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## THE RELATION OF HERTZIAN CONTACT PRESSURE TO FRICTION BEHAVIOR OF SELF-LUBRICATING BORIC ACID FILMS\*

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THE RELATION OF HERTZIAN CONTACT PRESSURE TO FRICTION BEHAVIOR OF SELF-LUBRICATING BORIC ACID FILMS

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**ABSTRACT**

The effect of Hertzian contact pressure on the friction coefficient of self-lubricating boric acid ( $H_3BO_3$ ) films was investigated by sliding steel and ceramic balls against boric oxide ( $B_2O_3$ ) coated steel and ceramic disks under a wide range of contact loads. Self-lubricating  $H_3BO_3$  films result from a spontaneous chemical reaction between water molecules and  $B_2O_3$  coatings in humid air. Mean initial Hertzian contact pressures in the range of 0.3 to 1.6 GPa, were created between balls and  $B_2O_3$ -coated disks by varying applied load and the radius of balls. It was demonstrated that an inverse relation exists between friction coefficient and Hertzian contact pressure. Using the Hertzian contact model, the shear strength of  $H_3BO_3$  films was estimated to be approximately 22.9 MPa, which is comparable to that of  $MoS_2$ , reported as 24.8 MPa.

## INTRODUCTION

A comprehensive review of the self-lubricating mechanisms of solids by Kanakia and Peterson has demonstrated that the friction coefficients of tribosystems using layered-lattice and soft metal lubricants tend to decrease with increasing contact pressure [1]. A detailed study of the phenomenon by Singer et al. [2] has provided further evidence that the friction coefficient of sliding pairs with a layered solid lubricant film, e.g.,  $\text{MoS}_2$ , indeed decreased with increasing contact pressure. Erdemir et al. [3] observed a similar trend on the friction coefficients of steel-steel and ceramic-ceramic pairs that used a  $\text{H}_3\text{BO}_3$  film at the sliding interface. These observations are in contradiction to the Amonton's law of friction which states that the friction coefficient of a sliding interface is independent of the contact pressure. However, using the Hertzian contact model, some explanation was provided for the decrease in friction coefficient with increasing contact pressure. For example, Kanakia and Peterson [1] and Singer et al. [2] used this model to describe the pressure dependent shear strength, hence the friction behavior of layered solid and soft metals. Based on a regression analysis of 629 friction data points, Singer et al. estimated the shear strength of  $\text{MoS}_2$  as 24.8 MPa which was in good agreement with the actual shear strength of bulk  $\text{MoS}_2$  reported in the open literature.

The primary objective of this study is to investigate the pressure-dependent friction behavior of  $\text{H}_3\text{BO}_3$  films. Furthermore, an attempt will be made to estimate the shear strength of  $\text{H}_3\text{BO}_3$  by using the Hertzian contact model that has previously been used by Singer et al. [2] to estimate the shear strength of  $\text{MoS}_2$ .

Like  $\text{MoS}_2$ ,  $\text{H}_3\text{BO}_3$  is a layered-solid lubricant whose crystal chemistry and lubrication mechanism were described in a recent paper [4]. Specifically, it was shown that  $\text{H}_3\text{BO}_3$  possesses a layered triclinic crystal structure. The atoms lying on the same plane (i.e., B, O, and H) are closely packed and strongly bonded to each other. Whereas, the layers themselves are widely spaced (e.g., 0.318 nm) and held together with weak van der Waals' forces [4]. When subjected to tangential forces, the atomic layers can align themselves parallel to the direction of relative motion; once so aligned, they can slide over one another with relative ease, thus providing low friction [3-6]. In addition to its bulk form,  $\text{H}_3\text{BO}_3$  was shown to form naturally on the surface of boric oxide ( $\text{B}_2\text{O}_3$ ) coatings by a spontaneous chemical reaction between moisture in open air and  $\text{B}_2\text{O}_3$  [3,5]. Recent friction tests by Erdemir et al. have demonstrated that these naturally occurring  $\text{H}_3\text{BO}_3$  films can provide sliding steel and ceramic interfaces with friction coefficients of 0.02 to 0.07, depending on applied load [3].

## EXPERIMENTAL DETAILS

### Test Materials

The pin and disk materials used in this study were AISI 52100 and 440C steels, polycrystalline  $\alpha$ -alumina, and sapphire. Except for sapphire, the balls were 9.5 mm in diameter and had surface roughness values less than 0.05  $\mu\text{m}$  center-line-average (CLA). The sapphire balls were 6.35 mm in diameter and had a surface finish of 0.001  $\mu\text{m}$  (CLA). The disks were 50 mm-diameter and exhibited surface finishes ranging from 0.002 (in the case of sapphire) to about 0.05  $\mu\text{m}$  CLA (in the case of alumina). The mechanical properties of the pin and disk materials are

given in Table 1.

### Deposition of B<sub>2</sub>O<sub>3</sub>

B<sub>2</sub>O<sub>3</sub> was deposited on the steel and ceramic disks in a high-vacuum deposition system equipped with an electron-beam-heated evaporator. Before deposition, disks were sputter cleaned with a flux of Ar ions emitted from a Kaufman-type ion gun operated at 1000 V. Vacuum evaporation was carried out at room temperature and at a chamber pressure of  $5 \times 10^{-4}$  Pa. A quartz-crystal rate monitor was used to control and estimate the evaporation rates. Coating thickness was in the range of 1 to 2  $\mu\text{m}$ . Substrates were not externally heated, however because of convection from the electron beam-heated evaporator, they attained temperatures in the neighborhood of 60°C. Further details of the deposition system can be found in Ref. 3.

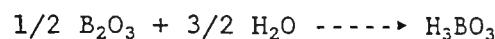
### Friction Tests

Friction tests were performed in a ball-on-disk tribometer at a constant rotational speed of 10 rpm. Depending on the track diameter, sliding velocity varied between 0.01 to 0.04  $\text{m.s}^{-1}$ . The relative humidity and temperature of the test room were  $50 \pm 5\%$  and  $23 \pm 1^\circ\text{C}$ , respectively. The dead weights applied on top of the ball holder ranged from 1 N to 20 N. Depending on the ball radius (e.g., 3.18 to 4.77 mm) and the combination of ball and disk materials, the initial mean Hertzian contact pressure varied between 0.3 and 1.6 GPa. The balls were firmly secured to a stationary holder for the ball-on-disk configuration. Disks were attached to a horizontal chuck driven by a variable-speed electric motor. Frictional force was monitored by a linear-voltage displacement transducer

attached to the ball holder and was recorded continuously.

## RESULTS AND DISCUSSION

One feature that makes  $H_3BO_3$  unique is its ability to self-replenish on the surface of  $B_2O_3$  coatings. When we first took the coated-substrates out of the deposition chamber, we noticed that the  $B_2O_3$  coatings were colorless and transparent. However, they became opaque and took on a color similar to that of the mother-of-pearl in a few minutes in open air. As described in Ref. 7, the change in appearance is due to the formation of a very thin  $H_3BO_3$  film (approximately 10 nm thick) on the surface of boric oxide coatings. Because, when exposed to open air at room temperature,  $B_2O_3$  reacts spontaneously with environmental moisture, resulting in a thin  $H_3BO_3$  film. The chemical reaction for  $H_3BO_3$  formation is



$$\Delta H_{298} = -45.1 \text{ kJ.mol}^{-1}.$$

It is interesting to note that moisture is known to be detrimental to the self-lubricating capability of  $MoS_2$  but is essential for the initial formation and continuous self-replenishment of  $H_3BO_3$  lubricant.

The self-lubricating mechanism of  $H_3BO_3$  is governed by its unique crystal structure. As shown in Fig. 1, it crystallizes in a layered triclinic structure. The atoms lying on each crystalline layer are closely packed and strongly bonded

to each other (e.g., covalent, ionic, and hydrogen bonds). Each layer can be regarded as a rigid, two-dimensional sheet of strongly bonded atoms. The atomic sheets are widely spaced (e.g., 0.318 nm) and held together by weak van der Waals' forces [4].

When these sheets of atoms are present on a sliding surface, they can slide over one another with relative ease (because of the weak bonding between atomic sheets) and thus provide low friction. In addition, strong interatomic bonding and rigidity in each layer prevents direct contact between sliding asperities, thus inhibiting wear damage. Some evidence of interlayer slip was shown in Refs. 3 and 5.

Figure 2 presents the variation of friction coefficients of various balls during sliding against a boric-oxide-coated alumina disk under loads of 1, 2, 5, and 10 N. The friction coefficient decreases monotonically with increasing load. Furthermore, the harder and more rigid the ball (e.g., sapphire), the lower the friction coefficient. These observations are consistent with those of Singer et al. [2] who presented a similar trend for various balls sliding against a  $\text{MoS}_2$ -coated 440C steel disk.

In our study, a total of 38 friction tests were performed with various ball and disk combinations. The friction coefficients obtained from these tests were plotted against the inverse mean Hertzian contact pressure in Figure 3. One major goal of this study was to determine the approximate shear strength of  $\text{H}_3\text{BO}_3$ . To achieve this goal, we used the Hertzian contact model that was previously used by Singer et al. in Ref. 2 for the assessment of the shear strength of  $\text{MoS}_2$ . An approximate value for the shear strength of  $\text{H}_3\text{BO}_3$  will be of significant

importance for practical purposes. Specifically, it will allow one to predict the friction coefficient of a tribosystem using  $H_3BO_3$  as the solid lubricant.

### Shear Strength of Boric Acid

One assumption that we adopted during the use of Hertzian contact model was the presence of 1 to 2  $\mu m$  thick  $B_2O_3$  coatings with a 5 to 10-nm-thick  $H_3BO_3$  film on the surfaces did not violate the rules of Hertzian contact law. Specifically, it was assumed that the real contact area was determined by the elastic properties of rigid balls and disks, not by the elasto-plastic deformation of boric oxide and/or acid layers. The radius of the smallest Hertz contact area was calculated to be about 16  $\mu m$  for the sapphire ball sliding on a sapphire disk under 1 N load. Being at least 8 times larger than the  $B_2O_3$  coating thickness, it is reasonable to assume that the Hertz law was not grossly violated.

As is known, the frictional force ( $F$ ) between a rigid ball sliding against a rigid disk is determined by the product of the shear strength ( $S$ ) of the contact interface multiplied by the real contact area ( $A$ ). When a solid lubricant film is present, the shear behavior of the contact interface is governed by the shear strength of that solid lubricant film ( $S_f$ ) present at the interface [4]. Hence,

$$F = A \cdot S_f \quad (1)$$

The friction coefficient ( $\mu$ ) is

$$\mu = F/L = (A \cdot S_f)/(A \cdot P) = S_f/P \quad (2)$$

where  $L$  is the normal force and  $P$  is the contact pressure.

As mentioned earlier, several studies have indicated that the shear strengths of solids become increasingly load-dependent as contact pressure increases. This pressure-dependent shear strength was defined in Refs. 1,2,8 as

$$S_f = S_o + \alpha P \quad (3)$$

hence,

$$\mu = S_o/P + \alpha \quad (4)$$

where  $S_o$  is the shear strength of contact interface including a solid lubricant film, and  $\alpha$  is a constant and these parameters are the characteristics of a solid lubricant [1,2].

In terms of the Hertzian contact model, the friction coefficient of a sliding interface can then be expressed as:

$$\mu = A \cdot S_o/L + \alpha$$

$$\mu = (S_o/L) \cdot \pi (3L \cdot R/4E)^{2/3} + \alpha \quad (5)$$

where  $R$  is the radius of a ball sliding against a disk,  $E$  is the elastic modulus of the composite system including ball and disk materials, and  $L$  is the applied load.

Eq. 4 is an equation of the form  $y = ax + b$ . A plot of the friction coefficient ( $\mu$ ) against the inverse contact pressure ( $P$ ) yields  $S_0$  as the slope and  $a$  as the intercept. A regression analysis of 38 friction data in Figure 3 resulted in a least-square best-fit straight line with a mean slope ( $S_0$ ) of 22.9 MPa. The intercept,  $a$ , is 0.006.

The estimated shear strength, 22.9 MPa, of  $H_3BO_3$  could not be compared to the actual shear strength of  $H_3BO_3$ . A survey of published literature found no reports of a mechanically measured shear strength value of  $H_3BO_3$ . As mentioned earlier, using the same method, Singer et al. [2] estimated the shear strength of  $MoS_2$  as 24.8 MPa, a value which compared favorably to the measured bulk shear strength of fully dense  $MoS_2$  compacts. The constant  $a$ , in our case had a value of about 0.006 in contrast to a value of 0.001 for  $MoS_2$ . It is important to note that the number of frictional data points (i.e., 38) used in this work is much less than used by Singer et al. [2] in their  $MoS_2$  work (i.e., 629). Therefore, it is possible that these values of  $S_0$  and  $a$  might have been different if a large number of frictional data had been used. However, this was a first attempt to estimate the shear strength of  $H_3BO_3$  and to further demonstrate that the Hertzian contact model can be used to predict the shear and/or friction behavior of self-lubricating solids.

From a practical stand point, we think that the knowledge gained from this study may be helpful in the design of future tribosystems that may be using  $H_3BO_3$  as the primary solid lubricant.

## CONCLUSIONS

- \* The friction coefficient of sliding interfaces with a  $H_3BO_3$  film decreases with increasing pressure.
- \* Based on a regression analysis of frictional data, we found that the shear strength of  $H_3BO_3$  is 22.9 MPa.

## ACKNOWLEDGMENT

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Table 1. Some mechanical properties of the materials used in friction tests.

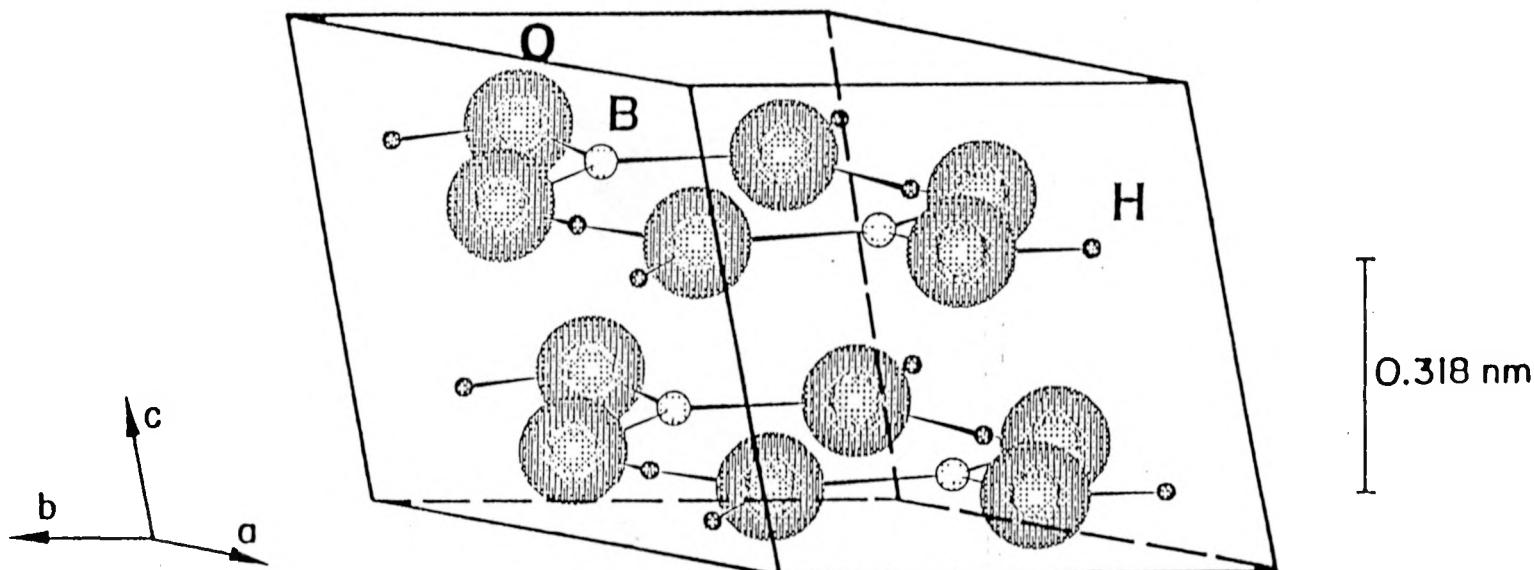
| MATERIALS                            | Modulus of Elasticity<br>(GPa) | Poisson's Ratio | Hardness<br>(GPa) |
|--------------------------------------|--------------------------------|-----------------|-------------------|
| AISI 440C                            | 210                            | 0.3             | 8.0               |
| AISI 52100                           | 210                            | 0.3             | 8.0               |
| Sapphire                             | 470                            | 0.24            | 22.5              |
| Policrystalline<br>$\alpha$ -alumina | 343                            | 0.24            | 16.2              |

FIGURE CAPTIONS

Fig. 1. Depiction of layered-crystal structure of  $H_3BO_3$ .

Fig. 2. Friction coefficients of various balls during sliding against a  $B_2O_3$ -coated alumina disk under load of 1, 2, 5, and 10 N.

Fig. 3. Plot of friction coefficient against inverse Hertzian pressure.



INTERLAYER BONDING : van der Waals

$$\begin{array}{ll} \alpha = 92.58^\circ & a = 0.7039 \text{ nm} \\ \beta = 101.17^\circ & b = 0.7053 \text{ nm} \\ \gamma = 119.83^\circ & c = 0.6578 \text{ nm} \end{array}$$

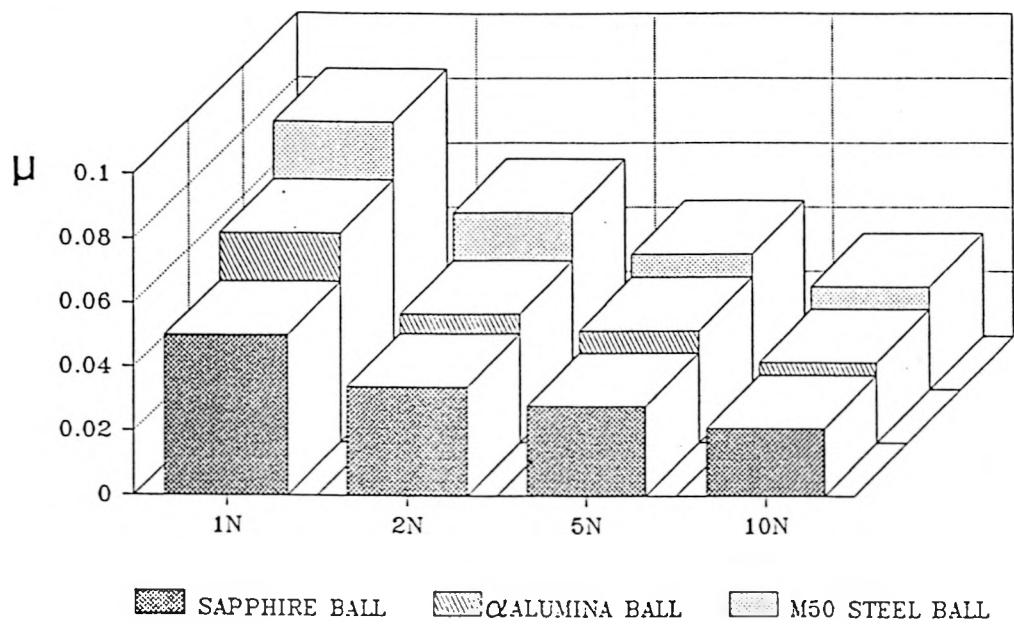


Fig. 2

FRICTION COEFFICIENT

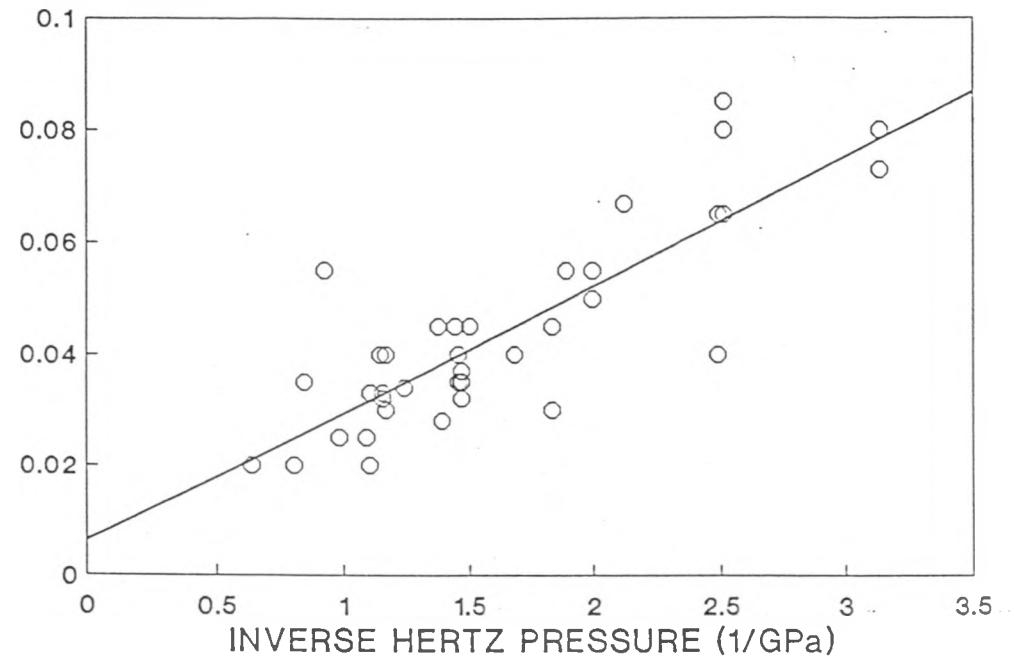


Fig. 3