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Effect of steel hardness on soot wear

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ABSTRACT

Due to incomplete combustion, high levels of soot can accumulate in engine lubricants between drain intervals. This soot can promote wear of engine parts such as timing chains and cam followers. One standard approach to reducing wear is to increase the hardness of the rubbing components used. According to the Archard wear equation, wear rate should be broadly inversely proportional to hardness.

To explore this approach for controlling soot wear, wear tests have been conducted in a High Frequency Reciprocating Rig (HFRR) with HFRR steel discs of various hardness against a hard steel ball. Carbon black (soot surrogate) dispersions in model lubricants based on solutions of ZDDP and dispersant in GTL base oils have been studied. Wear volumes have been measured and wear scars and tribofilms analysed using scanning white light interferometry and SEM-EDS.

It is found that, while most oils show wear that reduces with increasing hardness, for blends that contain both ZDDP and carbon black, wear rate markedly increases with disc hardness as the latter approaches the hardness of the ball. The results support the prevalence of a corrosive-abrasive wear mechanism when carbon black and ZDDP are both present in a lubricant and suggests that selection of very hard surfaces may not be a useful way to control soot.

1. Introduction

High levels of soot in engine lubricants are frequently reported to induce high wear rates on engine components. Engine bearings, camshaft and crankshaft, piston rings, cylinder walls and timing chain are some of the engine parts that are most affected by wear induced by soot [1–3].

There has been extensive research to determine mechanisms by which dispersed soot particles in lubricants increase wear. Early work focussed on a possible negative impact of soot on the effectiveness of the anti-wear additive in engine oil and it was proposed that soot might adsorb anti-wear additives [4,5] or compete with them for rubbing surfaces [6]. Other suggested mechanisms were enhanced oil degradation by soot [7], metal reduction from anti-wear Fe_3O_4 to prowear FeO promoted by soot [8], lubricant starvation due to increased viscosity with high soot loading [9–11] and abrasion, either of the rubbing surfaces [12–14] or anti-wear film [4,12–21] by the soot particles.

In recent years attention has focussed on the concept that soot particles abrade ZDDP films as rapidly as they form, leading to a high rate of corrosive-abrasive wear. The main evidence for this is that when both ZDDP and the soot surrogate carbon black are present in a lubricant, this can lead to much higher wear than if either ZDDP or carbon black is absent. Booth et al. studied the additive interactions with soot using factorial analysis which showed that primary ZDDP appeared to increase pin wear [22]. He observed that blends containing both ZDDP and carbon black exhibited high wear on the ball, which he ascribed to due to immature anti-wear film formation. In 2009 Olomolehin et al. investigated the influence of carbon black and other nanoparticles on wear in antiwear additive-containing model lubricants [19]. They found that when carbon black was added to an oil containing ZDDP, the combination gave more wear than when no ZDDP was present; *i.e.* ZDDP became prowear. They suggested an adhesive corrosive-abrasive mechanism in which the carbon black removes the initial iron sulphide and phosphate antiwear film as rapidly as it forms, leading to a rapid loss of ferrous compounds and thus high wear levels. Very recently Salehi et al. have shown a similar wear mechanism for carbon black in formulated engine oil [21].

The process of obtaining engine soot from lubricants is time-consuming and the soot extracted will be contaminated by additives specific to the lubricant and fuel used. Soot can also vary in the degree of graphitization and particle size depending on engine conditions. Therefore a soot surrogate such as furnace or channel carbon black is generally used for wear studies. There has been some discussion in the literature concerning the similarity of carbon black with soot. It has

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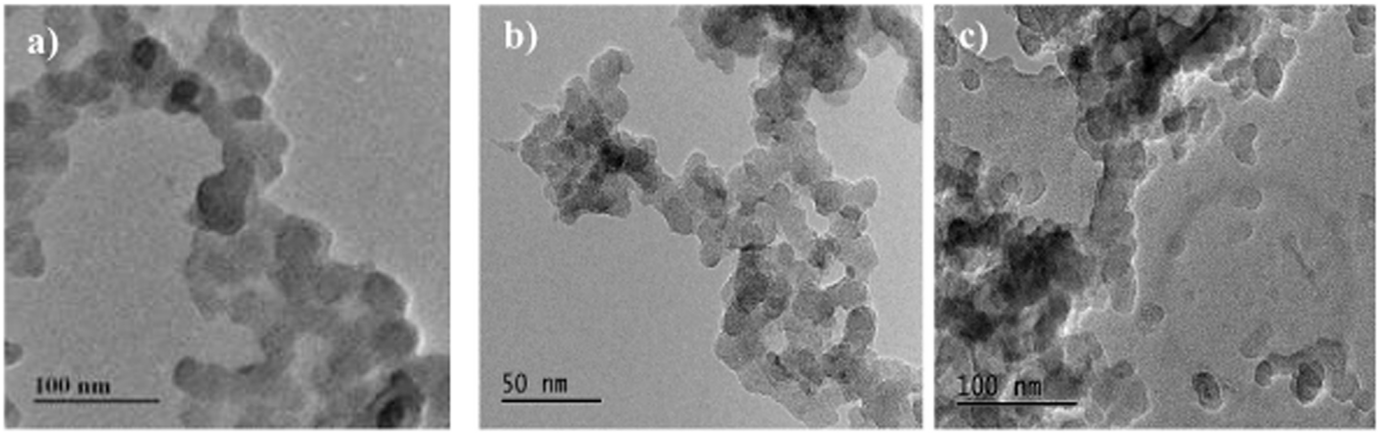

Fig. 1. TEM pictures of **a)** engine soot extracted from used diesel engine oil **b)** furnace CB (Cabot Vulcan XC72R) **c)** soot collected from cylinder walls of diesel engine.

Table 1
Test materials.

Base Oil	Gas to Liquid (GTL) 18.3 cSt at 40 °C, 4.2 cSt at 100 °C
ZDDP	Secondary zinc dialkyldithiophosphate antiwear additive at 0.08 wt% P
Dispersant	Polyisobutylene succinimide polyamine dispersant at 0.02 wt% N
Carbon Black	Carbon black Cabot Vulcan XC72R (soot surrogate) at 5 wt%
Ball hardness (HV)	880 ± 3
Disc hardness (HV)	196 ± 2, 295 ± 2, 398 ± 13, 658 ± 25, 772 ± 0.57
Ball Roughness, Ra (nm)	5 ± 0.1
Disc Roughness, Ra (nm)	5.6 ± 0.4 (196 HV), 6.2 ± 0.1 (295 HV), 4.9 ± 0.3 (398 HV), 5.8 ± 0.5 (658 HV), 5.1 ± 0.2 (772 HV)

* ± is standard deviation of repeats.

Table 2
HFRR wear test conditions.

Load (N)	3.92
Maximum Hertz contact pressure (GPa)	1.03
Frequency (Hz)	50
Stroke length (mm)	1
Test temperature (°C)	100
Test duration (min)	60

been suggested that some carbon blacks are similar in composition, size and morphology to engine soot [22] although considerable differences in surface properties have been noted between carbon blacks and exhaust soot, especially with respect to their combustion properties and toxicity [23–25]. In this study the furnace carbon black Cabot Vulcan XC72R was selected as being quite similar in primary particle size, structure, porosity and carbon content to engine soot [22] and because it has been used in previous soot-wear studies [19]. It also forms very similar secondary particles, as shown in Fig. 1, which makes it a realistic soot-surrogate in morphological terms.

In tribology in general, the material property that is found to improve wear resistance most reliably is hardness. This means that in engineering practice, one recognised approach to overcoming wear problems is to increase the hardness of the solid materials used. According to the Archard wear equation, the volume of material loss (V) during rubbing is directly proportional to the applied load, W, and the sliding distance, s, and inversely proportional to the hardness of the material, H:

$$V = KWs/H$$

where K is a wear coefficient. This equation is only approximate for most systems but can be derived theoretically from models of abrasive and adhesive wear [26].

No research appears to have been published to investigate the impact of hardness on soot wear although the hardness of engine components is considered crucial for the lifetime and durability of the engine. The minimum requirement limits of hardness for crankshafts and camshafts set by manufacturers and international standards range between 500 and 570 HV [27,28]. It is difficult to find definitive hardness values of some engine components since engine manufacturers hold these confidential. However, the research literature mentions finger followers in overhead camshafts with hardness of approximately 800 to

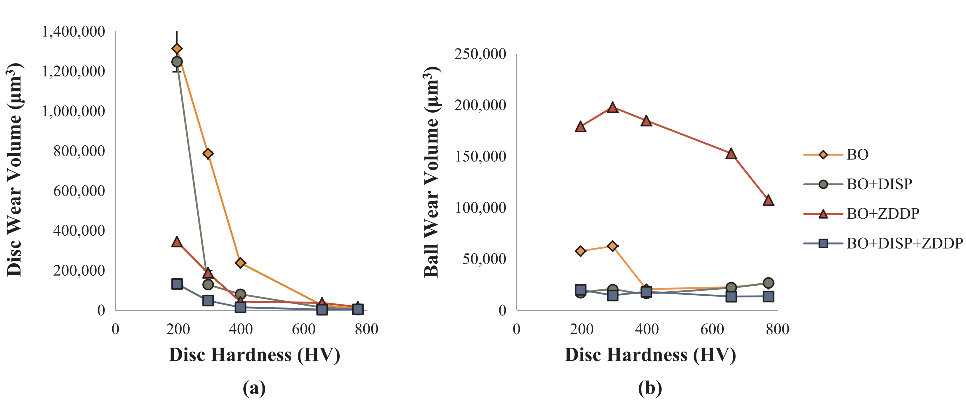

Fig. 2. HFRR disc (a) and ball (b) wear volumes from tests with different disc hardness for oils without CB.

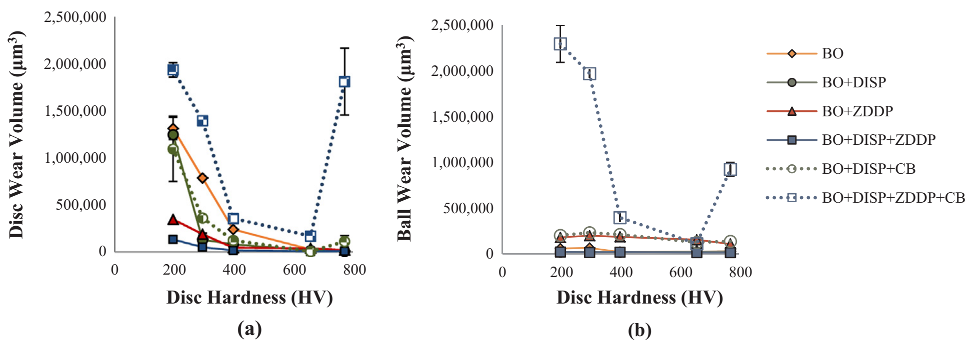

Fig. 3. HFRR disc (a) and ball (b) wear volumes with various disc hardness for all oil formulations. CB-containing blends are shown as dotted lines.

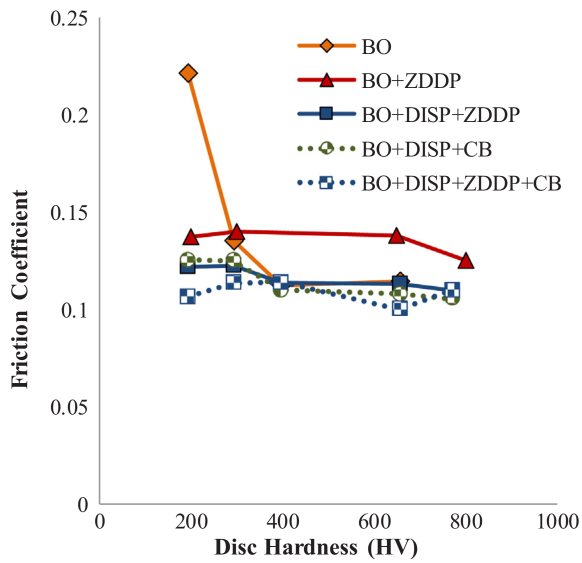

Fig. 4. HFRR average friction coefficient results of all oil formulations at various disc hardness.

850 HV [29] and timing chains of between 500 and 800 HV [30,31]. Pistons and piston rings have hardness ranging between 230 and 600 HV [32].

It is very difficult to measure the hardness of soot or carbon black. In early work Rounds suggested a very low value of less than 1 Moh, corresponding to about 30 HV, but this appears to assume an equivalence between soot and graphite [33]. Jao et al. used low loss electron energy-loss spectroscopy (EELS) to estimate the density of various carbon materials. Assuming a linear relationship between density and hardness they determined hardness values for soot, centred around 800 HV [34]. Quite recently Bhowmick and Biswas employed nanoindentation to estimate the hardness of soot from a flame and diesel soot [35,36]. While acknowledging the uncertainty of this approach [35] they estimated hardnesses in the range 350–500 HV for flame soot and 500–650 HV for diesel soot. Based on these it is probable that the hardness of carbon black lies in the range 300–600 HV.

The aim of this study is to explore the impact of material hardness on soot wear, both from the practical point of view and also to learn more about the prevailing mechanism of wear. Ball on disc reciprocating wear tests have thus been carried out with different hardness discs using partially-formulated engine oils containing base oil, dispersant, ZDDP and with dispersed carbon black as a soot surrogate.

2. Material and methods

2.1. Experimental materials

Samples containing base oil, anti-wear additive and dispersant were blended and stirred using a magnetic stirrer at 70 °C for 30–40 min until the solution was fully homogeneous. Carbon black (CB) was dried in an oven at 100 °C, cooled, and added to the samples and stirred on the magnetic stirrer for 30 min at 70 °C. The resulting dispersions were tested immediately. Table 1 lists the lubricant additives and test materials used. Lubricants studied were (i) base oil (BO), (ii) BO + dispersant, (iii) BO + ZDDP, (iv) BO + dispersant + ZDDP, (v) BO + dispersant + CB and (vi) BO + dispersant + ZDDP + CB. The wear tests were performed in a reciprocating ball on flat rig (HFRR, PCS Instruments, Acton, UK) using various disc hardnesses. The discs and balls specimens are made of LESCALLOY® 52100 VAC-ARC® high performance bearing steel. The balls were all of hardness of 880 HV while the discs were hardened at values ranging from 200 to 800 HV to span the range of engine component values. The different hardnesses were achieved by partial annealing of the hardened specimens followed by polishing. Clearly the rate of wear will be influenced by material composition as well as hardness but by using specimens of the same composition this study aimed to focus on the influence of hardness alone.

2.2. Experimental methods

2.2.1. High frequency reciprocating rig (HFFR) wear tests

The HFRR is a controlled reciprocating friction and wear testing device employed to assess the performance of fuels and lubricants. The test uses a 6 mm diameter steel ball loaded and reciprocated against the flat surface of a stationary steel disc immersed in lubricant. The HFRR test conditions are listed in Table 2.

All the tests were repeated twice and error bars using standard error, $\sigma/\sqrt{n}$, were plotted for each average value where σ is the standard deviation and n is the number of repeats. 95% confidence intervals were estimated for each pair of repeats using a t-distribution:

$$\bar{x} \pm t_{n-1}\frac{\sigma}{\sqrt{n}},\ \text{where } \bar{x} \text{ is the average value.}$$

All the average values fell within their estimated confidence intervals.

2.2.2. Scanning white light interferometer (SWLI) wear measurement

At the end of each test, the ball and disc were removed from the test rig, rinsed with toluene and iso-propanol, and then treated with a 0.05 wt% solution of ethylene diamine tetraacetic acid (EDTA) for 60 s. The last of these was to remove any ZDDP anti-wear film on the surfaces since this can interfere with optically-based wear measurement [37]. Topography images were then obtained and analysed to determine wear volumes and profiles of the wear scars on the ball and the disc using a SWLI Veeco Wyko model NT9100. For this project the machine was set in Vertical Scanning Interferometry (VSI) mode, calibrated to measure rough surfaces with a nanometre detection range.

The mean sliding speed in the HFRR under the test conditions used was 0.1 m/s, so the mean entrainment speed was 0.05 m/s. EHD film thickness measurements were made using optical interferometry on the soot-free test oils in pure rolling conditions at 100 °C and showed films

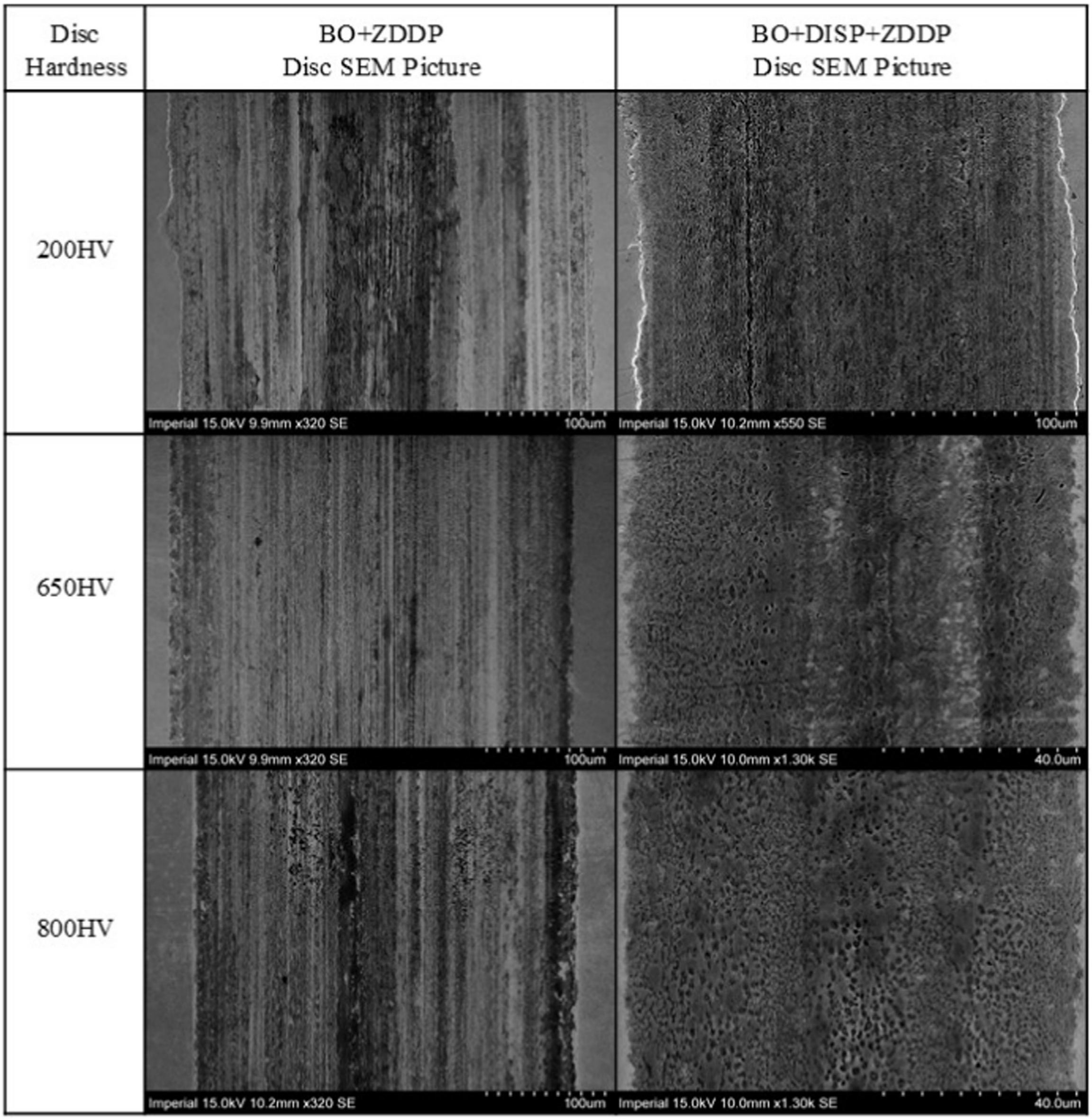

Fig. 5. SEM pictures of different hardness discs tested with BO + ZDDP and BO + DISP + ZDDP oils.

of thickness 4 nm and 5 nm at this entrainment speed for base oil and dispersant solution respectively. Allowing for the difference in ball radius between the HFRR (3 mm) and EHD tests (8.5 mm), this implies a mean lambda ratio of *ca* 0.2 at the start of an HFRR test, indicative of boundary lubrication conditions for all test fluids.

2.2.3. SEM-EDS analysis

An HITACHI S-3400N SEM (Scanning Electron Microscopy) was used to capture high resolution images of the wear scars and the tribofilm topography when ZDDP was used in the lubricant. Some imaging was also carried out using an LEO Gemini 1525 FEG-SEM (Field Emission Gun-SEM). This has higher resolution and was able to identify CB nanoparticles on the surface. EDS (Energy Dispersive x-ray Spectroscopy) from Oxford Instruments X-ray System INCA, was employed to detect any ZDDP film on the surfaces and also to analyse the chemical properties of anti-wear films. For EDS analysis, the same square area was selected inside the wear scars for all the samples. An accelerating voltage of 15 keV and a working distance of 10 ± 1 mm were used.

3. Results

3.1. HFRR results

A standard HFRR ball with a measured hardness of 880 HV was used in all the tests, while the disc hardness ranged between *ca* 200, 300, 400, 650 and 800 HV. Fig. 2a summarises the effect of disc hardness on disc wear volume for different oil formulations without CB. For all the oils, wear reduces as hardness increases from 200 to 400 HV, broadly in accord with the Archard wear law. For softer specimens, wear is much lower with the oils that contain ZDDP than those that do not, and lowest for the blend with ZDDP and dispersant. With hard discs of 650 and 800 HV, all the oils give similar, very low wear.

Fig. 2b shows the corresponding ball wear volumes for the oil formulations without CB. It should be noted that the wear volume scale is much smaller than in Fig. 2a, as expected since the ball is hard in each case. The wear volumes of the balls are relatively independent of disc hardness. For most oils, wear is very low, but interestingly it is highest for the oil containing only ZDDP. As discussed later in this paper, since the same position on the ball is in continuous contact throughout a test, a protective film is unable to stabilise on the ball surface, and this may

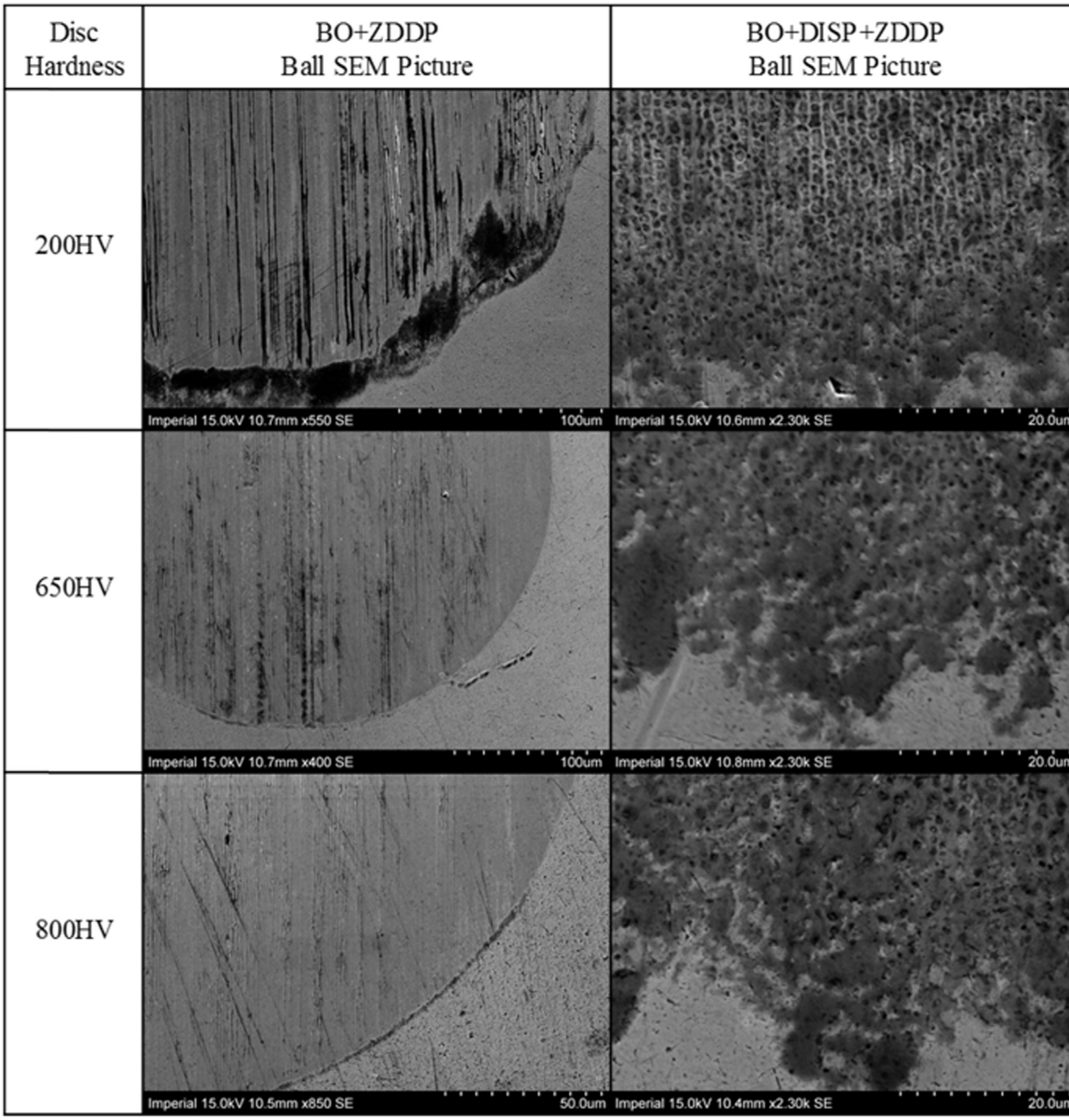

Fig. 6. SEM pictures of balls from tests with different hardness discs using BO + ZDDP and BO + DISP + ZDDP oils.

lead to continuous mild corrosive wear. It appears that dispersant is able to afford enough boundary film protection to mitigate this. This differs from what is observed in rolling-sliding contacts conditions where dispersant partially removes ZDDP films [38].

Fig. 3a shows the impact on disc wear of adding CB. Addition of CB to the dispersant solution has little additional effect on wear even with soft discs, indicating the effectiveness of the dispersant at the level used (0.02 wt% N with 5 wt% CB). Wear rate still appears to conform to the Archard wear equation. However when CB is added to the solution containing both ZDDP and dispersant, the wear volume is increased significantly above that of the base oil for all disc hardnesses. Wear rate still decreases with increase of disc hardness up to 400 HV, and then levels out. However there is then a very large increase in wear with the hardest disc used.

The fact that wear is greater when both CB and ZDDP are present than when one or other component is absent for all disc hardnesses supports the concept of a corrosive-abrasive mechanism. However, the most striking finding is the very large wear rate when ZDDP and CB are both present with the hardest disc. Here the wear rate becomes more than 20 times that found when either lubricant component is absent.

Fig. 3b shows the corresponding wear of the ball when CB was added to the blends. When CB is added to dispersant solution it has negligible effect – wear remains very low over the whole range of disc hardnesses. However, when CB is added to a solution containing ZDDP and dispersant a very interesting wear response occurs, with much higher wear when the disc is either soft or very hard but a much smaller increase in wear with intermediate hardness discs. This pattern is similar to that of the wear of the disc. It should be noted that a similar dependence of wear on disc hardness using ZDDP and CB-containing oils was previously reported by Olomolehin [39].

Fig. 4 shows friction coefficients from the HFRR tests. These are average values taken over the whole one hour test, although in practice they varied very little during each test. Friction coefficients lie in the range 0.10–0.15 for all lubricants except for the base oil with the softest disc where it exceeds 0.2. The latter indicates adhesion in the absence of any potential surface-adsorbing or surface-reacting species. The friction coefficients of the oils were little affected by the addition of CB or the level of disc hardness. Similar results have been also observed by previous researchers who concluded that there is no change in friction coefficient when using soot and CB [3,40,41]. Most recently, Honda

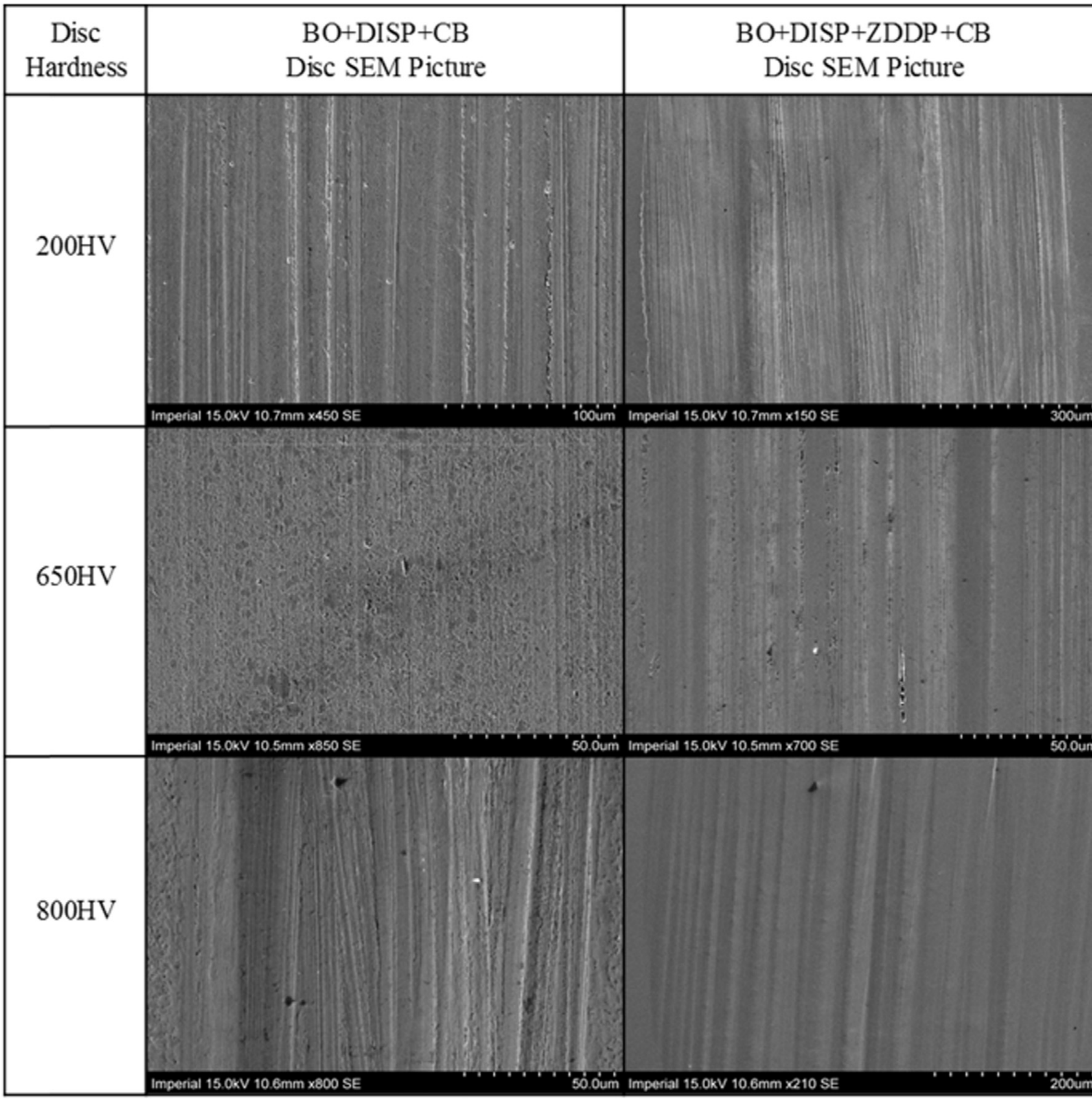

Fig. 7. SEM pictures of different hardness discs tested with BO + DISP + CB and BO + DISP + ZDDP + CB oils.

and Ogano [42] have suggested mechanisms of how soot in oils could act as friction modifier to reduce friction coefficient in low oil film thickness conditions.

It is noteworthy that the very large levels of wear seen for the oil containing both ZDDP and carbon black at high and low disc hardness are not reflected in the friction coefficient measurements which, for this oil, are quite independent of disc hardness. This lack of correlation between friction and wear is not typical of adhesive or abrasive wear but is often found where the prevailing wear mechanism is corrosive.

3.2. Surface analysis of HFRR discs with SEM-EDS and SWLI

The particular challenge of this project was to understand the mechanisms involved in the increase of wear volume with the oil containing dispersant, ZDDP and CB at 800 HV disc hardness. Therefore surface analysis was carried out using SEM (HITACHI S-3400N) high resolution images, EDS elemental analysis and SWLI profile analysis of the worn surfaces and of ZDDP films to help to understand these mechanisms.

Firstly the wear scars on discs and balls lubricated by the dispersant and ZDDP-containing oils without CB were analysed to investigate the effect of hardness on ZDDP film formation. SEM images are shown in Figs. 5 and 6 for the disc and ball respectively. The darker parts on the wear scars indicate an anti-wear film. It is interesting to observe that the oil containing both dispersant and ZDDP forms anti-wear films on both discs and balls, while that containing only ZDDP forms some traces of anti-wear films on the wear tracks on the discs only, with no detectable films on the balls. Wear scars are only evident for the oil containing just ZDDP and occur on both balls and discs in tests with all disc hardnesses. This is in accord with the wear measurements in Fig. 2. When ZDDP solution is able to form a protective film on disc surfaces, it gives low disc wear even for soft discs. However ZDDP solution cannot form a stable film on the ball since any reaction product is being continually removed, leading to relatively high wear; thus Shimizu et al. [43] have recently shown that a ZDDP film does not form on the ball in pure sliding, reciprocating contact and that this leads to quite high wear. When dispersant is present with ZDDP this protects the ZDDP film as it forms, so that a film is able to form on both ball and disc, with consequently low wear of both components.

The anti-wear films formed by oil containing both ZDDP and dispersant on 200 HV discs seem to be more uniform, while the films formed on 650 and 800 HV discs show a porous pattern, with the film having numerous, approximately circular holes of diameter *ca* 5–10 μm. Isotropic, porous films were also found on the balls rubbed against 200

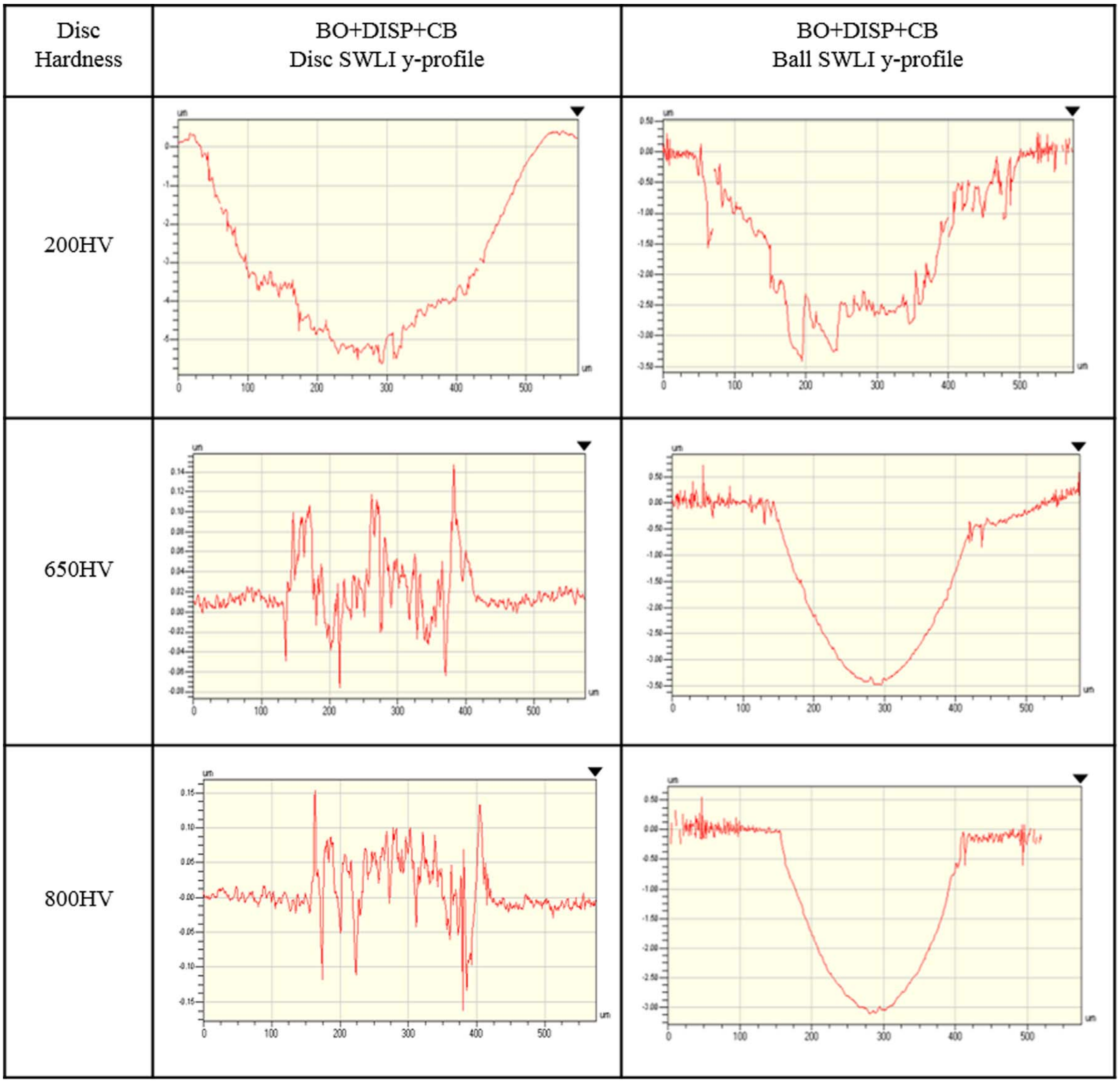

Fig. 8. SWLI y-profiles of discs and balls from tests with different hardness discs using BO + DISP + CB.

HV discs in oils containing both ZDDP and dispersant oil at 200 HV disc hardness, while similar but less compact films are seen on balls rubbed against 600 and 800 HV discs.

For the discs, EDS analysis showed the elements expected from ZDDP anti-wear film, *i.e.* S, P and Zn. EDS analysis of the balls showed the presence of S, P and Zn when oils containing ZDDP and dispersant were used but just traces of S when ZDDP-only solutions were employed. The latter cases correspond to those when no tribofilm was seen using SEM.

Fig. 7 shows SEM pictures of discs from tests using CB-containing oils with and without ZDDP. It is clear from the SEM pictures that there are no observable anti-wear films on any of the wear scars. This suggests that when ZDDP is present the CB must continuously abrade any anti-wear film as it forms. The EDS analysis showed traces of S but negligible P or Zn.

Figs. 8 and 9 show SWLI profiles across the contact transverse (y-direction) to the rubbing direction on both disc and ball for oils containing dispersant and CB, without and with ZDDP respectively. In these profiles the lengths of the horizontal axis are always 575 µm but the scales of the vertical axes vary.

For the ZDDP-free oil in Fig. 8 it is interesting to observe that at 650 and 800 HV only the balls experience material loss. With the ZDDP-containing oil in Fig. 9 it is clear that the disc profiles of 200 HV and 800 HV, which have similar HFRR wear volumes, have different surface topographies. The wear scar of 200 HV disc is smoother than the 800 HV one, which consists of large ridges. The wear scar profiles of the balls are smoother at low disc hardness and increase at higher disc hardness.

4. Discussion

HFRR results show that for all the oils without CB, disc wear reduces as hardness increases, in agreement with the Archard wear equation. Also wear is much lower on soft discs with the oils that contain ZDDP than with oils that do not, and lowest for the blend with ZDDP and dispersant. The high wear that occurs with the non-ZDDP containing oils is probably primarily adhesive wear and this is reduced by the tribofilm formed by ZDDP, while the dispersant also provides some boundary lubrication protection. Surface analysis confirms that ZDDP tribofilms form on the discs with both ZDDP and ZDDP + dispersant oils. With hard discs of 650 and 800 HV, all the oils give similar, very low wear, indicating the positive effect of high hardness on wear control.

The wear volumes of the corresponding HFRR balls using oils without CB are relatively constant with increasing disc hardness, which is unsurprising since the hardness of the ball is constant (880 HV) and always greater than that of the disc. For most oils, wear is very low, but

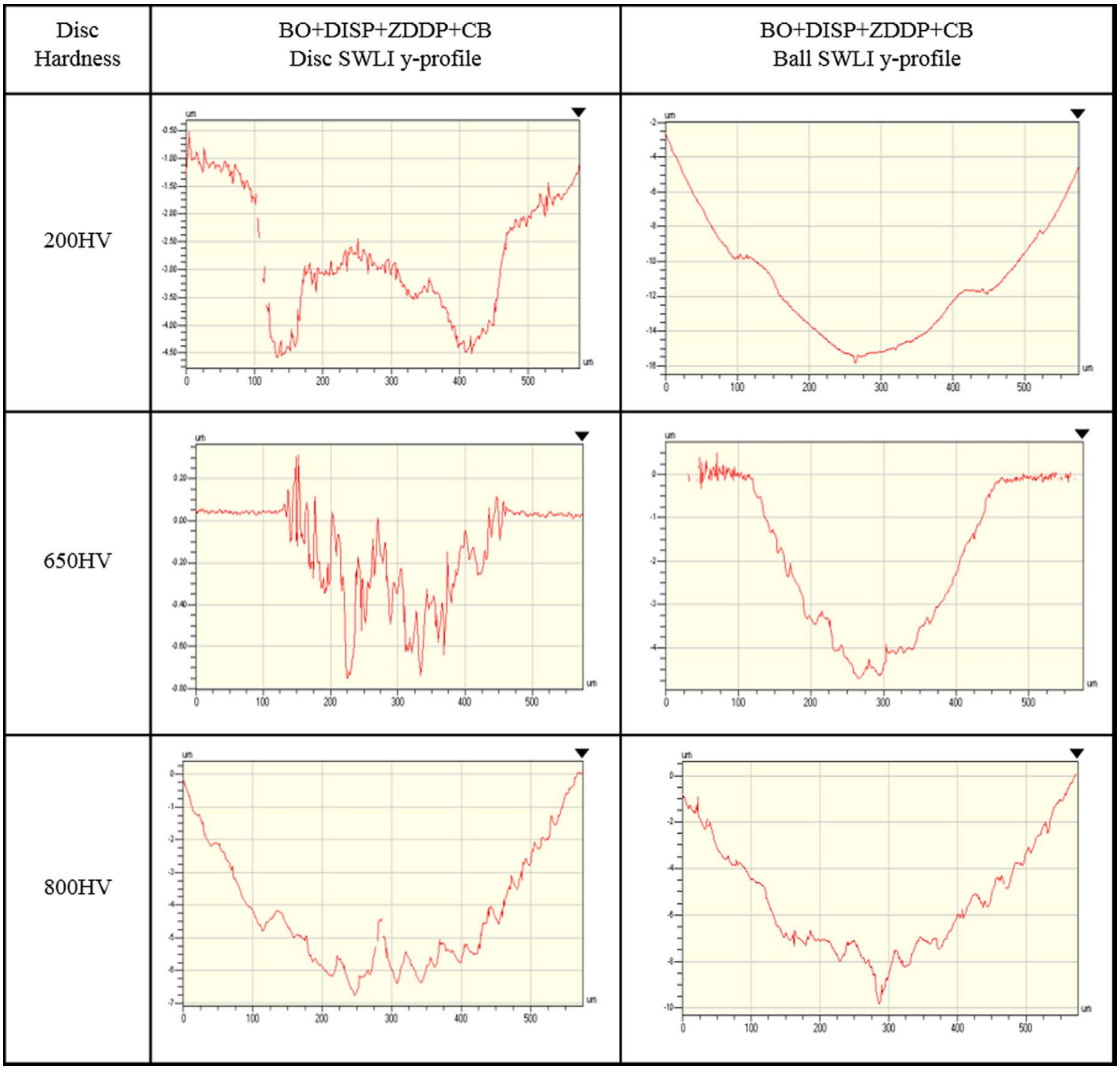

Fig. 9. SWLI y-profiles of discs and balls from tests with different hardness discs using BO + DISP + ZDDP + CB.

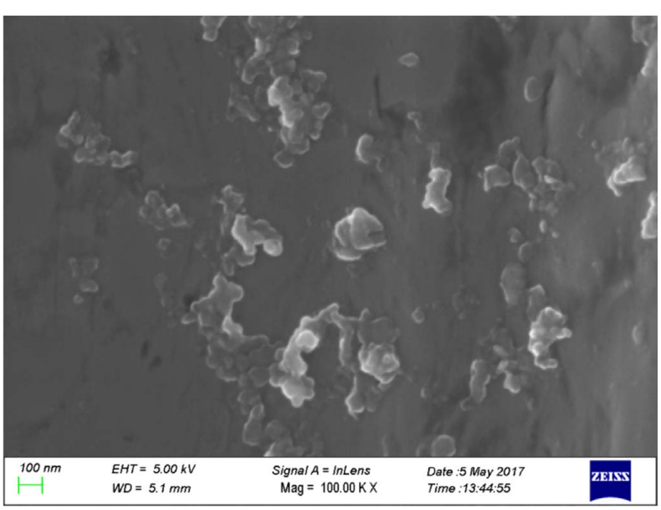

Fig. 10. FEG-SEM image of 200 HV disc after test with BO + DISP + ZDDP + CB.

interestingly it is highest for the oil containing only ZDDP. Since the ball is in continuous contact throughout a test, a protective film is unable to stabilise on the ball surface and this leads to continuous mild corrosive wear. Surface analysis confirms the absence of any measureable tribofilm on the ball. Oils containing both ZDDP and dispersant do not show this increased wear, suggesting either that dispersant is able to provide enough boundary film protection to allow a ZDDP tribofilm to form or that it prevents the ZDDP film from forming so that no corrosive wear takes effect. Surface analysis confirms the presence of a thin tribofilm for this system, supporting the former mechanism.

When CB is added to the dispersant solution, wear does not significantly increase on the softer discs, indicating the effectiveness of the dispersant (0.02 wt% N with 5 wt% CB). However when CB is added to solutions containing ZDDP the disc wear volume is increased to a value much greater than that without CB and even above that for the base oil alone, for all disc hardnesses. Wear rate still decreases with increase of disc hardness up to 400 HV, and then levels out. There is then a very large increase in wear with the hardest disc used.

The finding that when both CB and ZDDP are present wear is greater than when one or other component is absent is a confirmation of the previous work by Olomolehin et al. [19]. The mechanism involved is believed to be corrosive-abrasive, in which the carbon black nanoparticles remove the iron sulphide and phosphate anti-wear films as rapidly as they form, leading to a rapid loss of ferrous compounds and thus high wear levels. Surface analysis confirms that no measureable

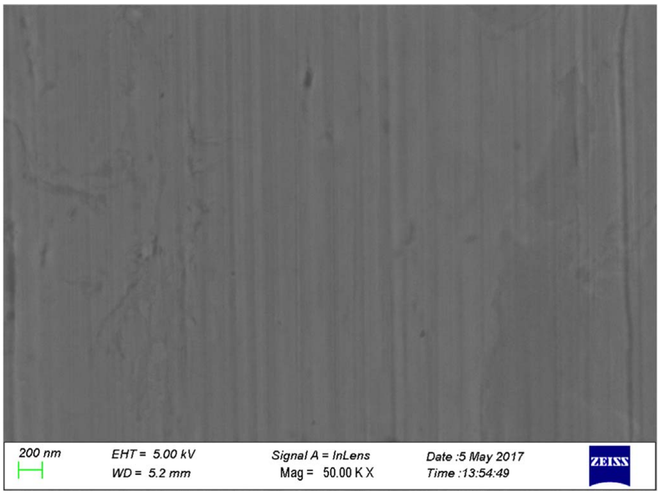

Fig. 11. FEG-SEM image of 400 HV disc after test with BO + DISP + ZDDP + CB.

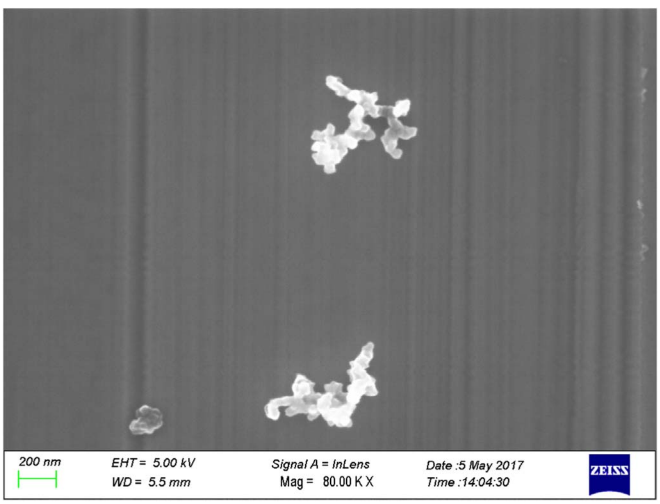

Fig. 12. FEG-SEM image of 800 HV disc after test with BO + DISP + ZDDP + CB.

ZDDP tribofilm forms when CB is present.

The most interesting finding of this study is the large wear rate on both ball and disc when ZDDP and CB are both present with the hardest disc. The wear rate increases more than 20 times compared to when either component is absent. This hard/hard surface combination is the one studied in all previous work and is present in many engine components. It is not evident whether this effect arises because both surfaces are hard or because both surfaces have similar hardness – unfortunately it was not possible to obtained softened balls. However the authors favour the former cause.

The shape of this dependence of wear on hardness, summarised in Fig. 3(b), suggests that two different effects are operating, although clearly the ZDDP must still be involved in promoting wear with both. With soft discs it is very likely that the CB particles are harder than the disc. In consequence they are likely to be embedded and accumulate in the disc surface, thus increasing the rate of abrasion of the ZDDP reaction product on the hard ball and so its wear rate. To test this conjecture, FEG-SEM, which has higher resolution than conventional SEM, was used to examine the disc surfaces after rubbing. The surfaces were cleaned in toluene in an ultrasonic bath for one minuted followed by rinsing isopropanol prior to analysis. Fig. 10 shows a rubbed 200 HV disc surface. The surface has numerous adhered or embedded CB particles. The CB present consist primarily of single or a few joined primary particles. Figs. 11 and 12 show corresponding images of 400 HV and 800 HV surfaces respectively. The 400 HV disc surface is smooth with no visible particles. The 800 HV is also smooth but with visible groove marks. There are very few particles including one primary particle that lies within a groove. There are also a few secondary particles that appear to lie apparently undamaged on the surface.

Such a soot-embedding mechanism does not, however, explain the correspondingly high rate of wear of the soft disc itself when ZDDP is present. Here it is probable that the high wear results primarily from normal adhesive/abrasive wear of the soft surface, as seen in dispersant solution without carbon black in Fig. 2a. This implies that the ZDDP is unable to form a protective tribofilm when CB is present, *i.e.* it is continuously removed. However wear is somewhat higher than the BO + dispersant case in Fig. 2a, so some additional corrosive-abrasive effect of the ZDDP/CB combination must also be present.

With discs of intermediate hardness this embedding process diminishes so that wear of the ball is reduced. However another process must come into play to cause the very large wear of both the ball and disc surface when both the disc and ball are hard. This hardness combination is, of course, the one studied in previous work [19,21]. One possibility is that the high contact stresses present at the contact of hard surface asperities, or that result when CB particles pass through the contact of a hard ball on a hard disc, generate very high local pressures and thus shear stresses that promote ZDDP reaction rate, thus accelerating the corrosion/abrasion process. Recent work has shown that ZDDP reaction is driven by shear stress and is thus a mechanochemical process [44]. It is thus envisaged the ZDDP forms an incipient sulphide/phosphate film very rapidly on both surfaces due to high local stresses resulting from the passage of CB particles between hard surfaces and this film is then immediately abraded by these same CB particles, resulting in high wear rate. From the results, in the absence of CB the ZDDP film on the 800 HV disc and ball seem to be thicker than the films formed on balls and discs with 650 HV and 200 HV hardness, supporting the concept that increased contact pressure leads to faster ZDDP film growth (Figs. 5 and 6).

5. Conclusions

HFRR wear tests have been carried out on discs with varying hardness against a hard ball, using oil formulations containing combinations of ZDDP, dispersant and CB. The worn surfaces and ZDDP films have been analysed using SEM high resolution pictures, EDS elemental analysis and SWLI profile analysis, to help understand the mechanisms involved. The main conclusions drawn from this study are:

- In the absence of CB, increase of disc hardness always results in a marked reduction in disc wear, such that when hardness is greater than 600 HV very low wear occurs even when the surfaces are lubricated by base oil. The addition of ZDDP enables low wear to be achieved even with soft surfaces.
- The addition of CB to a base oil containing dispersant has relatively little effect on wear. However when ZDDP is also present, higher wear ensues. The fact that higher wear takes place when both ZDDP and CB are present that when one or other of these components are absent supports a corrosive-abrasive mechanism of soot wear.
- When both ZDDP and CB are both present much more wear is found when the disc surface is either very soft or very hard compared to intermediate disc hardnesses. Unusually, this high wear is present on both the disc surface and the hard ball surface.
- With soft discs it is suggested that the CB particles that are harder than the disc embed and accumulate in the disc surface, thus increasing the rate of abrasion of the ZDDP reaction product on the hard ball and so its wear rate.
- When hard discs are used with oils containing both ZDDP and CB, at least twenty times more wear occurs compared to when either component is absent. It is suggested that high local pressures and thus shear stresses that occur in the contact between two very hard surfaces in contact promote the rate of ZDDP reaction and thus

accelerate the corrosion/abrasion wear process induced by ZDDP and CB.

Since ferrous-based engine components hardness generally lie in the range 400–800 HV, the results of this study should provide a possible way to mitigate the impact on wear of lubricants that contain both antwear additives and soot, by ensuring that one of surface of the tribopair is neither very hard nor very soft.

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