraction Analysis (XRD)**

Only a broad peak are observed at  $2\theta$  value of  $28^\circ$  in X-ray diffraction diagram of the samples indicating that they were amorphous. The small size of the crystals formed in the present study caused broadening of the diffraction lines . The crystal growth occurs in time at high temperature and at high initial concentration and an x-ray diagram with sharp diffraction peaks is obtained. Savrik *et al.* [2011] obtained sharp diffraction peaks for zinc borate obtained from  $1 \text{ mol dm}^{-3}$  initial concentrations at  $70^\circ\text{C}$  in two hours. Diffraction peaks for  $\text{Zn}(\text{B}_3\text{O}_3(\text{OH})_5)\text{H}_2\text{O}$  (JPDS PDF File Number 721789) were observed by Savrik *et al.*[ 2011].

### **The precipitates as lubricant additives**

Previous studies also had shown the lowering of the friction coefficient when zinc borate nanoparticles were added to the base oil [Dong and Hu, 1998, Tian et al, 2006]. The results of the four ball tests are shown for the lubricating oil prepared in the present study. The wear scar diameter for ball 1, 2 and 3 are  $662 \mu\text{m}$ ,  $704 \mu\text{m}$  and  $701 \mu\text{m}$  respectively. The average wear scar diameter was  $689 \mu\text{m}$ .

The change of the friction coefficient with time during the test is 0.079. The wear scar diameter was lowered from  $1402 \mu\text{m}$  to  $689 \mu\text{m}$  and the friction coefficient was lowered from 0.099  $\mu\text{m}$  to 0.079 by adding nanozinc borate to light neutral oil. The wear scar diameter and friction coefficient was lowered 50% and 20% respectively. Compared to inverse emulsion case the friction coefficient was 11 % lower, but the wear scar diameter was 15.6 % higher for the nanozinc borate case.

The visible spectrum of the lubricant before and after four ball tests indicated that the yellow color of the oil was darkened during the tests that was made at  $75^\circ\text{C}$ . The absorbance of the lubricating oil at 414 nm increased from 0.06 to 0.84 after the test. This discoloration was due to oxidation and crosslinking reactions in base oil. Thus it is necessary to add antioxidants other than zinc borates to the lubricant to avoid oxidation.

## **CONCLUSIONS**

The nano zinc borate particles were prepared in the present study by using low initial zinc and borate concentrations and low temperature to prevent particle growth. The templates span 60 and PEG 4000 has increases the aggregation state of nanoparticles of zinc borate in their mother liquor. The empirical formula of the nanoparticles was approximately  $3\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  from EDX analysis. However it could be a mixture of zinc borate and zinc hydroxide. X-ray diffraction diagram indicated the particles were in amorphous state. When the nanoparticles were added to light neutral oil the wear scar diameter and friction coefficient was lowered 50% and 20% respectively. However the oil color was darker after the four ball tests indicating addition of antioxidants is necessary. Further studies should be made in synthesis, characterization of zinc borate nano particles and their use in nanoparticle state as lubricant additives and formulating lubricants.

## **ACKNOWLEDGEMENT**

The authors thank to OPET A.Ş. for four ball tests.

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