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Formation of Boric Acid by Surface Oxidation of Amorphous Boron Powder: Characterization and Quantitative Estimation

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Abstract: Amorphous Boron Powder (ABP) is used as a fuel in air breathing propulsion systems due to its high gravimetric and volumetric heat value. ABP is sensitive to air and undergoes slow oxidation during storage and handling, leading to the formation of a boric acid layer on the particle surface. This paper describes an analytical method for the estimation of boric acid in ABP. In-house samples obtained from the pilot plant of this laboratory, as well as commercial samples, were assayed for their boric acid content. The study is substantiated by characterization of the ABP samples by SEM with EDX and FTIR. The ageing characteristics of in-house boron powder was also studied.

Keywords: Amorphous Boron Powder, B_2O_3, boric acid, FTIR, SEM, EDX

Introduction

Boron is well known as an advanced fuel in air-breathing propulsion systems due to its high gravimetric and volumetric heat value [1, 2]. This laboratory has developed a process at pilot plant scale to prepare Amorphous Boron Powder (ABP) by the magnesiothermic reduction of B_2O_3 using Self-propagating, High-temperature Synthesis (SHS) process [3-5]. The crude boron so produced (containing impurities such as B_2O_3, MgO, magnesium borides, magnesium orthoborates etc.) is crushed, pulverized and purified by sequential leaching processes using concentrated HCl, water and alcohol. The boron obtained by this process has a purity of 85-88%, with magnesium as the major impurity (9-11%) and is referred to as ABP Grade-II (Gr-II). The impurities of boron are further removed by an oxidative roasting process at 600 °C in air, followed by acid leaching [6, 7]. This gives ABP Gr-I of improved purity (>92%).

ABP particles have a tendency to undergo surface oxidation by atmospheric oxygen and form a B_2O_3 layer on their outer surface. This B_2O_3 is sensitive to moisture and gets converted to boric acid (H_3BO_3). The presence of B_2O_3 and H_3BO_3 on the surface of the boron particles poses problems during propellant processing, ignition and combustion [1, 2, 8-10]. The hydroxyl functional group of the propellant binder i.e. Hydroxyl Terminated Poly-Butadiene (HTPB) reacts with B_2O_3 / H_3BO_3 to form substantial cross linking with the boron particles, resulting in an increase in viscosity, making propellant processing difficult. Hence, boric acid is an undesirable impurity in ABP. Efforts have been made by various authors to inhibit the surface oxidation of boron particles by the use of various surface passivating agents such as organic amines, hydroxyamine [11] or with ceramic B_4C [12]. Efforts were also made to overcome this problem by the use of various coating agents adhering to the surface of the boron particles [13-15]. The coating materials react with the B_2O_3 layer and facilitate its quick removal during combustion.

This paper describes a method for assaying the boric acid content of ABP. The presence of boric acid in ABP was also characterized by FTIR and SEM with EDX. In-house boron samples as well as boron samples obtained from commercial sources were analysed and the results have been thoroughly compared. The ageing characteristics (with respect to boric acid formation) during storage of in-house boron powder were also studied.

Materials and Methods

An environmental SEM (made by FEI, Eindhovan The Netherland; Model: Quanta 200), that uses a tungsten filament as the source of electrons, was used for particle imaging. The morphological study of boron powder was carried out using an accelerating voltage below the charging limit. An Energy Dispersive Spectroscopy (EDS) study of selected boron samples was carried out using Energy Dispersive X-ray Analysis (EDS) accessories (EDX Inc. USA) fitted to the microscope. A ‘Shimadzu’ infrared spectrometer (FTIR-8400) was used for this characterization. Boron powder samples were thoroughly mixed with dry KBr to give a sufficiently homogeneous mixture.

Results and Discussion

ABP samples for characterization

Three ABP samples were obtained from commercial sources (produced in UK, USA and China). Two other samples (ABP Gr-I and ABP Gr-II) were production grade ABP manufactured in the pilot plant of this laboratory. Chemical analysis, such as boron and magnesium content, as well as physical property analysis (particle size, bulk density) were carried out for the above five samples as per the product specification prepared by this laboratory [16]. The results are tabulated in Table 1.

Table 1. Chemical analysis and physical properties of ABP samples obtained from different sources

Sample No.	Sample Name	Source description	Chemical analysis		Surface weighted mean particle size D[3,2], μm	Bulk density (g/cm^3)
			B content (%)	Mg content (%)		
1	ABP Gr-I	Manufactured at HEMRL, India	92.4	2.4	1.7	0.7
2	ABP Gr-II	Manufactured at HEMRL, India	85.6	9.5	1.1	0.7
3	UK Boron	Supplied by M/s Orion Chemicals Pvt. Ltd., Mumbai and Manufactured in UK	95.5	1.5	1.9	0.6
4	S B Boron	Supplied by M/s Deepkamal Chemiclas Ltd. Mumbai, India and Manufactured by M/s S.B.Chemicals Inc. USA.	92.1	3.0	1.4	0.4
5	Chinese boron	Supplied by M/s Barucha Chemicals Pvt. Ltd, Mumbai, India and Manufactured in China	91.9	3.6	1.0	-

Apart from the above, two more in-house ABP samples (roasted and fused) were collected from the various processing stages of the pilot plant and investigated. Additional six samples, collected from old stock (produced in the pilot plant of this laboratory), were studied for ageing characteristic with respect to boric acid formation.

Analytical method for the estimation of the boric acid content of ABP

A 250 ml round-bottom flask was loaded with the ABP sample (~1.0 g, accurately weighed). The flask was placed on a heating mantle. Distilled water (150 ml) was added to it and the flask was fitted with a glass condenser. The flask was heated in order to reflux the boron slurry. Heating and refluxing were continued for 1h. The slurry was hot filtered (using Whatman 42 filter paper) and the cake was washed (twice) with hot water (100 ml). The filtrate was collected in a 500 ml conical flask and it was allowed to cool. Mannitol (5.0 g) and phenolphthalein indicator solution (10 drops) were added to the filtrate. It was then titrated against 0.05 N standard NaOH solution (previously standardized with primary standard potassium hydrogen phthalate) until a faint pink colour appeared.

Calculation:

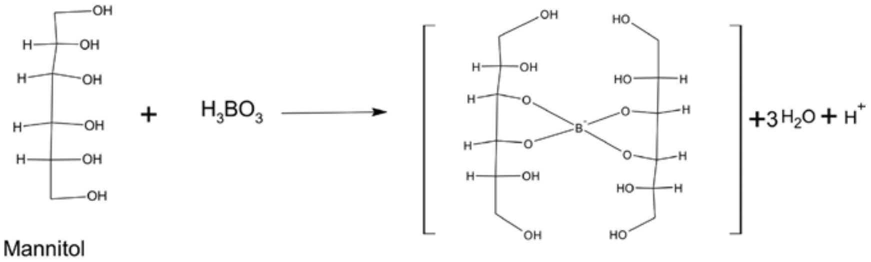
$$\%\ \text{Boric acid in ABP} = 6.2 \times \frac{R \times N}{M}$$

where R = burette reading, N = normality of sodium hydroxide solution, M = mass of the sample taken.

Results of boric acid content of ABP

For quantitative estimation of the boric acid content of ABP, it is essential to leach out the adhering layer of boric acid, present on the surface of the boron particles, into the solution. Accordingly, efforts were made to develop an effective leaching out method. The ABP sample was refluxed with water to leach out the surface boric acid (the solubility is high in water). The extracted boric acid present in the filtrate was estimated in a subsequent titration. Boric acid is a weak acid and cannot be directly titrated against sodium hydroxide solution. It is titrated with addition of mannitol, a poly-hydroxy alcohol. Borate forms a complex with mannitol and liberates H^+ as shown in Scheme 1 [17].

The boric acid content of five ABP samples (three from commercial sources and two in-house production grade samples) were assayed by this method and the results are summarised in Table 2. The boric acid content in HEMRL's Gr-I boron (old stock) and UK boron was found to be similar (~8.0%). The boric acid content in HEMRL's Gr-II boron (old stock) was found to be similar to SB and Chinese boron (~16%). Roasted boron shows a high boric acid content (~44%). This laboratory has developed an oxidative roasting method to improve the purity of ABP Gr-II from ~85% to ~92% [6]. Gr-II boron is placed on a SS-tray in the form of a thin layer and roasted inside a muffle furnace at 600 °C. In the roasting process, the outer surface of the boron particle is totally converted to B_2O_3. Thus, the material showed a high boric acid content. Occasionally, during the roasting process, the Gr-II boron particles become fused together on certain trays and form granular lumps. Due to uneven heat transfer, the material in certain trays becomes fully oxidized and gets fused. Thus, fused material showed a very high boric acid content (~99%).



Scheme 1. Formation of complex between mannitol and borate.

Table 2. Analysis results of boric acid content in various ABP samples

Sample name	No. of replicates	H_3BO_3 contain (%)	S D (%)
ABP Gr-I(old stock)	3	8.7	0.008
ABP Gr-II(old stock)	3	15.9	0.015
UK Boron	4	7.9	0.018
S B Boron	3	16.5	0.040
China boron	3	15.7	0.010
Roasted boron	3	43.7	0.008
Fused boron	3	99.2	0.009
Pure H_3BO_3	4	99.8	0.005

The re-analysis of % elemental boron content for a few batch samples from the old stock (stored for more than 2 years) gave a lower value than that of earlier reported values. This is due to incorporation of oxygen (through formation of boron oxide) into the sample. This prompted us to analyse six ABP samples from old stock (stored for different periods, 2-8 years) for their boric acid content. The results are shown in Table 3. The formation of boric acid was found to increase linearly with aging time. An empirical equation was formulated from the trend line (Figure1).

Table 3. Analysis results of boric acid content in ABP samples collected from old stock

Sample Name	No. of years of storage	H_3BO_3 content (%)
ABP Gr-II (freshly prepared)	0	0.7
ABP Gr II (B. No. 080201)	2	3.3
ABP Gr-I (B. No. HR-050721)	5	4.5
ABP Gr-I (B. No. HR-040916)	6	5.5
ABP Gr-II (batch No. ML 2003)	6.5	5.7
ABP Gr-I (B. No. HR-030308)	7	8.1
ABP Gr-II (B. No. 020410)	8	11.6

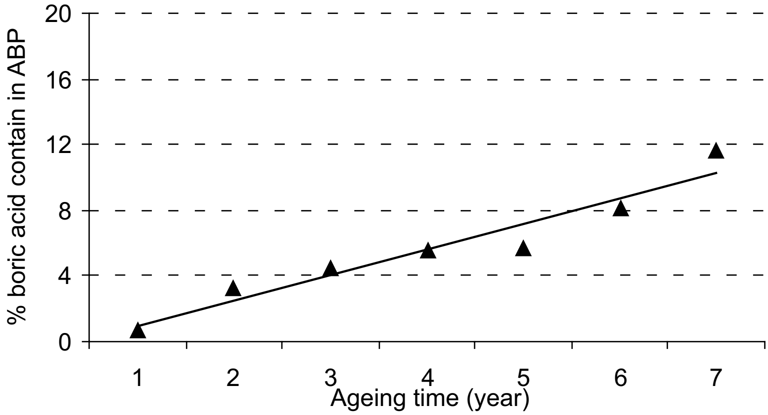


Figure 1. Boric acid contain in ABP with ageing (storage life).

% Boric acid in ABP = 1.42 × No. of years of storage

Fine ABP (particle size <2 μm, BET surface area 12 m^2/g) was stored in a plastic (HDPE) container with a closed lid. Apparently, there is no visible scope for exposure of this material to atmospheric oxygen (considering the very low permeability of oxygen gas through the plastic container). However, a substantial amount (~11%) of boric acid was found in the ABP after a storage life of 8 years

(Table 3). This may be due to surface oxidation by entrapped oxygen molecules, present in the micro-pores of the fine particles. To avoid such an oxidation process, it is recommended to apply vacuum to the powder followed by argon flushing prior to packaging. Application of vacuum will remove the oxygen from the micro-pores and the subsequent argon flushing will protect the surface from oxidation [Argon (Mol. wt. 39.9 g/mol) being heavier than air (Mol. wt. ~29 g/mol) will not allow oxygen into the micro-pores]. Moreover, it is also recommended to use a three layered plastic pouch having a metallic foil at the centre (polyester-aluminum-polyethylene) for boron packaging (1 kg/packet for single use/consumption). This laboratory has adopted this methodology and it is found to be effective in preventing surface oxidation of boron.

SEM characterization

A cloudy layer of boric acid was observed with all of the samples in their SEM photographs (Figures 2-7). Figure 2 shows the SEM photograph of ABP Gr-I boron (old stock) where the fine particles are covered with boric acid. The same observation was also made with UK boron (Figure 3). Unlike Gr-I boron, fine particles are well dispersed in UK boron. In a fresh Gr-I sample, nascent boric acid whiskers were observed on the boron surface; these were just formed by topochemical reaction with atmospheric oxygen and moisture (Figure 4). The particle shape, size and morphology are quite different in SB and Chinese boron (Figures 5 and 6). The samples all have well developed crystals. Chinese boron is crystallized with a layer structure (Figure 7). However, boric acid clouds were also observed on both samples.

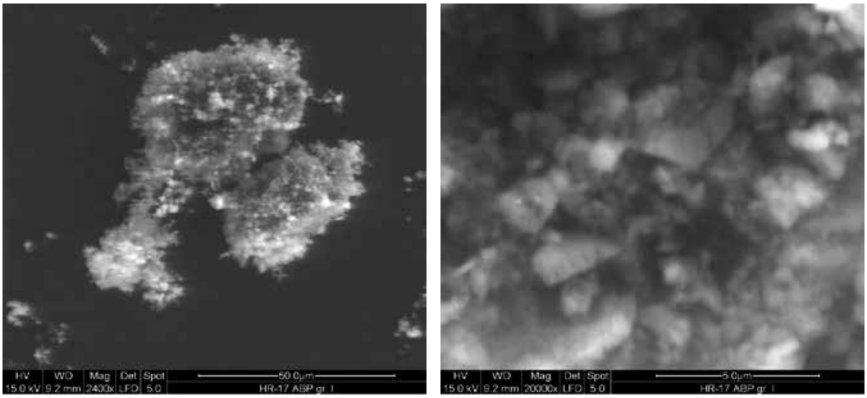


Figure 2. SEM photographs of ABP Gr-I (old).

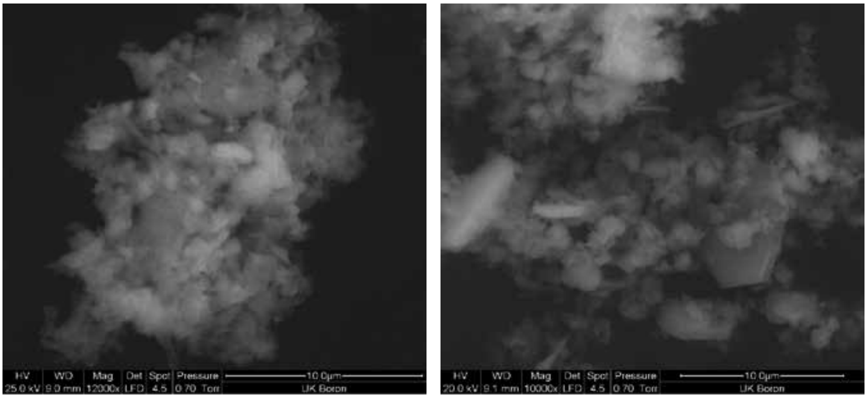


Figure 3. SEM photographs of UK boron.

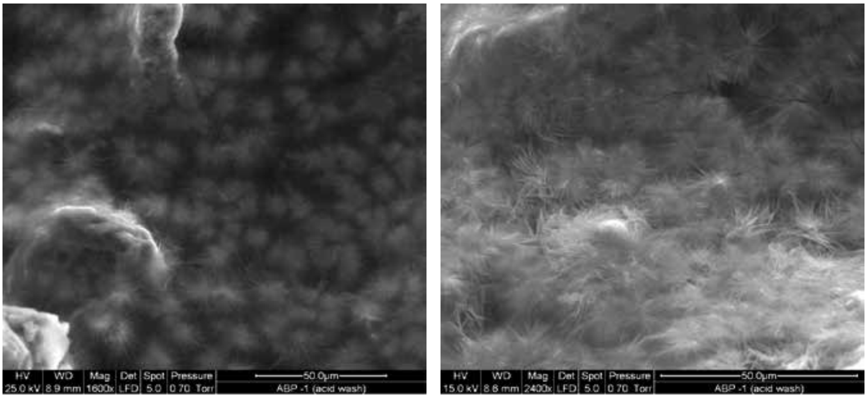


Figure 4. SEM photographs of ABP Gr-I (freshly prepared).

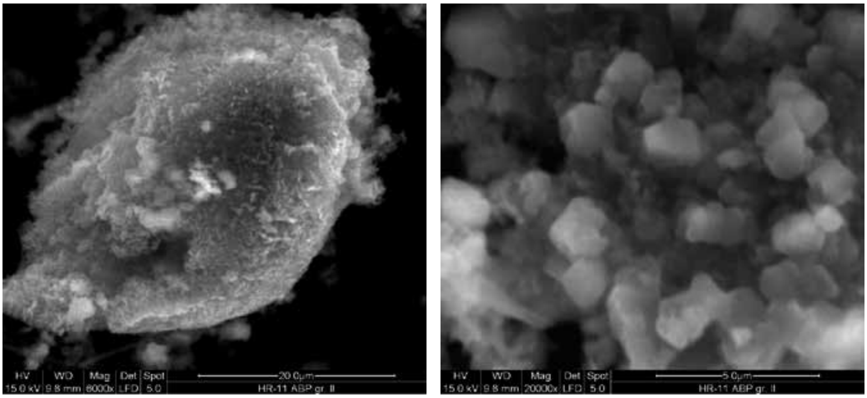


Figure 5. SEM photographs of SB boron.

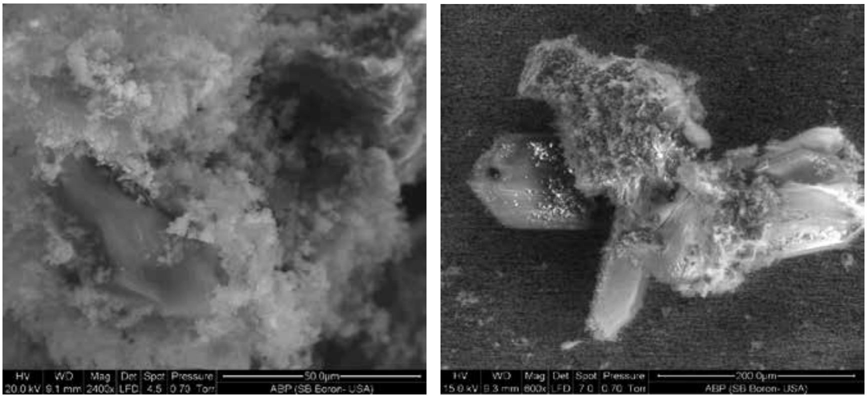


Figure 6. SEM photographs of Chinese boron.

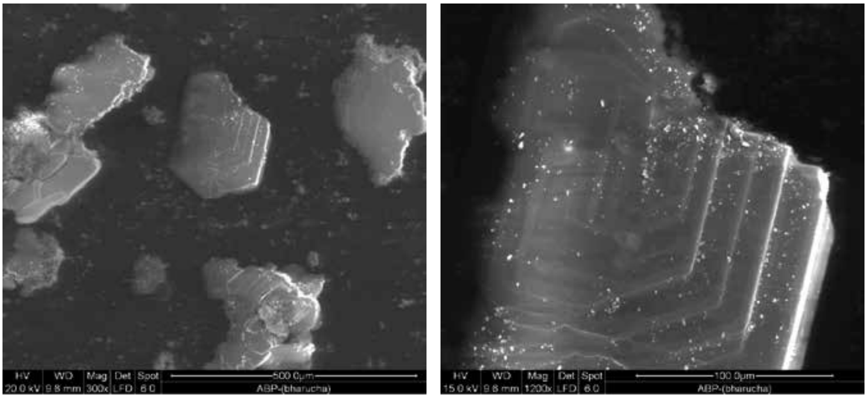


Figure 7. Layered structure of Chinese boron as seen in SEM photographs.

EDX elemental analysis of all ABP samples revealed the presence of the elements B, O and Mg. A typical EDX spectrum is compared with that obtained with pure B_2O_3 and is shown in Figure 8. Boron gives a very weak signal in EDX spectra due to its low atomic number and shows its presence both in atomic (0.172 eV) and B^{3+} (0.266 eV) states, whereas oxygen shows as O^{2-} (0.515 eV) and magnesium as Mg^{2+} (1.252 eV). The EDX study qualitatively supports the presence of the boric acid layer in ABP samples. Mg is present in ABP as an HCl insoluble impurity MgB_x (x = 2, 4 and 6) [6, 7].

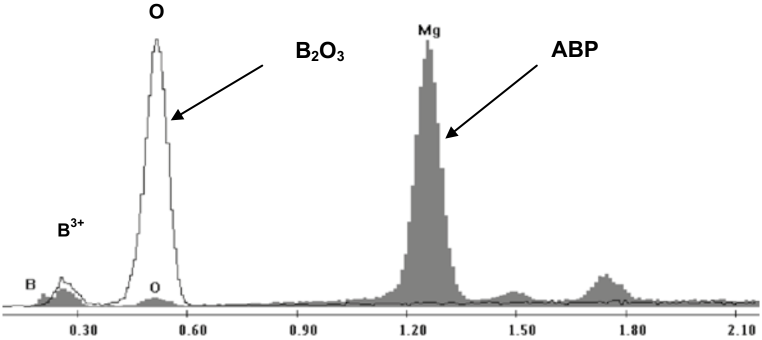


Figure 8. Typical EDAX spectra of ABP (compared with pure B_2O_3).

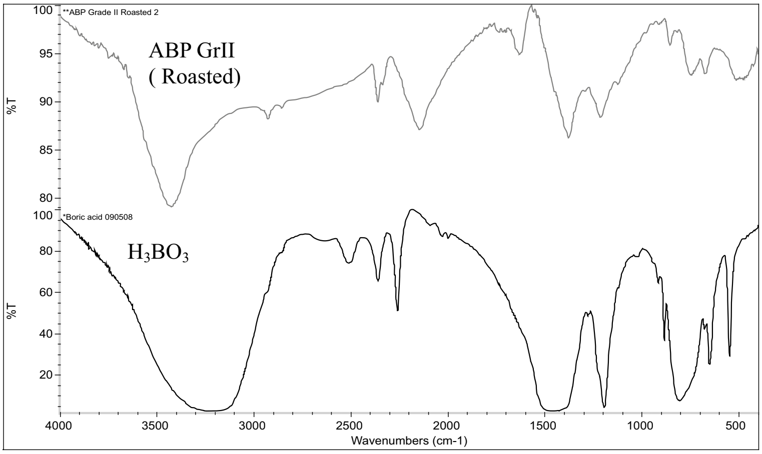


Figure 9. Typical FTIR spectra of ABP (compared with pure boric acid).

FTIR characterization

FTIR analysis was carried out on all samples and the spectra were compared with the FTIR spectrum of standard boric acid (99% pure). The IR bands of ABP almost match those of standard boric acid. A typical FTIR spectrum of ABP Gr-II (roasted) is shown in Figure 9.

Conclusions

All boron samples invariably contain a thin layer of boric acid which is formed by surface oxidation with atmospheric oxygen followed by absorption of moisture. The wet chemical analysis of the boric acid content of ABP samples reveals that the percentage of this impurity may vary from 2-16%. Boric acid is an undesirable impurity in ABP and hence this analytical method may be incorporated in the product specification for its acceptance for final application in propellant formulation. The SEM, EDX and FTIR studies give qualitative assessment of the boric acid present in the ABP sample, as well as the particle morphology.

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