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Effect of Zero-Sap Antiwear/Ep Lubricant Additives on Nano-Mechanical Properties of Tribofilms Formed on AISI 52100 Steel Grade

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ABSTRACT

Numerous nations have recently passed stricter environmental legislation due to excessive release of harmful emissions like sulfur (S), phosphorus (P), and zinc (Zn) in conventional lubricating oil additives used in contemporary internal combustion engines. Use of borate ester lubricant additives with no sulfated ash, phosphorus, or sulfur effect (zero-SAPS) is one way to reduce this effect. The resistance of tribofilms from oils containing borate esters on AISI 52100 steel grade to plastic deformation is not entirely understood, yet. This study compares Zinc Dialkyl Dithiophosphate (ZDDP) to the tribological performance and Nano-mechanical behavior of tribofilms made from each of the antiwear/extreme pressure borate esters in Polyalphaolefin (PAO6) base oil. According to tribological test findings on a reciprocating steel pin-on-steel plate sliding rig, the boundary films formed by the borate esters reduced friction and wear in a manner similar to that of ZDDP. On the wear scar, the Nano-indentation technique was used to characterize the Nano-mechanical properties of the tribofilms. The ratios of reduced elastic modulus to hardness (E'/H) for the tribofilms of both borate esters are not only higher than the steel substrate but also comparable to ZDDP. This shows that boron-containing tribofilms offered ZDDP-like tribological performance and also have the ability to release absorbed frictional energy when moving across elastic asperity contacts. Consequently, using borate additives in lubricating oils in IC engines is a method of reducing exhaust emission modern vehicles without adversely affecting tribological performance.

Key Words: Anti-wear Additives, Borate Esters, Plasticity Index.

1. INTRODUCTION

One of the ways of minimizing the excessive release of harmful emissions from internal combustion engines (ICE) is by imposing stricter environmental legislation on the quantities of sulfur (S), phosphorus (P), and zinc (Zn) in conventional lubricant additives. Emissions from automotive exhaust system into the atmosphere is a major global challenge presently facing humanity. This causes: melting of glaciers, rising sea levels, drying forests and extreme weather conditions; more rain followed by longer droughts. In many parts of the world that could results in economic instability of many countries. The IC engines are used as prime movers to provide power in machines for the transportation of goods and people by land, air and sea that accounted for about 22% of the global primary energy consumption. Lubricating oils in IC engines serves to cool the engine parts, reduce friction and wear between moving parts, seal gaps between piston rings and cylinder walls, clean the engine parts of carbon and debris, and absorb shocks and noise from engine operation. Lubricating oils consists of mixtures of base oil and additives (chemical agents) which are organic or inorganic compounds dissolved or suspended as solids in oil to improve the physical properties of the base oil. One of the additives used in lubricating oils of IC engines since 1940s is Zinc Zinc dialkyldithiophosphates (often referred to as ZDDP with its antiwear, antioxidant and extreme pressure (EP) properties. The chemical reacted layers (Tribo-films) formed by ZDDP between rubbing surfaces is known to form soft polymeric materials similar to soft sacrificial coatings deposited on hard substrate. However, ZDDP contains a large proportion of Zn, P, and S. The oxides and phosphates formed by the combustion products of these additives have an irreversible and deleterious effect on particulate filters and/or three-way catalytic converter (TWC) system of modern vehicles [1-3]. The TWC is an emission control system that ensures the concurrent oxidation and reduction of exhaust toxic fumes from internal combustion engines (IC) into the atmosphere. A research study on vehicles running on boron-based lubricant additives yielded lower tailpipe emissions than vehicles running with lubricating oil containing ZDDP [4].

2. LITERATURE SURVEY

An earlier study on the extreme pressure action of the tribofilms formed by tri benzyl borate additives in solvent-neutral oil on steel surfaces was characterized as heterogeneous, non-descript, and non-sacrificial [5]. In addition, micro-hardness evaluation of the tribofilms formed by these additives estimated their hardness as being higher than the steel substrate [6]. Tribo-chemically generated boron-containing boundary films were noted to absorb on tribo-components surfaces by various studies which indicated that boron-containing boundary films consist of boron trioxide (B_2O_3) and orthoboric acid (H_3BO_3) [7-8]. The formation of boron trioxide within the tribofilms was noted to react with moisture in the surrounding air to form a low shear strength orthoboric acid (22.8MPa) [9]; having a crystal structure similar to graphite or molybdenum disulfide (MoS_2). However, boric acid is much more favorably disposed of with moisture than MoS_2 and hence does not require oxidative attack with the ferrous substrate to form its tribofilms [6, 10].

Physical characterization studies on the individual components of boron-based tribofilms revealed bulk-phase hardness values for glassy-boron trioxide of 1.5-2.0 GPa [11-12], β-boron trioxide of 16 $\pm$ 5 GPa [11], γ-boron trioxide (30 $\pm$ 5 GPa) [11], orthoboric acid (1.5GPa) [12], iron borides (1.4–21 GPa) [13, 14] and boron nitride (>7.0 GPa) [15-16].

3. PROBLEM DEFINITION OR EXPERIMENTAL WORK

Micro-hardness characterization of tribofilms from tribenzyl borate (organic borate ester) gave higher hardness than the steel substrate by a factor of 1.6 [5] while another test results indicated that tribofilms from metal borate nano-particle was not harder than the steel substrate [17]. However, these tests were carried out under a different set of conditions. The two studies had used different types of borate ester additives; one is organic and the other is inorganic. In addition, the two studies had used different techniques to analyze the hardness of the tribofilms formed by the borate esters. With this inconclusive results with regards to the mechanical properties of tribofilms from borate esters used as additives in lubricating oils, it is imperative to determine the tribological properties of the borate esters in comparison to ZDDP and also elucidate on whether their tribofilms have the ability to release absorbed frictional energy when moving across elastic asperity contacts

One of the objectives of this study is to investigate the tribological performance of organic and inorganic borate ester in comparison to ZDDP on AISI 52100 steel-grade surfaces under boundary lubrication conditions. Another objective is to use instrumented Nano-indentation to investigate changes in elastic modulus with the hardness of the tribofilms from the antiwear additives. The ratio of reduced elastic modulus to hardness elastic known as strain to failure characteristics (E'/H) of the tribofilms could provide a better understanding of the Nano-mechanical properties of the borate esters concerning their tribological behavior. Also, given environmental restrictions limiting the use of conventional lubricant additives, this study will consider boron-containing antiwear/EP lubricant additives as a possible alternative.

3.1 TEST MATERIALS

The ferrous materials chosen for this study are AISI 52100 steel pins and plates. The plates were rectangular in cross-section with dimensions measured as 15 x 6 x 3 mm^3. Cylindrical cross-sectioned pins of lengths of 20 mm and 6 mm diameters were machined on the sliding end to a 40 mm radius of curvature and surface roughness of 0.3-0.5 µm range. By using a pneumatically actuated automatic polishing machine with P120 and P320 polishing abrasive papers sequentially, a surface roughness range of 0.4-0.6 µm was achieved for the plates. Nano-indentation hardness measurements of the steel samples gave an elastic modulus of 209 $\pm$ 39.3 GPa and hardness of 9.21 $\pm$ 3.2 GPa.

3.2 TEST LUBRICANTS

Three separate antiwear/EP lubricant additives were evaluated. Each lubricant additive was based on a wax-free, high-performance synthetic hydrogenated olefin polymer (Polyalpha olefin oil). A measure of momentum transfer rate through the base oil at 100℃ is about 6mm^2/s. Two of the antiwear lubricant additives are boron-based, while the third is a commercially available secondary ZDDP. One of the two boron-containing lubricant additives is an organo-borate ester composition (ABE) supplied by R.T. Vanderbilt Company, Inc. Norwalk, CT. The other boron-based additive is composed of potassium borate nanoparticles dispersed in a fatty acid ester carrier (KBE); supplied by ARCHOIL Inc. Wallingford, CT. US with molecular structures shown in Fig 1.

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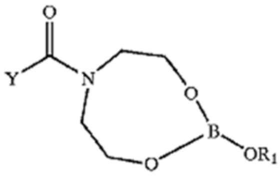

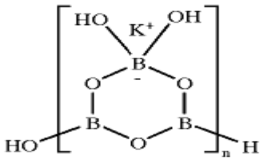

(ABE) **(KBE)**

Figure 1: Molecular structure of the boron additives [18, 19]

For ABE, R_1 = H or C_xH_y for which; x=1 to 60 and y = 3 to 121, Y = represents a glycerol ester of higher fatty acids containing at least 12 carbon atoms; derived from vegetable oils from coconut, corn, cottonseed, linseed, peanut, soybeans, and sunflower seed [18]. However, KBE has values of n in the range of 1.0 to 10 with the specific ratio of potassium to boron limited to between 1: 2.75 and 1:3.25 while the ratio of hydroxyl to boron ranges from 1.2:1 to 2.2: 1 [19]. The physical properties of the lubricants used in this experiment as provided by the manufacturers are highlighted in Table 1. The inclusion of these additives in PAO at 0.5wt%, 1.0wt%, and 2.5wt% concentrations did not result in significant changes to the base oil viscosity.

Table 1 Physical properties of the test oils

Description	ABE (Only)	KBE (Only)	ZDDP (Only)	PAO (Only)
KV at 40℃ (mm^2/s)	458		407	31.0
KV at 38℃ (mm^2/s)	-	32	-	-
KV at 100℃ (mm^2/s)	22.3		13.5	5.9
Density (g/cm^3) at 15.5℃	0.990	-	1.060	0.826
Density (g/cm^3) at 25℃	-	1.0	-	

3.3 FRICTION MEASUREMENTS

In this study, a reciprocating pin-on-plate test rig was used to produce boundary films from sliding steel-steel tribo materials lubricated by antiwear/EP lubricant additives in PAO. The tribometer consists of a multipurpose adjustable pin holder that holds the pin rigidly against a reciprocating flat plate specimen of different sizes. It is also equipped with a force-post assembly with a bi-directional load cell in the range of 58.8 N with a combined error of -0.0037 N. The combined error is the combination of non-linearity, temperature effect, load cell sensitivity, and hysteresis [20]. The load cell measures frictional force, where signal conversion from analog to digital takes place using a data acquisition card (DAQ). The digital data will then be finally processed and stored in a LABVIEW Window-based software program on a computer. With a stroke length of 10 mm, readings of frictional force are taken every 10 min. for 2 s (120 points), corresponding to two-stroke cycles. The frictional force is the average of the 120 data points which is used by the software program to calculate the friction coefficient. This average friction coefficient for the last hour of each experiment is plotted as a function of time for the duration of the test. The schematic diagram of the pin-on-plate reciprocating apparatus is shown in Fig 2.

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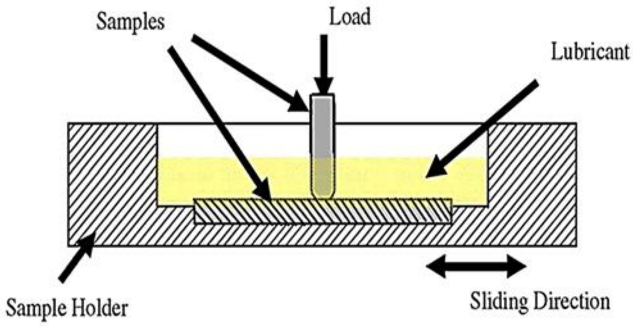

Figure 2 A schematic view of the pin-on-plate reciprocating test rig [21]

The relative tribological performances of the boundary films formed with these boron-based additives were to be compared to ZDDP with additives concentrations at 0.5 wt%, 1.0 wt%, and 2.5 wt% in PAO base oil. In determining the boundary lubrication regime under which the test was performed, the dimensionless film parameter, the lambda ratio (λ) is evaluated as the ratio of the composite root mean square surface roughness obtained from the surface roughness (R_Q) of each starting steel sample in tribo-contact as shown in 1 to the minimum film thickness ((h_{min}) defined for point contact by 2.

$$\sigma_{rms} = \sqrt{{R_{Q1}}^2 + {R_{Q2}}^2} \qquad 1$$

$$h_{min} = 3.63 \times R_Q \times U_{\Sigma}^{0.68} \times G_{\Sigma}^{0.49} \times W_{\Sigma}^{0.073} \left(1 - e^{0.68k}\right) \qquad 2$$

Where the respective dimensionless speed, material, and load parameters are $U_{\Sigma} = (\eta_o . u_s / E.R)$, $G_{\Sigma} = \alpha_p . E$ and $W_{\Sigma} = (F/E.R^2)$. In addition, R represents the radius of the pin (40mm), η_o is the viscosity at ambient pressure assumed to be the same for the three additives (4.03 x 10^{-3} Pa.s at 100°C) [20, 22], u_s is the entrainment speed (0.02m/s), α_p is the viscosity-pressure coefficient (11 x 10^{-9} Pa^{-1} at 100°C), F is the normal load (176 N), k is the elliptical parameter (1.0339 for point contact), E* is the effective modulus of elasticity (230 GPa) obtained from Poisson's ratio of 0.3 for steel. By using a load of 176 N, the initial maximum Hertzian contact pressure was evaluated to be 0.66 GPa, while the minimum film thickness is calculated using Hamrock and Dawson equation for elasto-hydrodynamic point contact in 2. The lambda ratio must be less than unity, for the tests to be in a boundary lubrication regime. In this case, the calculated film thickness parameter was less than unity (0.0041).

Tests were carried out at a maximum sliding speed of 0.02 m/s, stroke length of 10 mm, and frequency of 1 Hz for six hours' duration. By using 3 ml of lubricant, the bulk temperature within the sample holder is heated and regulated at 100℃ throughout the test using a thermocouple connected to the lubricant bath. For good repeatability, the tests were replicated three times with a standard deviation of ± 0.003 of friction coefficient in the last hour of the six hours' tests.

3.4 WEAR MEASUREMENTS

At the end of each test, the pin and plate samples were dipped in n-heptane for 1-2 s to remove excess oil from the surface before each surface analysis. Wear measurements were carried out to determine the antiwear effectiveness of the additives in the lubrication system. The wear volumes on the wear scars for pins and plates were measured after the tribological tests by using the NPFLEX optical white-light interferometry (Bruker Inc.). The dimensional wear coefficients were calculated from Archard's wear equation as shown in 3.

$$V_{PL} = k_{PL} \times F_N \times L \;\; ; \; V_{Pi} = k_{Pi} \times F_N \times L \qquad 3$$

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Where the; measured wear volumes for both the plates and pins are, V_{Pi} V_{PL} in m^3 Dimensionless wear coefficients for plates and pins being k_{PL} and k_{Pi} in m^3/N-m. The normal load is denoted by F_N in Newton and sliding distances are represented by L in meters.

3.5 NANO-INDENTATION EXPERIMENTS

In characterizing the hardness and elastic modulus of the tribofilms formed from the tribological tests, an instrumented Nano-indentation technique was employed using the Nano-mechanical test instrument from Micro-Materials Ltd on the wear tracks formed by plate samples of ABE, KBE, and ZDDP tribofilms. The instrument is equipped with an optical microscope for sample imaging before the test to locate a flat indent area on top of the tribofilms. In addition, the indenter used for this instrument is equipped with a Berkovich diamond tip with a nominal radius of curvature in the range of 50 nm that was calibrated before the test to determine the area function in the contact depth.

The hardness, reduced elastic modulus, and other mechanical properties were determined from the load-displacement curves using an algorithm based on the method of Oliver and Pharr [23]. Where the hardness (H) was calculated by dividing the maximum indentation load by the resulting projected contact area at this maximum indentation load; provided by the area function algorithm. In addition, an estimation of the reduced elastic modulus was possible from the slope of the unloading part of the indentation curves at the maximum indentation load

In this experiment, a series of sequential indentations around the same location on the wear track was made at various indentation loads which were 50 μm apart on various worn samples from the three antiwear additives. The loading and unloading time was 10s with each at 0.5 µm/s velocity and sequential loading rate of 0.5mN/s based on ISO 14577-1 protocol.

Indentations at 100 indents on a flat section of the central part of the wear scars were carried out on the wear scars of tribofilms formed on reciprocating steel plates/pins lubricated by oils containing ABE, KBE, and ZDDP additives at different concentrations (0.5, 1.0 and 2.5 wt.%). The mechanical properties measurements at an indentation load of 600µN and maximum indentation depths in the range of 10-50nm were utilized but limited to about 25% of the estimated thicknesses of the tribofilms to capture the nature of this influence.

An assessment of the tribofilms' resistance to plastic flow due to sliding was possible through information provided from the variation of the ratio of hardness to reduced elastic modulus [24-28]. A measure of the wear resistance ability of the tribofilms of boron antiwear/EP additives concerning its mechanical properties is compared to that obtained for ZDDP using the material property factor of plasticity index.

4.0 RESULTS AND DISCUSSIONS

4.1 TRIBOLOGICAL PERFORMANCE - FRICTION, AND WEAR

The instantaneous coefficient of friction response of the tribofilms formed by 0.5 wt.% of each additive in the base oil is shown in Figure 3 (a) while samples of typical wear scars from optical interferometry experiment for the wear scars of the worn plates samples from the three antiwear additives are shown in Figure 3 (b). The results of the changes in the instantaneous coefficient of friction with time as indicated in Figure 3 (a), shows that at 0.5 wt.% additive concentration, the running-in period for tribofilms formed by the borate ester (ABE) is shorter than those formed by KBE (metal borate ester) and ZDDP. In addition, the steady-state coefficient of friction of the tribofilms formed by the ZDDP at low concentrations is in good agreement with that obtained in previous studies [21, 29] with the Amine Borate Ester providing about 26% lower friction than ZDDP tribolayer.

A relative comparison of the wear tracks formed on the plates lubricated by oils containing ABE additives to KBE and ZDDP is shown in Figure 3(b). The results indicated that at 0.5 wt.%, the reacted tribolayer formed by ABE additive in the base oil can provide better friction-reducing characteristics and wear protection on AISI 5210 steel surface than KBE and ZDDP tribofilms.

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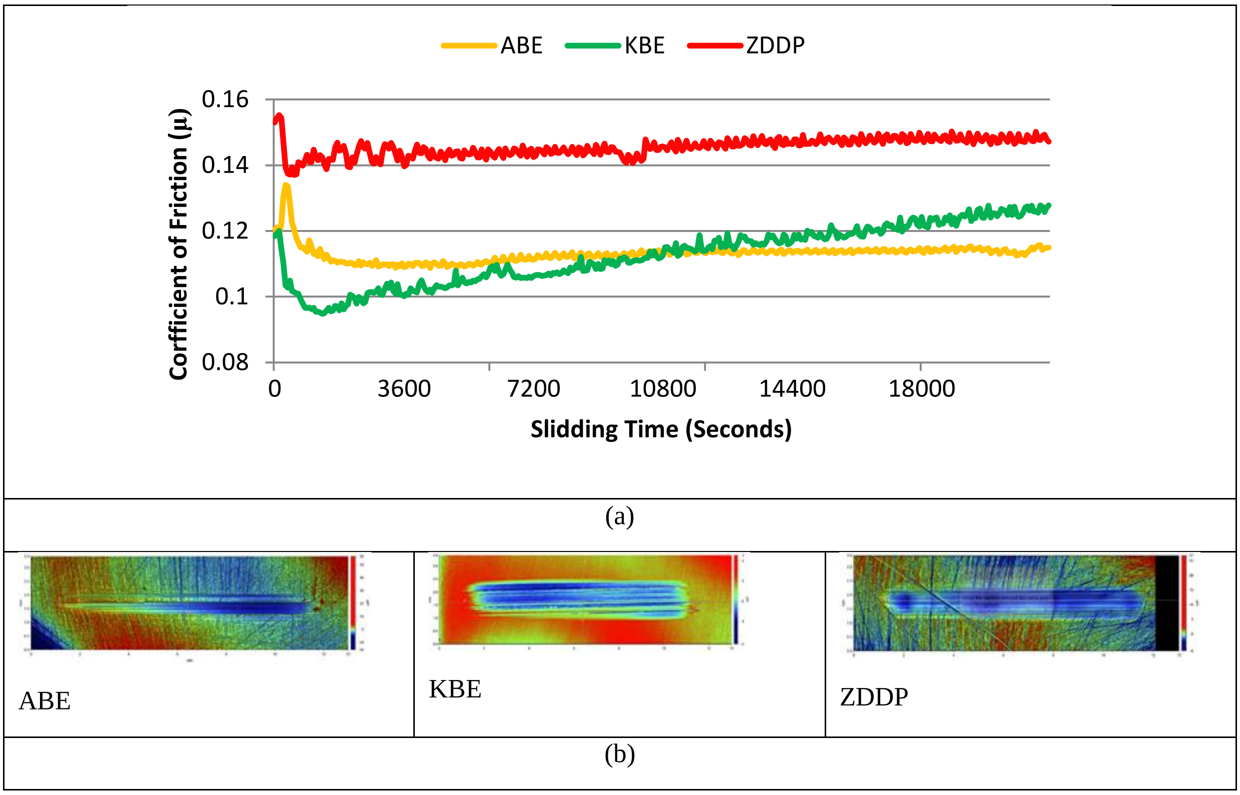

Figure 3 Tribological test results at 0.5wt.% (a) friction behavior and (b) plate wear scars

Figure 4 and Figure 5 show the averages of the coefficient of friction and wear rates provided by the tribofilms for each of the three additives at different additives concentrations on steel plates and pins respectively. The results indicated that at 0.5 wt. %, tribofilms formed by ABE additives gave a significant difference in coefficient of friction compared to KBE and ZDDP. However, at higher additive concentrations, this difference was not greatly significant.

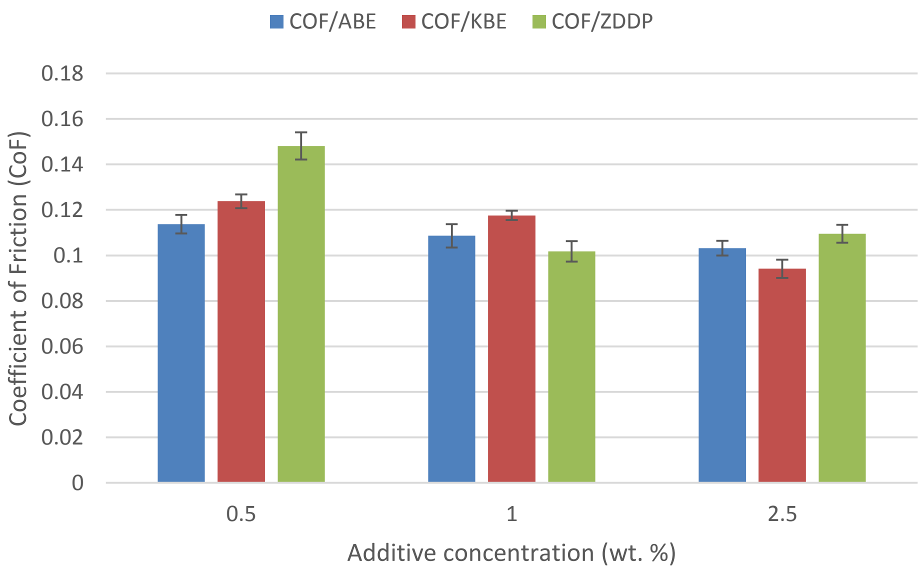

Figure 4: Variation in average coefficient of friction with additive concentration

The wear rates of the plates and pins shown in Figure 5 indicated that at 0.5 wt.% additive concentrations, tribofilms formed by oils containing ABE additive gave the lowest wear rates on both plates and pins, while the highest wear rates occurred on the pins lubricated by oils containing KBE at 0.5 wt. % in the base oil.

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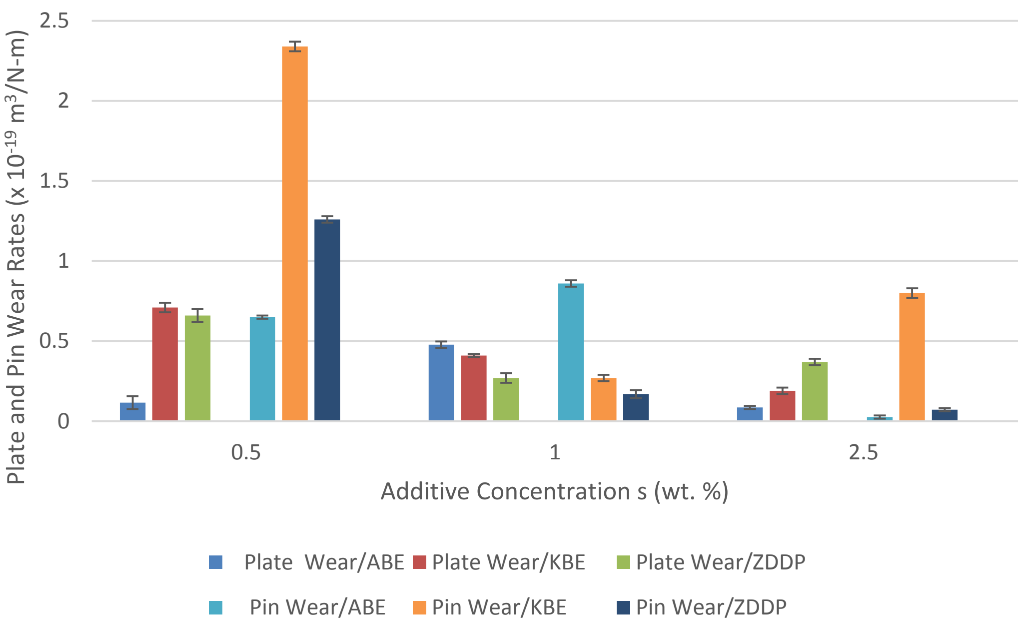

Figure 5 Changes in wear rates of steel samples at different additive concentrations

This is unlike the tribolayer formed by KBE and ZDDP additives in the oil. As the additives concentrations in the oil are increased, the wear rates on the plates reduce, except for the wear rates on the pins at 0.5 wt. % for KBE, 1.0 wt.% for ABE, and 2.5 wt.% for KBE tribolayers are consistent with the observations from similar studies [30, 31]. The pin counter-face of the tribo-pair lubricated by the borate additives appears to tend to give higher wear rates than ZDDP; especially, the Nano-particles metal borate (KBE).

4.2 NANO-INDENTATION RESULTS

The results of Nano-indentation measurements yielded force hysteresis curves which after eliminating pop-ins and pile-ups curves [32, 33] gave hardness values and reduced elastic modulus (E*); obtained from indentation modulus (E) and Poisson ration (v), as E* $= E/(1 - v^2)$. Figure 6 represents typical loading and unloading curves from nano-indentation experiments that permit an estimation of the reduced elastic modulus at maximum indentation load. A measure of the tribofilms elastic strain to failure characteristics due to sliding was determined by evaluating the ratio of elastic modulus-to-hardness (material factor of the plasticity index = E*/H) [25, 34] for the worn plate samples of different antiwear additives formed at various concentrations (0.5, 1.0 and 2.5 wt. %). These are all compared to the plasticity index of unworn steel plate samples shown in Figure 7.

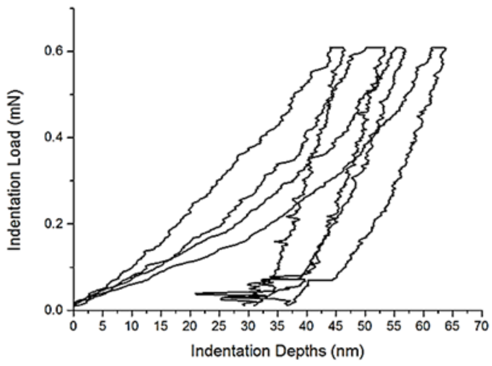

Figure 6 Nano-indentation loading and unloading curves

The results shown in Figure 7 indicated that elastic strain to failure of the tribofilms formed under load which can deflect with the substrate's deformation is higher at 0.5 and 2.5 wt. % than at 1.0 wt. % additive concentrations. At 1.0 wt. % of KBE additive in the oil, the plasticity index of tribofilms formed was 21.0 compared to 20 for the steel substrate. This is an indication that tribofilms formed on AISI 52100 steel tribo-pair lubricated by both borate additives and ZDDP in lubricating oils are heterogeneous and 'aluminum-like' [32] when compared to the substrate.

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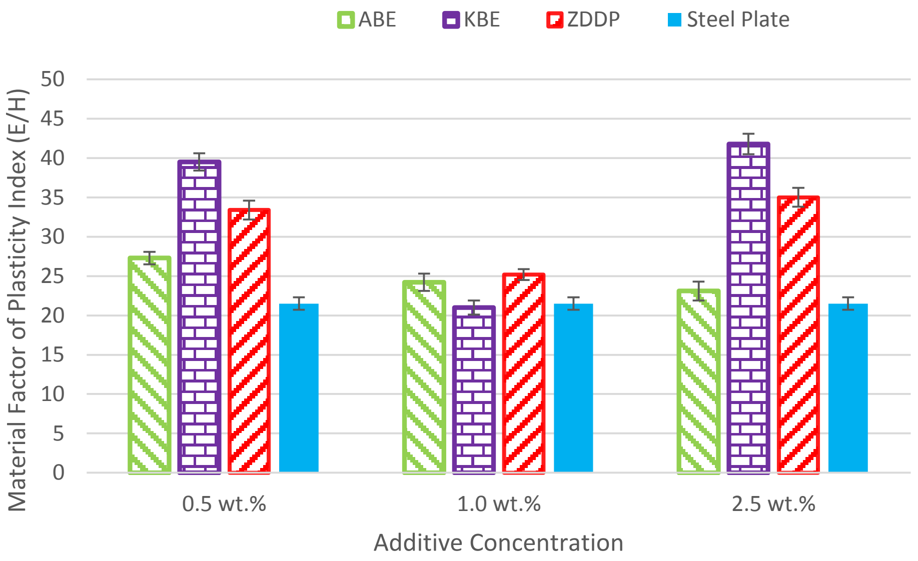

Figure 7 A comparison of the material factor of plasticity index of wear scar regions for tribofilms formed by different additives at different concentrations

4.3 DISCUSSION

The results of the friction coefficient performance of the boron-containing additives shown in Figure 4 indicated that the tribo-layers formed at the low additive concentration on AISI 52100 steel surfaces are more lubricious than ZDDP. This could be attributed to the different friction-reducing mechanisms of the borate esters additives compared to ZDDP. The friction-reducing mechanism of borate-containing oils was attributed to boric acid (H_3BO_3) formation when diboron trioxide (B_2O_3) reacts with moisture in the air of the surrounding environment. However, the lubricious boric acid is known to reduce friction based on a weak van der Waal mechanism [35-37] and edge-passivation or edge-unlocking mechanism [38, 39] where the passivation of high energy edge sites on boric acid by physisorbed water molecules that allows lamellar sheets of boric acid to easily shear to provide friction reduction [38]. The antiwear behavior of borate-containing tribofilms is more different on the plates than pins as additive concentration increases as shown in Figure 5. This could be related to dissimilar Nano-mechanical characteristics of tribofilms from these antiwear additives as shown in Figure 7.

The tribofilms formed under boundary-lubricated conditions at different additive concentrations by the borate additives gave comparable wear-resistant behavior to ZDDP on the plates. Enhanced antiwear performance by tribofilms from organo-borate additive (ABE) was attributed to the formation of wear-resistant boron oxide-iron oxide glass [10]. On the other hand, tribofilms from metal borate nanoparticle dispersion are known to provide wear-resistant due to the shear effect and tribo-chemical reaction between boron oxide and metallic iron to form iron borides [40].

In this study, a point contact between the plates and the pins was maintained. This may not be the case if it is line contact. For the borate additives, the formation of wear-resistant boron oxide-iron oxide glass will be limited to the friction zones. On the plates, this will be distributed over a relatively larger area under load compared to the pins. Hence, some of the abrasive iron oxides outside the contact points of the pins that are unloaded may not be digested by diboron trioxide in the additives to give higher wear rates. In this study, a higher wear rate was more pronounced in oils containing KBE additives than in ABE. The results from this study about the antiwear behavior of tribolayer formed by metal borate as lubricant additives as dependent on its concentration in the oil are supported in the literature could be affected by its [31, 41].

The tribological results shown in Figure 4 and Figure 5 indicated that at low additive concentrations, friction and wear-resistant performance of ZDDP tribofilms was below those of the borates. At this low additive concentration, the amount of sulfur and phosphorus within the tribofilms is reduced. The results from Figure 7 indicated that a mechanically protective film of ZDDP is formed. However, the removal of abrasive iron oxide could be slower due to a reduction in zinc polyphosphate polymer glass to reduce wear as suggested in the literature [42]. Hence, complying with environmental regulations on emission control in IC engines could lead to poor tribological performance, unlike the borates that do not have any zinc, phosphorus, or sulfur in their composition.

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The changes in the Nano-mechanical properties of the tribofilms formed by the additives are greatly affected by additive concentrations. A result from a similar study on ZDDP additive based on test durations had the average E/H around 25.3 [24], while another study got 24.7 [43]. However, diboron trioxide (B2O3); the major component of the borate additives in humid air was shown to have an E/H of about 23 [12]. In relating the wear of contacting surfaces in relative motion to the total area of contact, Archard's assumed the contact to be entirely plastic. However, asperities were identified in this study to deform plastically initially as shown in Figure 3 (a) during the running-in process but were noticed to reach a steady state in which the load was supported elastically [44] as shown in Figure 7. This indicated that antiwear films formed by the borates can deflect with the substrate's deformation as ZDDP exhibits similar Nano-mechanical properties.

5.0 CONCLUSIONS

The friction coefficient and wear characteristics of the tribofilms from boron-containing antiwear/EP additives were compared to ZDDP in PAO on the steel-steel tribo-system in this study. Nano-mechanical characterization of the boundary films along with tribological test resulted in the following conclusions;

- At low additive concentrations, some borate esters as antiwear/EP lubricant additives can provide better friction and wear performance to the conventional ZDDP.
- The tribofilms formed by all the antiwear additives are heterogeneous with mechanical properties that vary with additive concentrations.
- The mechanical protective films formed by the borate additives did not have elastic strain-to-failure characteristics lower than the steel substrate.
- A way of preventing the early deactivation of the emission control system in lubrication oils of IC engines is the use of boron-containing oils as antiwear additives in lubricant formulations.

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