Influence of boric acid additive size on green lubricant performance

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As the industrial community moves towards green manufacturing processes, there is an increased demand for multi-functional, environmentally friendly lubricants with enhanced tribological performance. In the present investigation, green (environmentally benign) lubricant combinations were prepared by homogeneously mixing nano- (20 nm), sub-micrometre- (600 nm average size) and micrometre-scale (4 $\mu$m average size) boric acid powder additives with canola oil in a vortex generator. As a basis for comparison, lubricants of base canola oil and canola oil mixed with MoS$_2$ powder (ranging from 0.5 to 10 $\mu$m) were also prepared. Friction and wear experiments were carried out on the prepared lubricants using a pin-on-disc apparatus under ambient conditions. Based on the experiments, the nanoscale (20 nm) particle boric acid additive lubricants significantly outperformed all of the other lubricants with respect to frictional and wear performance. In fact, the nanoscale boric acid powder-based lubricants exhibited a wear rate more than an order of magnitude lower than the MoS$_2$ and larger sized boric acid additive-based lubricants. It was also discovered that the oil mixed with a combination of sub-micrometre- and micrometre-scale boric acid powder additives exhibited better friction and wear performance than the canola oil mixed with sub-micrometre- or micrometre-scale boric acid additives alone.

Keywords: green lubricants; green additives; micro- and nano-boric acid; canola oil

1. Introduction

According to the US Energy Information Administration, the US consumed a total of 7.14 billion barrels of oil in 2008 (refined petroleum products and bio-fuels), which was about 23 per cent of total world oil consumption (http://tonto.eia.doe.gov/ask/crudeoil_faqs.asp). Fifty-four per cent of these were automotive lubricants—engine oils and transmission fluids—whereas 44 per cent were industrial lubricants such as hydraulic fluids and gear oils (http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Harvesting_Lubricants).

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One contribution of 11 to a Theme Issue ‘Green tribology’.
Nearly all lubricants used in the automotive and manufacturing sectors are oil- or grease-based. Since these lubricants are usually toxic and not readily biodegradable, they can introduce significant quantities of pollutants into the waste stream. The long-term impacts that these lubricants have on the environment are cumulative and ultimately are detrimental to humans, plants, fish and wildlife. For this reason, the Environmental Protection Agency and other government agencies have imposed increasingly stringent regulations on the use, containment and disposal of oil- and grease-based lubricants. These regulations have changed the landscape of the lubrication marketplace over the last decade as new lubricants are being developed to address a combination of environmental, health, economic and performance challenges. Since traditional lubricants often carry a health risk to humans during their primary use and disposal, and because disposal costs are nonlinearly increasing, it has become essential to develop and implement lubricants that come from non-toxic, natural resources.

2. Background

(a) Green liquid lubricants

The term ‘green lubricants’ is generally used for lubricants manufactured from vegetable or other natural sources. The development of green lubricants to displace petroleum-based products is presently an emerging area of research in the engineering community. Among other factors, this development has been driven by dramatic increases in the price of crude oil and the movement towards using biodegradable oils from renewable resources. With better biodegradable and toxicity properties than conventional petroleum-based products, green lubricants have tremendous potential for use in the industrial sector (Bartz 1998; Barriga et al. 2005; Battersby 2005; Grushcow 2005; Grushcow & Smith 2005; Jayadas et al. 2005; Lovell et al. 2005, 2006; Puscas et al. 2005; Deshmukh et al. 2006; Kabir et al. 2008). Although industry standards do not exist, engineers desiring to use green lubricants must consider specific applications and products individually. The highest volume of green lubricant production is presently for hydraulic applications. Most of these products are produced from vegetables (e.g. rapeseed/canola, corn or soybean oil), synthetic esters, polyalkylene glycols or severely hydrotreated petroleum-based oils. Vegetable oils have a long history of use as lubricants—together with animal fats—as they dominated the lubrication industry before the petroleum age (Grushcow 2005). Problems of limited oxidative stability and poor low-temperature performance gradually led to their replacement by fossil oils and later by synthetic oils. When compared with mineral and synthetic oils, vegetable oils have a number of distinct advantages including higher lubricity, lower volatility, higher shear stability, detergency and dispersancy and a substantially higher viscosity index. In fact, vegetable oils offer a large range of kinematic viscosities, from 2.37 to 8.53 mm² s⁻¹ at 100°C and from 7.85 to 35.01 mm² s⁻¹ at 40°C (Puscas et al. 2005). Today, vegetable oils represent a nearly inexhaustible source of raw materials for lubricants. In 2004, world production of vegetable oil exceeded 100 million tonnes (Battersby 2005). Most of this oil was used by the food industry, with only a small percentage entering the lubrication market, making it an under-used commodity.
The physical structure of ‘green’ vegetable oils is very different to that of traditional lubricants. Plant oils are composed of triacylglycerol, which consists of three fatty acids esterified to a glycerol molecule. Most of the oilseed crops produce triacylglycerol containing a mixture of fatty acids that have varying chain lengths; the most common lengths of carbon chains in these triacylglycerols are 16, 18 and 20. It is the fatty acid composition of the oil that determines its characteristics. In most lubricant applications, vegetable oils are used either as the intact triacylglycerol molecule or the oil is reacted with methanol to produce methyl esters and glycerol (Grushcow 2005). A triacylglycerol molecule containing saturated 18-carbon fatty acids is solid at room temperature. The presence of the double bonds makes the oil liquid, but also increases oxidative instability. The recent introduction of ultra-high oleic (more than 80%) varieties of oilseed crops such as sunflower and canola has made a new type of oil available with characteristics far superior to the oil from existing temperate crops. Oils highly enriched in this monounsaturated fatty acid have improved lubricity and an oxidative stability that surpasses Group 1 petroleum-based oils (Grushcow 2005). Despite their significant promise, these improved vegetable oils still have lower oxidation stability and poorer low-temperature performance than many conventional oils (Neff et al. 1994; Petlyuk & Adams 2004). These and other limitations must be further researched and addressed before a new class of green lubricants can be used to replace traditional grease and oil lubricants.

(b) Green powder lubricants

Over the past 30 years, dry powder lubricants have been employed in a variety of sliding contacts as an alternative to conventional liquid lubricants. The name ‘powder lubricants’ is usually given to lamellar solids that have low interlayer friction (Woronyh et al. 2007). Powder lubricants have been known to: (i) adhere to surfaces to form a protective boundary layer that prevents wear (Johnson & Vaughn 1956; Lancaster 1965, 1966; Heshmat 1995; Dareing & Atluri 1997), (ii) act as a lubricant in sliding contacts by accommodating relative surface velocities (Godet et al. 1980; Godet 1984; Heshmat & Dill 1992; Heshmat 1995; Brendle et al. 1996; Higgs et al. 1999), and (iii) lubricate at high temperatures (Centers 1987; Heshmat & Shapiro 1989; Heshmat 1991a; Heshmat & Dill 1992; Heshmat & Walton 1993; Higgs et al. 1999; Higgs & Tichy 2004). Several of these lubricants—molybdenum disulphide, tungsten disulphide, titanium oxide and boron nitride—were evaluated for their lubrication behaviour at a variety of sizes and found to exhibit excellent tribological performance (Prasad & Zabinski 1993; Shao et al. 2004; Hu 2005; Hu et al. 2005; Ilie & Tita 2008; Shankara et al. 2008). Due to similar health, economic, environmental, and disposal issues encountered with liquid lubricants, efforts are being made to develop and implement powder lubricants that come from natural resources. These lubricants, such as boric acid, have excellent lubrication properties without requiring expensive disposal techniques (Erdemir 1991; Erdemir et al. 1991b, 1997, 1999; Wei et al. 2000). The effectiveness of boric acid can be attributed to its low friction and shear strength values. As reported in the literature (Barton et al. 2004), the shear strength of boric acid has been experimentally determined to be 23 MPa, and its coefficient of friction has been measured to be less than 0.02 in ambient environments. These values are very similar to the more commonly used and synthetic-based

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Figure 1. Lamellar structure of boric acid.

molybdenum disulphide, which has a measured shear strength value of 24 MPa. Two other important characteristics of boric acid for use as a lubricant are that it is readily available and environmentally safe. It is very inexpensive, as finely ground technical grade boric acid powder (more than 99% pure) is commercially available for less than US$ 4.5 kg$^{-1}$. The Environmental Protection Agency has established that boric acid is benign (Deshmukh et al. 2006; Sawyer et al. 2006) and the Clean Water Act does not classify it as a pollutant. The United States is the world’s largest producer of boron compounds, as large domestic reserves of boron materials reside in lake sediments and brines.

Several studies related to the lubrication properties of boric acid have been carried out over the past several decades (Peterson et al. 1960; Johnson & Sliney 1962; Erdemir 1991; Erdemir et al. 1991b; Sawyer et al. 2006). These works have primarily focused on the performance of boric acid in high-temperature applications. Research specifically aimed at the use of boric acid in engineering systems has also been undertaken (Erdemir et al. 1997, 1999; Wei et al. 2000). These studies have indicated that boric acid’s unique layered inter-crystalline structure (see figure 1) makes it a very promising solid lubricant material because of its relatively high load carrying capacity and low steady-state friction coefficient. Other important research has investigated the use of boric acid as a lubricant in manufacturing processes such as forming, drilling and machining. In metal-forming applications (Branneen et al. 1990; Liang & Jahanimir 1995; Rao & Wei 2000; Rao & Xie 2006), it was shown that boric acid powder provided very low friction (0.04) between an aluminium workpiece and a steel-forming tool. During these processes, the post-fabrication cleaning of the boric acid lubricant was environmentally safe, non-toxic and water soluble. In work done by Liang & Jahanimir (1995), drilling experiments with sapphire tools indicated that the addition of boric acid to distilled water increased the rate of drilling of polycrystalline alumina by a factor of 2. In addition, boric acid was found to help reduce friction and corrosion when mixed with cutting and grinding fluids (Fischer & Tomizawa 1985; Barton et al. 2004). In Barton’s work, pin-on-disc experiments were conducted at high speeds using the test apparatus shown in figure 2. In the experiments, the sliding contact consisted of an alumina pin on
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Figure 2. Results obtained from interrupted pin-on-disc tests (Barton et al. 2004).

an AISI-M50 bearing steel disc at a maximum central Hertzian contact pressure of 1.9 GPa. For sliding speeds of approximately 1 m s\(^{-1}\), the resulting friction revealed a reduction in friction from 0.4 for the dry contact, to approximately 0.15 for the boric acid lubricated contact. As illustrated in the figure, continuous powder delivery of the boric acid successfully produced a lubricous surface film and low friction until the delivery of powder was halted. It is very important to note that as with Barton’s findings, the success of boric acid as a lubricant in all of the previously mentioned studies was dependent on the continuous replenishment of the boric acid into the contact region.

Despite its known benefits, it is demonstrated that there are difficulties associated with using boric acid alone as a lubricant in repeated or extended duration contacts (Deshmukh et al. 2006). These drawbacks are owing to the fact that boric acid powder can be dehydrated or forced out of the contact zone during sliding contact. Thus, the widespread use of boric acid in the metal-forming community has been limited by the fact that it must be continuously replenished, which requires the development of expensive spray and recovery systems that would significantly change present manufacturing process lines. To minimize changes to present processes, a logical alternative is to replace presently used oil/grease lubricants with an environmentally friendly liquid lubricant that carries the solid boric acid crystals.

(c) Green powder-based lubricant additives

As conceptually depicted in figure 3, a natural fluid lubricant (canola oil) can carry the third body boric acid particles, providing a mixed lubrication system between contacting surfaces. Hence, efforts have been made to analyse a green, petroleum-free lubricant that was produced by mixing two environmentally benign components—canola oil and boric acid powder (Kabir et al. 2008).
The boric acid powder and canola oil lubricant mixture demonstrates multifunctional lubrication performance, where surfaces are separated by a liquid lubricant film and protected by a solid powder. In Kabir’s work, micrometre-scale (100–700 μm) boric acid particles were added to canola oil. To determine the optimum composition of the boric acid–canola oil lubricant mixture, a series of experiments were conducted at different volume fractions of canola oil with a constant particle size distribution. Based on these experiments, a mixture of 7 per cent by volume was found to outperform the other lubricant mixtures. The experiments were conducted using a pin-on-disc apparatus with spherical copper pins and aluminium discs, where figure 4 shows the variation of friction with sliding distance. The most effective lubricants in the experiments were the canola oil and canola oil–boric acid mixture.

Other efforts have been made by the authors to evaluate the interfacial friction characteristics of canola oil and boric acid lubricants. To simulate their performance in metal-forming operations, a strip tensile friction simulator (Lovell et al. 2006) was used. By means of the simulator, the friction coefficient between a die (carbon steel) and a steel sheet was measured for four different
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Figure 5. Variation of coefficient of friction with sliding distance for various lubricants obtained in the metal-forming experiment (Lovell et al. 2006; filled square, unlubricated; filled triangle, transmission oil; filled diamond, canola oil; filled circle, canola oil with boric acid).

lubricant conditions: unlubricated, canola oil (viscosity of $33 \text{mm}^2\text{s}^{-1}$ at $20^\circ\text{C}$), transmission fluid (viscosity of 0.028 Pa.s at $40^\circ\text{C}$), and a combination of boric acid and canola oil (viscosity of 0.276 Pa.s at $20^\circ\text{C}$). As shown in figure 5, a lubricant consisting of canola oil mixed with boric acid crystals (5 wt% and $100 \mu\text{m}$ average particle size) significantly outperformed several other lubricants with respect to the measured friction coefficient in the specialized experiments. Such a finding indicated that the novel lubricant may be used in manufacturing processes where replenishment is not feasible and disposal of non-environmentally friendly lubricants is expensive. Studies were also conducted to determine the relative performance of boric acid and different oil combinations in a commercial brake valve assembly (Deshmukh et al. 2006). As depicted in figure 6, a lubricant combination of transmission fluid and boric acid (5% by weight) was found to provide optimum friction and wear properties. The friction coefficient for a combined boric acid and canola oil lubricant was comparable but slightly larger than the combined boric acid and transmission fluid case. The boric acid and canola oil case showed no degradation over the entire range of the sliding tests and demonstrated the lowest wear rate of any of the lubricants tested. Such a finding is extremely important as it indicates that the lubricant can be used in extended duration applications where replenishment is not feasible.

Based on the success of using micrometre-scale boric acid particles as an additive, the present investigation focuses on determining the relative performance of sub-micrometre-scale boric acid particles in canola oil for metal-forming applications. The rationale for such an endeavour lies within the fact that numerous studies in the literature have indicated that sub-micrometre particulate additives of graphite, MoS$_2$, and other lamellar solids have improved the performance of base oils (Sunqing et al. 1999; Hu 2005; Huang et al. 2006; Xiaodong et al. 2006). In addition, despite several patents (Erdemir 1995, 2004) on the subject, there are no studies in the archival literature that quantitatively

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investigate the performance of boric acid particle additives in the colloidal size range. In the literature, considerable efforts have been made to study the effect of powder lubricant size on system performance at both the microscale and sub-micro/nanoscale (Shao et al. 2004; Hu 2005; Hu et al. 2005; Ilie & Tita 2008). Sub-micrometric forms of these powder lubricants have been synthesized using chemical vapour deposition, liquid precipitation, electronic chemistry deposition, thermal desulphurization and mechanical grinding or milling. In many cases, sub-microscale powder lubricants offer an enhanced tribological performance because their size is of the order of the asperities for surfaces (Cizaire et al. 2002; Leshchinsky et al. 2002, 2004; Rapoport et al. 2003a,b).

3. Experimental investigation

In the present study, frictional performance of nanoscale (20 nm), sub-microscale (average size 600 nm), microscale (average size 4 μm) and combined sub-microscale/microscale boric acid additives in base canola oil was investigated using a pin-on-disc apparatus. To create the sub-microscale and microscale size boric acid powder additives for the canola oil lubricants, 250 μm sized crystals of boric acid (figure 7a) were milled using an 1800D SPEX Mill/Mixer. The mill used two 1/2 inch and four 1/4 inch steel balls, incorporated a 6 mass ratio between the balls and the crystals, and operated at a rotational speed of 1060 r.p.m. The different sized particles were produced by milling the boric acid powder over different time periods; the 600 nm average-sized particles (ranged from 400 to 800 nm) were produced by milling for 1800 min while the 4 μm (figure 7b) average-sized particles (ranged from 1 to 8 μm) were milled for a duration of 900 min. The nanoscale (20 nm average as shown in figure 7c) particles were produced using a proprietary freeze drying technique in which 250 μm boric acid particles were initially dissolved in water. As a basis for comparison with
the boric acid, 5 \( \mu \)m size MoS\(_2\) powder additives were purchased and mixed with canola oil. The lubricant combinations studied were then produced by homogeneously mixing the canola oil with the powder additives in a vortex generator. Thus, five different lubricants were prepared by combining canola oil with (i) 5.0 wt% of 4 \( \mu \)m boric acid particles, (ii) 5.0 wt% of 5 \( \mu \)m MoS\(_2\) particles, (iii) 5.0 wt% of 600 nm boric acid particles, (iv) a 5.0 wt% mixture of the 4 \( \mu \)m (2.5 wt%) and 600 nm (2.5 wt%) boric acid particles, and (v) 5.0 wt% of 20 nm boric acid particles.

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Once prepared, friction and wear experiments were carried out on the lubricants using the pin-on-disc apparatus (Falex tribometer) at ambient conditions with an average temperature and humidity of $23^\circ C$ and 68 per cent, respectively. The pin-on-disc investigation used spherical Cu pins (6.5 mm diameter) and Al discs (66 mm diameter) that were machined with a standard lathe to an initial average roughness ($R_a$) of 1.5 $\mu$m. These pin and disc materials were specifically chosen to match prior experiments conducted by the authors (Lovell et al. 2006). Before each experiment, the pin and disc surfaces were cleaned with ethanol. Based on prior experiments by the authors, a 4ml homogeneous mixture of particulate lubricant was then carefully dispersed on the rotating disc so that the surface of the disc was in a fully immersed condition. In the experiments, a 100g normal load was applied and a constant sliding velocity of 120 mms$^{-1}$ was used. These operating conditions generated peak and mean Hertz pressures of 60.1 and 47.1 kPa, respectively, when considering non-lubricated, virgin conditions. The friction force was continuously recorded for a sliding distance of 7500 m (65 000 disc revolutions). Although this sliding distance adequately captured the variation and performance of the lubricants over time, it does not represent the maximum distance for which the lubricants should ultimately be investigated; automotive and industrial applications often operate for several hundred hours and over extremely long sliding distances. All experiments were repeated three times. After the experiments, the contact regions of the pins were examined using an optical microscope to study the pin morphology.

4. Results and discussion

The variation of coefficient of friction values for the five lubricants studied is shown in figure 8. Although the exact sliding distance location of the minimum friction varies for each lubricant tested, figure 8 shows that—with the exception of 20 nm boric acid—each of the lubricants follows a similar trend where the coefficient of friction significantly decreases to a minimum value before slightly increasing over the remainder of the sliding distance. Consider the shape of the coefficient of friction curve of the microscale (i.e. 4 $\mu$m size) additive lubricant in figure 8. A maximum friction coefficient of 0.14 is observed at the start of the experiment and then the friction decreases with increasing sliding distance to a minimum value of 0.09 at a sliding distance of 5800 m. After this sliding distance, there is a modest increase in coefficient of friction up to the completion of the experiments. Such a trend suggests that the powder additives in the canola oil form a thin ‘protective layer’ between the pin and disc surfaces as the microscale and sub-microscale particles are squeezed into the contact interface. This powder layer, which helps carry the load and provides low shear resistance, increases over time as more particles are forced between the contacting asperities which naturally round off over time. The fact that the friction increases after a minimum value is attained demonstrates that the boric acid and MoS$_2$ particles ‘run out’ and are no longer available to enter the contact interface; this causes the protective layer to wear away over time which leads to the increase in friction at the latter stages of the experiments. For the case of the 20 nm boric acid particles, the shape of the curve in figure 8 is unique because the friction continuously

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Figure 8. Variation of coefficient of friction with sliding distance for various lubricants (open square, boric acid 4 μm; open circle, boric acid 600 nm; open triangle, boric acid mix (4 μm and 600 nm); open inverted triangle, MoS2 5 μm; open diamond, canola oil; filled circle, boric acid 20 nm).

decreases to an asymptotic value at the end of the sliding experiments. It is possible that if the experiments had been run to a greater sliding distance, then the 20 nm particles would have exhibited a behaviour similar to the other additives. Unlike the other additive cases, however, the 20 nm particles go to colloidal suspension within the canola oil; this allows the lubricant particles to easily enter between the asperities of the pin and disc throughout the sliding experiments. Thus, the 20 nm solution is able to prevent asperity interaction over the entire sliding distance so that no degradation occurs over time. The 20 nm particle lubricant also opens the possibility of additional friction reduction mechanisms that are unique to nanoparticles (Rapoport et al. 1997).

In terms of the magnitude, the coefficient of friction substantially varied with the type of additives used with the canola oil. As shown in figure 8, the best frictional performance was exhibited by the 20 nm boric acid particles, followed closely by the MoS2 powder additives (0.5–10 μm) and the combination of sub-microscale (0.6 μm) and microscale (4 μm) boric acid additives. The largest measured coefficient of friction over the sliding distance tested was found for the microscale (4 μm) boric acid particles and the sub-microscale (0.6 μm) boric acid powder. As described previously, the 20 nm boric acid lubricant combination exhibits the lowest friction because it consists of a colloidal solution that is able to enter into the pin–disc contact interface and provide optimum lubrication without degrading over time. Considering the mixed sub-microscale and microscale powder additives, the reason for the stark differences in frictional performances of the additives can be explained by examining the physical phenomena at play between the different sized particles (see figure 9). As described in prior work by the authors (Kabir et al. 2008), boric acid additives that are larger than the asperity size decrease friction by carrying some of the load between contacting asperities (see figure 9a). The smaller sub-microscale particles, in contrast, will ‘fill’ the asperity valleys and provide a thin,
smooth, solid lamellar film between the contacting surfaces (see figure 9b). Since the protective sub-microscale particles are a better lubricant than individual microscale particles, they exhibited a lower coefficient of friction. As shown in figure 9c, the combined sub-microscale and microscale powder additives exhibited strong frictional performance because both physical phenomena were at play; the small particles formed a protective boundary film while the larger particles helped support the load while being sheared with their well-known low interlayer friction. It is important to note that an identical trend was observed by Hu (2005) while studying the frictional behaviour of 1.5 μm, 30 nm, and mixed 1.5 μm and 30 nm MoS₂ additives in paraffin.

Figure 10 shows the optical micrographs of the Cu pins slid against Al discs in the presence of various lubricants. The wear rate of the pin was assessed by measuring the wear scar radius (r) and then applying the wear volume (V) equation as described by Fischer & Tomizawa (1985):

\[ V = \frac{\pi r^4}{4R}, \]

where R is the original pin radius. The wear volume results are shown in figure 11 for the different lubricant mixtures, while table 1 shows the wear volume as a function of the size of the powder additives. As shown in figure 11 and...
Table 1, the 20 nm boric acid particle lubricant clearly demonstrated the best wear resistance. In fact, the wear rate of the 20 nm lubricant was at least an order of magnitude lower than those of the other lubricants. This again highlights the benefits of placing the nanometre scale particles into a colloidal solution that is able to readily enter the pin–disc contact interface throughout the experiments. In figure 11, it is interesting to note that unlike the coefficient of friction, the lubricant mixtures with the combined sub-microscale and microscale powder additives exhibited higher wear than the individual microscale and sub-microscale boric acid powder. The sub-microscale boric acid powder exhibited the lowest
Figure 11. Variation of wear rate of the Cu pins slid against Al discs in the presence of various additives in canola oil-based lubricants at the interface. BA, boric acid.

Table 1. Calculated wear rate of the pin.

<table>
<thead>
<tr>
<th>test conditions</th>
<th>avg. powder additive size (µm)</th>
<th>avg. wear rate of the pin (mm³ mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>canola oil with sub-microscale boric acid</td>
<td>0.6</td>
<td>4.4592 × 10⁻¹²</td>
</tr>
<tr>
<td>canola oil with microscale boric acid</td>
<td>4</td>
<td>8.1519 × 10⁻¹²</td>
</tr>
<tr>
<td>canola oil with sub-microscale and microscale boric acid</td>
<td>0.6 and 4</td>
<td>1.2827 × 10⁻¹¹</td>
</tr>
<tr>
<td>canola oil with MoS₂</td>
<td>0.5–5</td>
<td>9.699 × 10⁻¹¹</td>
</tr>
<tr>
<td>canola oil</td>
<td>—</td>
<td>1.02 × 10⁻¹¹</td>
</tr>
<tr>
<td>canola oil with nanoscale boric acid</td>
<td>0.02</td>
<td>7 × 10⁻¹³</td>
</tr>
</tbody>
</table>

wear rate. While this trend might not seem intuitive, similar phenomena have been observed in reports on dry (i.e. no carrier fluid or oil) powder lubrication. For example, a tribo-system consisting of two surfaces separated by dry third-body powder has been known to exhibit multiple tribological regimes as a function of the particle size (relative to the surface roughness; Heshmat 1991b, 1995). If the third-body powder particles are smaller than a critical size $P_{d1}$, the surfaces may begin to experience adhesive wear, and if they are greater than the higher critical size $P_{d2}$, they will probably experience abrasive wear. This is because below $P_{d1}$, the particles are smaller than the asperities and can compact and form solid ‘rigid-like’ bodies that can promote adhesive wear. Above $P_{d2}$, in contrast, the particles are greater than or equal to the surface roughness which leads to more abrasive wear. When the particle size range is $P_{d1} < P_d < P_{d2}$, a regime known as ‘quasi-hydrodynamic’ powder lubrication (Heshmat 1991b) exists, where the particles undergo shearing to accommodate surface velocity differences similar
to that of hydrodynamic fluids and oils. Thus, the combination of sub-microscale and microscale mixtures in our experiments will promote wear owing to the larger microscale particles being squeezed between the pin and disc while sitting on top of the smaller sub-microscale particles (see figure 9c). The fact that the microscale boric acid powder exhibits lower wear than the combined sub-microscale and microscale boric acid is probably owing to the contact between the microscale boric acid powder additive and the disc surface being more disposed to induce the layered-lattice shearing behaviour of boric acid powder. It is worth noting that the MoS2 additives, which consisted of particle sizes between 0.5 and 10 μm, exhibited significantly greater wear than any of the boric acid additives. In principle, the MoS2-based lubricants followed a similar trend and can be explained by the combined sub-microscale and microscale boric acid additive discussion above. The wear rate for MoS2, however, increases to a much greater level than the combined boric acid particles and will be the focus of future research by the authors.

5. Conclusion

In order to study the relative tribological performance of different sized boric acid powder additives in a green lubricant liquid carrier (canola oil), pin-on-disc experiments were carried out to determine friction and wear behaviour. Based on the experiments, it was determined that a colloidal solution of 20 nm particles in canola oil provided optimum frictional and wear performance. This was explained by the fact that the colloidal solution did not degrade over time and was therefore able to continuously separate the asperities of the contacting surfaces. With respect to the lubricants with non-nanoscale particles, it was determined that the presence of smaller particles that are able to fill the surface asperities is much more important than the larger additives’ ability to carry contact loads between the surfaces. Additionally, the larger particles may act abrasively since they are larger than the surface roughness. Since this enhanced frictional performance by sub-microscale/microscale powder mixtures was previously shown for MoS2 additives in paraffin oil, the authors hypothesize that mixing sub-microscale/microscale powder lubricant additives may suggest a novel lubrication technology with favourable low and enhanced friction characteristics. As both boric acid and canola oil are environmentally benign and renewable, this work may also serve as a precursor to the development of multi-functional green lubricants by optimizing the particle size of the lubricant additives.

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