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ZDDP and MoDTC interactions in boundary lubrication—The effect of temperature and ZDDP/MoDTC ratio

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Abstract

Tribofilms formed under boundary lubrication from ZDDP and MoDTC additives alone or in different ratios in the lubricant have been studied. The tribological performance is linked to the tribofilm properties and consequently to the lubricating conditions. Tribofilms are formed using a reciprocating pin-on-plate tribometer. Surface sensitive analytical techniques, such as energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) have been used for tribofilm characterisation. The XPS peaks have been deconvoluted to characterise the species formed in the wear scar. The formation of species with different tribological properties, due to the decomposition of ZDDP and MoDTC molecules as a result of testing temperature, is shown. Surface analyses have shown that MoDTC decomposes, even in low-lubricant bulk temperature tests (30 °C), forming the same species as in high-lubricant bulk temperature tests (100 and 150 °C) but the tribofilms give different tribological performance. The effectiveness in friction reduction is shown to depend on the ratio between what are defined as high- and low-friction species in the tribofilm.

Keywords: Additive interactions; ZDDP; MoDTC; Tribofilm; Tribochemistry

1. Introduction

In the mixed to boundary lubrication regime, use of the MoDTC additive results in a very low friction coefficient of around 0.05 [1–11] making it a very effective friction modifier additive and an essential component of current engine lubricant technology. Its effectiveness in friction reduction comes primarily from forming an MoS_2-containing tribofilm on the wear scar. The layer-lattice structure of the MoS_2 contributes to low friction [12]. In MoS_2 there is powerful covalent bonding between atomic species, but between lattice layers there is only very weak Van der Waals attraction. The weak Van der Waals forces between MoS_2 layers maintain easy shear within the molecule and are responsible for the low-friction properties.

When a lubricant with only MoDTC additive was tested [3,10,13], the friction coefficient values could be separated into two distinct regions: a high friction, induction phase followed by a step to a second region with reduced friction. An increase of MoDTC concentration in the lubricant was shown to reduce the induction time prior to friction reduction [10] and not the final friction value, which is in contrast to the findings of Sorab et al. [14] that suggested that a MoDTC percentage higher than 500 ppm Mo is necessary for the most effective friction reduction. In other work, a minimum concentration of MoDTC for friction reduction was found to be approximately 180 ppm Mo [3] and this was shown to be dependent on temperature. It was observed that the MoDTC additives are most effective in reducing friction at a combination of high additive concentration and high temperature [3]. An increase in temperature from 80 to 160 °C was found to decrease the induction time prior to the friction drop [15] but the effectiveness of MoDTC to reduce friction was lost later during the test resulting in an increase of friction. This loss of effectiveness was evident only when testing the MoDTC lubricant in unidirectional linear sliding and not in reciprocating tests. One of the reasons for this is suggested to be some kind of conditioning of the contact surface after

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which the reactivity towards MoDTC is reduced. Yamamoto et al. [11] showed that an increase in temperature above 100 °C required a longer rubbing period for the friction to drop but once friction dropped, the values were lower than in low-temperature tests (50 °C). Both these studies were done in sliding conditions in the boundary lubrication regime with the difference being that in [11] the tests were in reciprocating mode, while in [15] they were in unidirectional linear sliding mode. These contrasting results highlight the need for further studies to understand the complete mechanism of MoS_2 formation from this additive.

Great attention has been paid to the performance of MoDTC when used in the additive package since its effectiveness may be strongly affected by synergistic or antagonistic effects from the interactions with other additives [16]. A substantial number of studies have focused on the interactions with anti-wear additives (ZDDP). There are a number of reports in the literature that show that MoDTC alone is not as effective in friction reduction as it is when used together with the ZDDP additive [6,9,17]. Recent work by the authors [7,8] on the interactions between ZDDP and MoDTC on tribological performance, testing at 100 °C, showed no synergy in final friction coefficient but the use of ZDDP with MoDTC was shown to reduce the length of the induction phase prior to friction reduction.

Engine lubricants and their additives need to operate over a range of temperatures. Temperature, in most chemical processes, is known to affect reaction kinetics, and thus the tribochemical reaction process involved in tribofilm formation. In the authors' previous study [7], the interactions between ZDDP and MoDTC additives in film formation at 100 °C were shown. This paper is a continuation of that work where (a) the change of MoDTC concentration in a ZDDP lubricant and (b) the effect of temperature are studied.

2. Experimental

2.1. Tribological experiments

A reciprocating pin-on-plate tribometer was used to test the lubricant in boundary lubrication conditions. This tribometer is instrumented to measure friction force via a bi-directional load cell with measuring range to 58.8 N and combined error of −0.0037 N. Combined error is an envelope of several errors such as non-linearity, hysteresis and temperature effects on load cell sensitivity. The load cell is connected to a computer programme that controls the time elapsed and number of points in each data set. Readings of the friction force were taken every 10 min for 2 s (120 points), which corresponds to two stroke cycles. The stroke length is 10 mm. An average of the 120 points gives the friction force, which is used to calculate the friction coefficient. Then the calculated friction coefficient is plotted as a function of time for the duration of the test. Fig. 1 shows the schematic of the contact obtained in pin-on-reciprocating plate apparatus.

As in the first part of this work [7], the material used for pins and plates was bearing steel AISI 52100. The pins were 20 mm in length and 6 mm in diameter and the ends of the pins were machined to a 40 mm radius of curvature. The rectangular plate measured $15 \times 6 \times 3\,mm^3$. The components were through-hardened to 60–64 HRC and surface finish tolerances were specified as $R_a = 0.15$–$0.2\,\mu m$ in the direction of sliding. The contact pair was immersed in the lubricant to be tested. For each test 3 ml of lubricant was used.

A load of 188 N was used to give an initial maximum Hertzian pressure of 640 MPa, which is comparable to the pressures obtained between cam and follower in the internal combustion engine. The tests were undertaken at a sliding speed of 0.1 m/s. All the tests were performed at three temperatures: 30, 100 and 150 °C. Lambda ratios, determined as a ratio of minimum lubricant film thickness and starting composite root mean square surface roughness (σ_{rms}), were well under unity showing that lubrication is in the boundary regime. The minimum film thickness is determined using the Dowson and Hamrock minimum film thickness equation [18] for an elastohydrodynamic point contact. The duration of tests was 6 h. Average friction coefficient from the last hour of the test and wear calculated measuring the volume loss from the pin after the test were used as an indication of the tribological properties of the lubricant tested. The tests were replicated at least three times and a good repeatability (average $\pm$0.004) for the friction coefficient in the last hour of the test was recorded.

The lubricants used are defined in Table 1. The base oil used was synthetic oil Polyalphaolefin (PAO6) of viscosity 31 cSt (mm^2/s) at 40 °C and 5.8 cSt (mm^2/s) at 100 °C. Incorporating the additives did not result in significant change of base oil viscosity.

The concentration of MoDTC additive is given as a concentration of Mo in the blend.

2.2. Post-test surface analyses—EDX and XPS

The tribofilms formed on the plate were chemically analysed using energy dispersive X-ray analysis (EDX) and

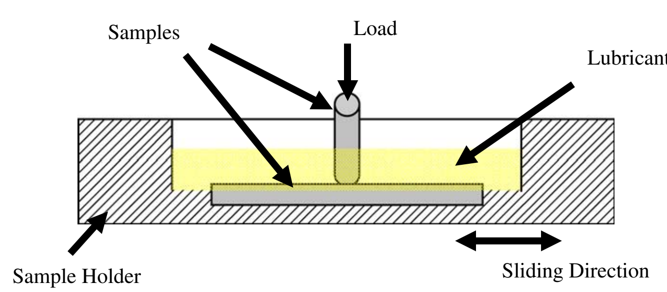

Fig. 1. Schematic of the contact obtained using the pin-on-reciprocating plate apparatus.

Table 1
Lubricant composition and designation

Designation	Lubricant
001A	PAO6
002A	PAO6 + 1.2 wt% ZDDP
003A	PAO6 + 250 ppm MoDTC
004A	PAO6 + 1.2 wt% ZDDP + 250 ppm MoDTC
005A	PAO6 + 1.2 wt% ZDDP + 50 ppm MoDTC

X-ray photoelectron spectroscopy (XPS) analytical techniques. The EDX technique has a probing depth in excess of 1 μm; hence will probe the substrate composition as well as the tribofilm itself. Use of this technique is important to obtain the composition of the entire tribofilm. XPS is used to complement EDX to provide very surface sensitive (~5 nm) information by probing only the wear film and analysing the composition as a function of depth.

XPS analyses were performed using the Scienta ESCA300 facility in Daresbury, UK. The instrument employs a high-power rotating anode and monochromatised Al*Kα* X-ray source. A large, seven crystals, double focusing monochromator focuses the X-rays to a line image, 6 mm × 0.5 mm, on the sample, which is then focused in the middle of the wear scar in an area of 400 μm × 300 μm. Energy resolution of the spectrometer is ~0.3 eV. The binding energy of 284.8 eV for adventitious C is used as a reference for charge correction. Prior to XPS analysis, the excess lubricant was drained from the surface and then the surface was immersed in heptane for about 2 s, in order to eliminate the residual lubricant. In a typical XPS analysis, a survey scan is obtained first in order to identify elements present, and then long scans of the selected peaks are obtained in order to determine a more comprehensive picture of the chemical composition. Acquisition conditions for the survey spectra were 300 eV pass energy, 2.9 mm slit size and 1.0 eV step interval. For the region spectra, the acquisition conditions were 300 eV pass energy, 2.9 mm slit size and 0.05 eV step interval. All the spectra were acquired in spatial mode. Chemical analyses as a function of depth were performed. Ar ion etching at 2 kV energy was done to facilitate this.

CasaXPS software [19] was used for performing the curve fitting procedures on XPS peaks obtained. The data obtained were compared with standard spectra and with the tabulated spectra from Refs. [20–22]. Peak area ratio, difference between binding energies of the doublets and full-width at half-maximum (FWHM) were constrained in order to obtain information with the most appropriate chemical meaning [23]. The value of FWHM of XPS peaks obtained in this work was a convolution of analyser resolution [23] and of natural FWHM of the peak [20].

A Gaussian–Lorentzian product function component line shape was found to provide a satisfactory fit to the data from the Scienta instrument. All fitted spectra subsequently underwent a linear background subtraction, using limits spanning the entire analysed region, to aid presentation. Quantitative analysis was performed utilising peak area sensitivity factors.

3. Results

3.1. Effect of ZDDP/MoDTC ratio

3.1.1. Effect on tribological properties

In Fig. 2a and b, the change of average friction coefficient and wear coefficient as a function of the MoDTC percentage present in the ZDDP lubricant tested is shown.

Fig. 2a shows that 005A lubricant is not as effective in friction reduction as the 004A lubricant. The presence of just 50 ppm MoDTC in the ZDDP lubricant reduces friction but not to the same extent as 250 ppm MoDTC. The wear observed in all tests conducted in this study was very low and a very small increase was seen when adding MoDTC to the ZDDP-containing lubricant. There was no real difference in wear between the high and low concentrations of MoDTC.

3.1.2. Effect on tribofilm formation

The chemical composition of the tribofilms formed, obtained using EDX and listed in Table 2, shows that an increase of MoDTC percentage in the lubricant reduces the ZDDP elements such as Zn and P, which is interesting in relation to the slightly increased wear observed when MoDTC was added to ZDDP.

EDX quantification is a good way to assess the *total* elemental composition of the film formed from the additives since it probes to a depth well in excess of the tribofilm thickness. Fe, Cr and Si in Table 2 are elements from the substrate, bearing steel. Zn and P are key constituents of the ZDDP tribofilm and so lower amounts in the presence of the MoDTC additive (004A lubricant) suggest that less ZDDP tribofilm is formed.

The more surface sensitive quantification of these tribofilms, obtained by XPS, is shown in Table 3.

From XPS measurements of the top layer of the tribofilm, analysed after 0.5 min etching, it can be seen that the C-rich layer is related to the higher MoDTC percentage in the lubricant. The lack of iron shows that a tribofilm with uniform thickness is formed when the 004A and 005A lubricants were used. The molybdenum signal from the 005A tribofilm was shown to be very weak.

3.2. Effect of temperature

3.2.1. Effect on tribological properties

Fig. 3 shows the friction coefficient as a function of temperature for all lubricants used. A clear effect of temperature can be seen. An increase in temperature when 002A was tested gives higher friction whereas in the case of 003A and 005A a contrasting trend is seen; an increase in temperature reduces friction. When 004A lubricant was tested at low temperature (30 °C), friction was shown to be

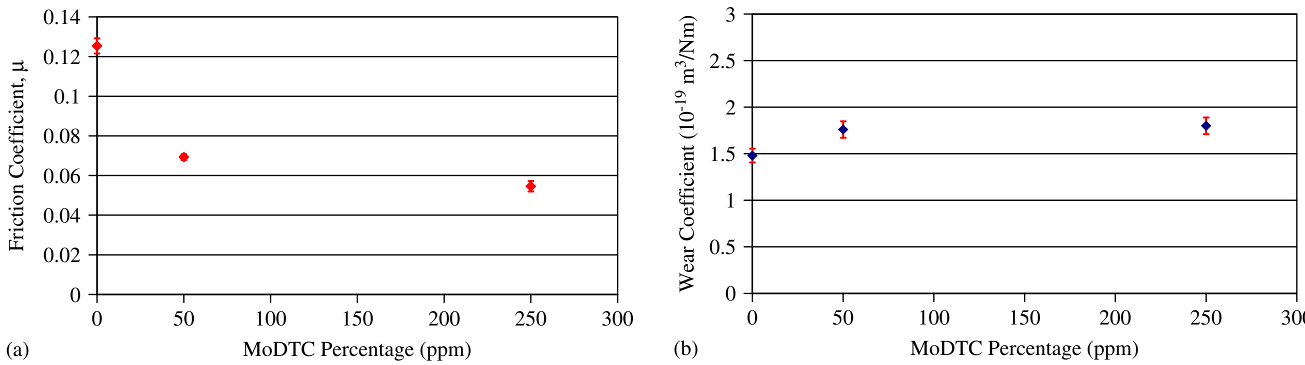

Fig. 2. Effect of MoDTC percentage in the ZDDP lubricant in (a) friction coefficient and (b) wear coefficient. Comparison of 002A, 005A and 004A lubricants. Tests conducted at 100 °C.

Table 2
Effect of MoDTC amount in tribofilm composition—EDX quantification. Comparison of 002A, 005A and 004A lubricants

Mo Conc. (ppm)	Lub.	EDX (wt%)									
		P	S	Zn	Fe	O	C	Cr	Si	Mn	Mo
0	002A	1.2	0.5	2.4	83.8	5.9	0	4.1	0.5	1.6	—
50	005A	1.1	0.2	2	77.2	6.2	5.2	5.2	0.6	2	0.3
250	004A	0.3	0.3	0.7	82.5	4.6	3.7	4.8	0.5	2.1	0.4

Table 3
Effect of MoDTC amount in tribofilm composition—XPS quantification. Comparison of 002A, 005A and 004A lubricants

	Etching time (min)	XPS (at%)							
		C 1s	O 1s	S 2p	P 2p	Fe 2p	Zn 2p	Mo 3d	N 1s
002A	0.5	14	51.7	5.5	14.9	4.9	9	—	—
	2	7.1	52.1	6.3	13.5	10.7	10.2	—	—
	5	5.5	46.8	6.9	12	19.5	9.3	—	—
005A	0.5	25.2	43.7	4.7	15.8	0	10.1	0.6	0
	2	13	49.9	5.4	16.7	0	14.2	0.8	0
	5	9.4	49.4	4.4	13.4	9.4	13.3	0.7	0
004A	0.5	91.1	4.1	1.6	2.2	0	0.3	0.8	0
	2	74.9	8.1	3.1	4	0	2.1	1.7	3.7
	5	54.7	15.6	4	5.4	1.8	4.3	3.3	5.13

lower than when 003A lubricant was used. An increase in temperature to 150 °C surprisingly led to an increase in friction compared to the 100 °C test. A value similar to the friction reached with 005A lubricant was recorded.

Wear results as a function of temperature also show the same complexities, Fig. 4. When ZDDP and MoDTC additives are used together, Zn phosphate glass, formed from the ZDDP additive, is not the only tribofilm species having anti-wear performance ability [7]. The presence of S- and N-containing species formed from MoDTC has also been suggested to reduce wear. The wear values measured in these tests were very low but a clear difference could be seen when the additives were used compared with wear obtained with just base oil (001A).

The wear values obtained testing the base oil (001A) at three temperatures show that increase in temperature caused increased wear. This is primarily due to the reduction of viscosity which will result in harsher lubrication conditions with more asperity contact. The wear was seen to be similar when 002A lubricant was tested at 30 and 100 °C. These values were much smaller than the wear using 001A, as expected. The wear at 150 °C, when 002A lubricant was used, reduced to about 50% of the values at 30 and 100 °C. This is likely to be due to the increase in the

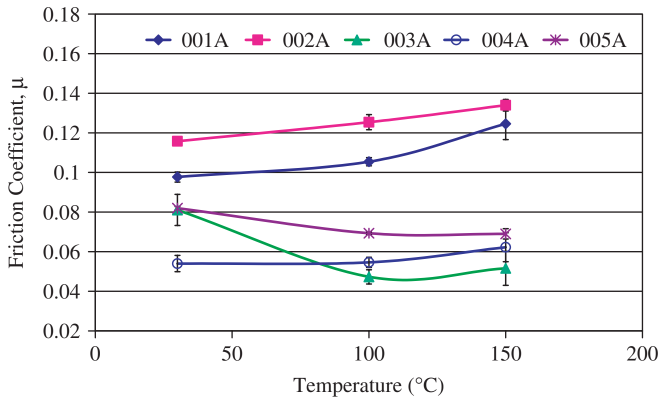

Fig. 3. Friction coefficient as a function of temperature. The curves are for guidance only.

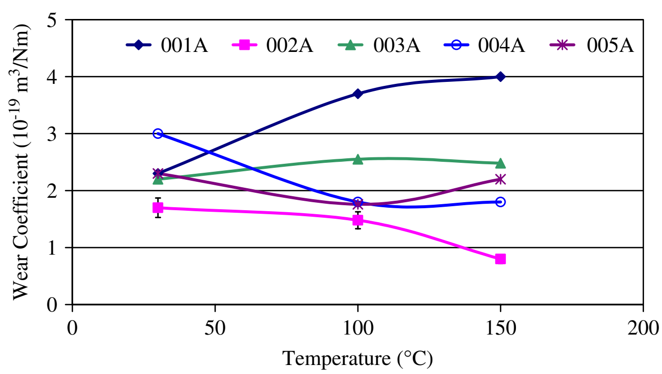

Fig. 4. Wear coefficient as a function of temperature. The curves are for guidance only.

rate of chemisorbed ZDDP film formation triggered by the higher temperature, as proposed by So et al. [24] who reported that above 80 °C a chemisorbed ZDDP film is formed.

When 003A lubricant was used, at all temperatures wear was reduced compared to the base oil, confirming the reported anti-wear properties of MoDTC [7]. Wear was seen to increase with increase of temperature but levelled out after 100 °C.

In order to understand the contributions of additives to the tribofilm formation and how the tribofilm constituents are related to temperature, firstly the film formation from lubricants with ZDDP and MoDTC only and then the film formation from a combination of these two additives as a function of temperature were assessed.

3.2.2. ZDDP (002A) tribofilm as a function of temperature

From Figs. 3 and 4, a clear effect of temperature on friction and wear of 002A lubricant can be observed. In these tests, an increase in temperature caused an increase in friction and at the same time wear was reduced. With the only component in this lubricant being the ZDDP additive, a possible cause for the change in tribological properties with temperature could be related to the different rate of formation of ZDDP tribofilm as a function of temperature.

Fig. 5 shows the EDX quantification of the tribofilms formed at three temperatures.

The P and Zn values increase with increase in temperature to 100 °C but seem to level out with further increase in temperature.

Quantification of the species in the ZDDP tribofilms formed at three temperatures obtained by XPS is shown in Table 4. An increase in concentration of Zn at 150 °C and the lack of iron until 5 min etching indicate that at 150 °C the tribofilm is at its thickest.

Another possible factor that could affect the tribological properties is the specific species formed from the ZDDP additive as a result of its decomposition. The XPS peak curve fitting procedure, results of which are shown in Fig. 6 and Table 5, determines the species formed in each tribofilm.

Zn and P binding energies from tribofilms formed at three temperatures are similar and correspond to Zn phosphate glass [20,21].

An important parameter for glass characterisation is the ratio of bridging oxygen (P–O–P) to non-bridging oxygen (–P=O and P–O–Zn), which is equal to BO/NBO = $(n-1)/2(n+1)$ [25]. From this the glass polymerisation number (n) can be calculated. In the cases where $n = 1$, the glass is an orthophosphate, $n = 2$ is a pyrophosphate and in the case that n is higher than 2 it is a metaphosphate [26]. Fig. 7 shows the phosphate glass polymerisation number (n) as a function of etching time, determined by calculating the ratio of bridging oxygen to non-bridging oxygen, values of which are shown in Table 5.

At 100 and 150 °C a longer chain polyphosphate chain is formed, this layer being thicker at 150 °C. Even after 5 min etching, no significant change of the polymerisation number was recorded.

From XPS data the key characteristics of the tribofilms formed at the three temperatures can be obtained:

- Zn and P binding energies from tribofilms formed at the three temperatures are similar and correspond to Zn phosphate glass [20,21]. At higher temperatures (100 and 150 °C), longer chain polyphosphates are formed.

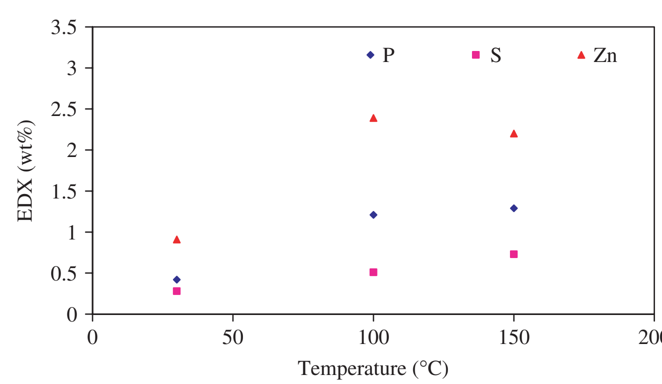

Fig. 5. 002A lubricant's tribofilm EDX quantification as a function of temperature.

Table 4
002A lubricant's tribofilm XPS quantification as a function of temperature

002A	Etching time (min)	XPS (at%)					
		C 1s	O 1s	S 2p	P 2p	Fe 2p	Zn 2p
30 °C	0.5	21.8	48.3	3.8	14.8	5.4	5.9
	2	9.7	52.1	5	15.4	10.7	7.1
	5	7.9	48.4	5.4	11.8	20.8	5.7
100 °C	0.5	14	51.7	5.5	14.9	4.9	9
	2	7.1	52.1	6.3	13.5	10.7	10.2
	5	5.5	46.8	6.9	12	19.5	9.3
150 °C	0.5	36	36.8	4.1	15.3	—	7.6
	2	15.9	47.7	4.8	17.2	—	14.4
	5	7.9	50.1	5.5	16	3.2	17.4

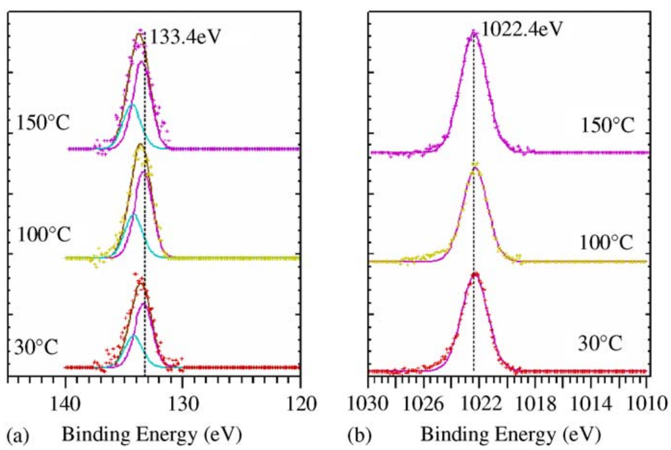

Fig. 6. Curve fitting of P 2p (a) and Zn 2p (b) XPS spectra recorded in tribofilms formed when 002A lubricant was used after 0.5 min etching at three temperatures.

- S 2p binding energy corresponds to ZnS and to FeS_2 [20,27,28]. Observing Fe 2p peak quantification and binding energy, it can be concluded that FeS_2 is found only at the base of the ZDDP 30 and 100 °C tribofilm. The S in the tribofilm formed at 150 °C and in the top layers of the tribofilms formed at 30 and 150 °C is mainly ZnS.
- No Fe peak could be detected in the tribofilm at 150 °C which is indicative of its greater uniform thickness. Iron could be detected only after 5 min etching.
- No oxides were detected on the tribofilm surface formed at 150 °C. The curve fitting shows an emergence of oxides with etching. With etching, the top tribofilm layers (phosphate and sulphide) are removed and the oxides start to appear.

A clear relationship between temperature, tribofilm composition and the tribological performance of the ZDDP lubricant is shown. Increase in temperature increased the formation rate of phosphates and longer chain polyphosphates are formed. In these conditions friction was seen to increase and wear to decrease.

3.2.3. MoDTC (003A) tribofilm as a function of temperature

In the case of the 003A lubricant tests, a reduction in friction is observed as the temperature increases from 30 to 100 °C and levelled when the temperature was increased further, Fig. 3. The EDX quantification of the tribofilms formed when a 003A lubricant was tested at 30, 100 and 150 °C is shown in Table 6.

Even at low temperature (30 °C) the formation of a film from MoDTC can be observed. Amounts of MoDTC constituents, Mo and S, increase with temperature increase.

In Table 7, the quantification of the top layer of the tribofilms analysed by XPS is shown.

The increase in temperature increased the C-rich layer at the top of tribofilm. This layer was found to be very uniform since no Fe from the substrate is detected. With etching of this layer, the MoDTC elements start to appear. The lower amount of MoDTC additive elements (Mo and S) found at 100 and 150 °C could be due to the high C amount, suggesting that a C-rich film covers the Mo species formed in the wear scar.

A comparison of the Mo 3d peaks obtained from the 30 and 100 °C tribofilm is shown in Fig. 8.

The higher shoulder on the left of the doublet (at higher binding energies) is due to the Mo oxide peak. With etching, Fig. 9, it can be seen that the oxides are reduced in relation to MoS2. This shows that when MoDTC lubricant was used at 30 °C, the surface of the tribofilm is dominated by Mo oxide.

3.2.4. ZDDP/MoDTC (004A) tribofilm as a function of temperature

In the case of the 004A lubricant tested at 30 and 100 °C, friction dropped to around 0.05 showing the effectiveness of the MoDTC additive in friction reduction, Fig. 3. Friction was seen to be higher at 150 °C than the friction at lower temperatures. EDX analysis of the tribofilms formed

Table 5
Curve fitting of O 1s and S 2p XPS spectra recorded in tribofilms formed when 002A lubricant was used at three temperatures

Etching time (min)	Binding energy (in eV) at			Species
	30 °C	100 °C	150 °C	
O 1s				
0.5		530.3 (5.5%)		Oxide–Fe_2O_3
	531.6 (87%)	531.6 (76%)	531.8 (76%)	NBO
	533.8 (13%)	533.1 (19%)	533.3 (24%)	BO
2	530.3 (4%)	530.3 (15.2%)		Oxide–Fe_2O_3
	531.7 (88%)	531.6 (73%)	531.7 (44.1%)	NBO
			532.5 (42.6%)	C–OH
	533.5 (8%)	533.1 (11.8%)	533.7 (13.2%)	BO
5	530.3 (16%)	530.5 (32.4%)	530.3 (5.2%)	Oxide–Fe_2O_3
	531.6 (81%)	531.7 (59.7%)	531.8 (38.4%)	NBO
			532.7 (40.4%)	C–OH
	533.8 (3%)	533.2 (7.9%)	533.4 (11.7%)	BO
			534.6 (4.3%)	C–O
S 2p				
0.5	162	161.8		Sulphide
		162.5	162.5	
2	162	161.8		Sulphide
			162.5	
5	162	161.8		Sulphide
		162.5	162.5	

BO and NBO stand for bridging oxygen and non-bridging oxygen, respectively.

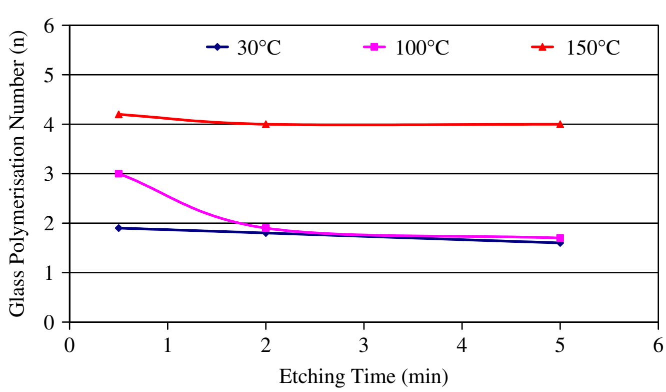

Fig. 7. Polymerisation number (n) values of the phosphate glass formed at three temperatures using the 002A lubricant.

at these temperatures, shown in Table 8, shows an increase of ZDDP elements (P and Zn) with increase in temperature to 150 °C.

Fig. 10 shows the wear and friction as a function of P and Zn amount for the tests performed at 30, 100 and 150 °C.

An increase in temperature resulted in a higher amount of P and Zn in the tribofilm and consequently higher friction. No effect on wear can be seen when the testing temperature was increased above 100 °C. The tribofilm formed from ZDDP dominates over the MoS_2 formed from MoDTC and because of that reduces the ability of MoS_2 to reduce the friction to the lowest value.

Table 9 shows the XPS quantification of the top tribofilms layers after different etching times.

The main points that can be observed are

- An increase of C amount is found in the 100 °C tribofilm.
- Quantification of P, Zn and Fe with etching suggests that a tribofilm with greater uniform thickness is formed at higher temperatures.
- Less Mo element is found in the tribofilm formed at 150 °C.

The higher friction recorded in the 150 °C tests could be due to the domination of the tribofilm by the ZDDP species or due to the preference to formation of other molybdenum species besides MoS_2.

The deconvolution of the Mo 3d peak, detected in 004A tribofilm formed at 150 °C, showed that besides formation of Mo sulphide and Mo oxide, Mo phosphate also forms as verified by the presence of the peak with binding energy at 233.5 eV [29] (Fig. 11).

The curve fitting for Mo 3d peaks was performed and results are shown in Table 10.

Formation of Mo phosphates is also seen at other temperatures. The amount of Mo phosphates, in relation to Mo sulphide and Mo oxide, is seen to increase in the tribofilm formed at 150 °C.

Table 6
003A lubricant's tribofilm EDX quantification as a function of temperature

003A	EDX (wt%)							
	S	Fe	O	C	Cr	Si	Mn	Mo
30 °C	0.3	82.1	5.9	3.1	4.9	0.6	2.1	1.2
100 °C	0.5	75.8	5	8.8	4.8	0.6	2.1	2.4
150 °C	0.7	79.6	6.1	4.1	4.8	0.6	2	2.1

Table 7
003A lubricant's tribofilm XPS quantification as a function of temperature

003A	Etching time (min)	XPS (at%)					
		C 1s	O 1s	S 2p	Fe 2p	Mo 3d	N 1s
30 °C	0.5	58.8	10.4	4.7	1.7	7.9	7.7
	5	43.8	9.5	5.1	4.9	11.2	15.7
	20	18.5	17.1	2.9	35.4	6.3	12
100 °C	0.5	99.4	0	0.4	0	0.2	0
	5	91.2	2	2	0.6	2.1	2.2
	20	75	5.5	3.9	3.7	7.2	4.7
150 °C	0.5	100	0	0	0	0	0
	5	90.7	2.3	0.8	0.9	1.3	3
	20	56.8	7	3.6	4	7.6	13.9

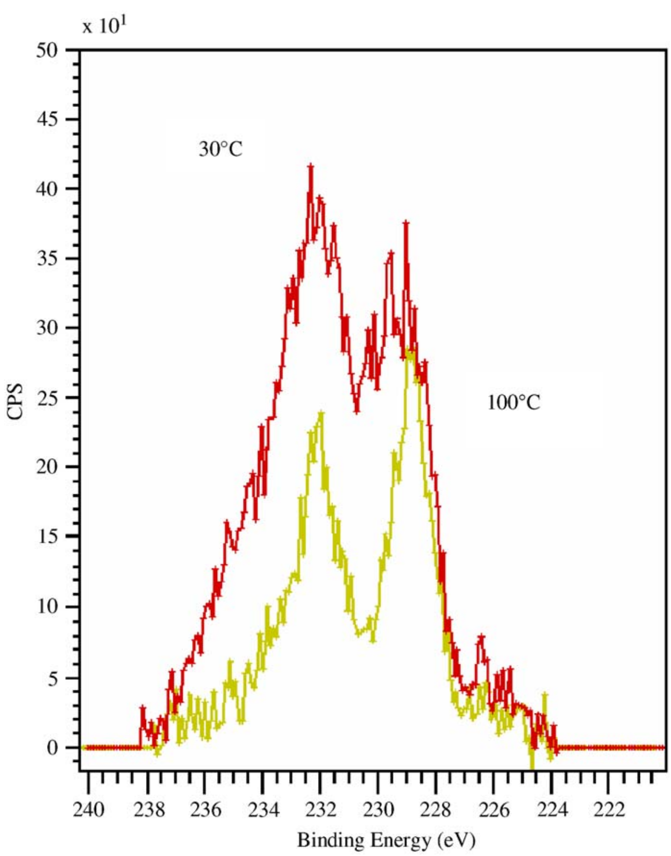

Fig. 8. Mo 3D XPS spectra recorded in tribofilm formed when 003A lubricant was tested at 30 and 100 °C. Higher left shoulder of Mo 3d peak detected in the 30 °C tribofilm is due to the higher amount of oxides formed in relation to sulphides.

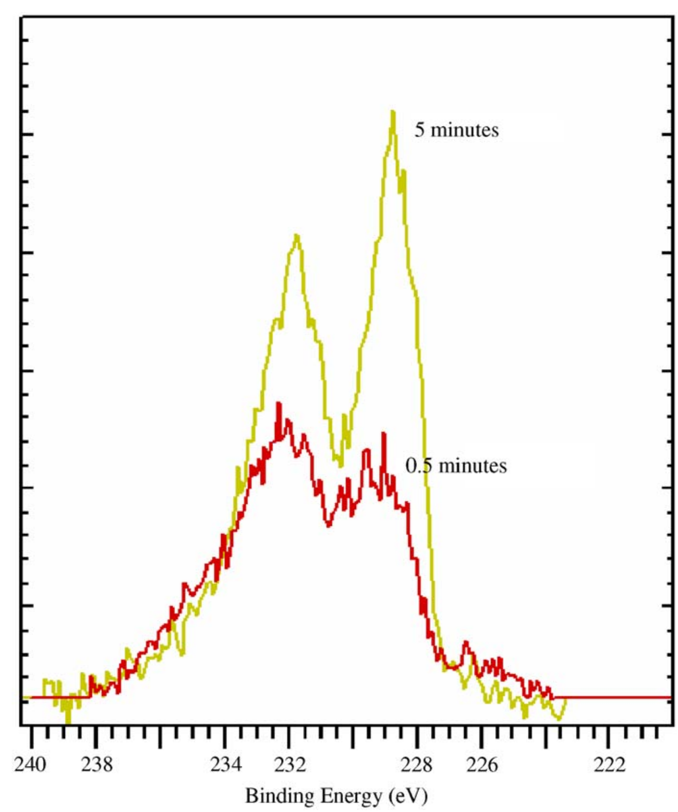

Fig. 9. Mo 3d XPS spectra recorded in tribofilm formed when 003A lubricant was tested at 30 °C after Ar^+ etching.

Table 8
004A lubricant's tribofilm EDX quantification as a function of temperature

004A	EDX (wt%)									
	P	S	Zn	Fe	O	C	Cr	Si	Mn	Mo
30 °C	0.4	0.3	0.9	83.5	4.9	2.3	4.8	0.4	1.8	0.6
100 °C	0.3	0.3	0.7	82.5	4.6	3.7	4.7	0.5	2.2	0.4
150 °C	1.6	0.5	2.8	75.2	6.5	6.9	3.7	0.5	1.7	0.5

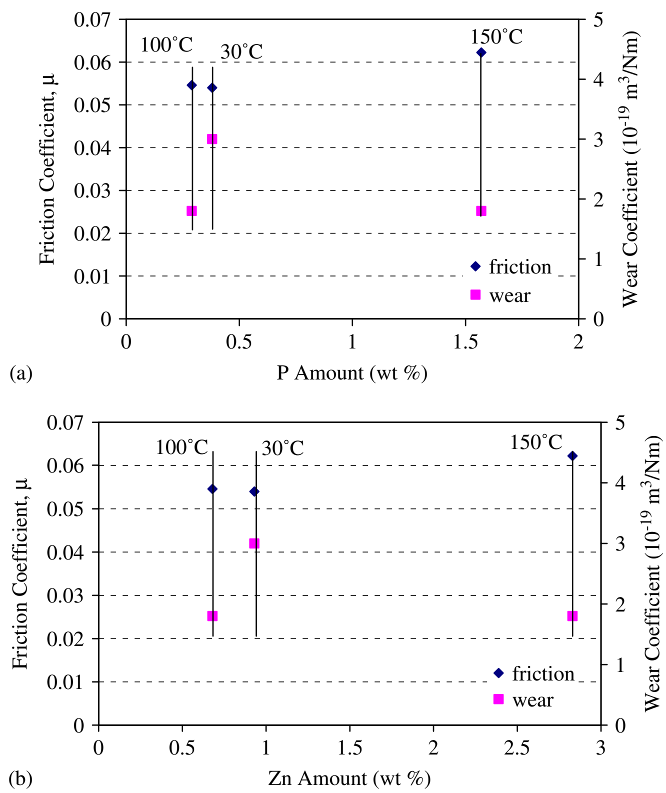

Fig. 10. Friction and wear coefficient as a function of (a) P and (b) Zn amount, quantified using EDX, detected in the 004A tribofilms formed at 30, 100 and 150 °C.

4. Discussion

4.1. Effect of ZDDP/MoDTC ratio in friction reduction

The friction results obtained from different MoDTC ratios in ZDDP-treated lubricant have shown that even 50 ppm MoDTC can cause a reduction in friction although not to the same extent as 250 ppm MoDTC. The link between increase of MoDTC concentration in the ZDDP lubricant to the level of friction reduction has been observed before by Muraki et al. [30] and Kasrai et al. [6]. There is no agreement about the minimum amount of MoDTC in ZDDP lubricant for achieving low friction. Muraki et al. [30] and Kasrai et al. [6] showed lowest friction to be achieved only after adding 700 ppm MoDTC and 500 ppm MoDTC, respectively. In the present work, optimum friction reduction is achieved even with 250 ppm MoDTC. The increase of MoDTC percentage in ZDDP-treated lubricant led to a reduction in the amount of Zn and P found, suggesting that less ZDDP tribofilm has been formed, while the Mo amount was seen to increase. Formation of a thinner ZDDP tribofilm when MoDTC is present in the lubricant has been reported by Muraki et al. [30] and is proposed to be due to the competitive adsorption between ZDDP and MoDTC to active surfaces in the wear scar. In general, an increase of MoDTC percentage in the ZDDP lubricant has shown to increase the extent of friction reduction as a result of more MoS_2 forming in the wear scar.

4.2. Effect of temperature

4.2.1. ZDDP tribofilm

When the ZDDP-containing lubricant (002A) was tested at the three temperatures, a clear effect of temperature on both friction and wear was seen. The friction was seen to increase while wear to decrease with lubricant temperature increase (Figs. 3 and 4).

Chemical analysis of the ZDDP tribofilms shows a steady increase of S in the tribofilm, while the amount of P and Zn increased in the tribofilm formed at 100 °C, when compared to the one formed at 30 °C. An increase of temperature has been shown to increase the ZDDP decomposition rate [31] thus increasing the film thickness [32,33]. The increase of temperature from 100 to 150 °C could trigger the formation of different ZDDP species. Gao et al. [34] showed that increase of P gave increase of friction when tested at temperatures higher than 80 °C and lower friction when tested at temperatures lower than 80 °C, suggesting that different P species form at these temperatures. In this study, the deconvolution of the Zn and P XPS peaks showed that in tribofilms formed at all three temperatures, a Zn phosphate glass has been formed. The increase of bulk lubricant temperature from 30 to 100 °C formed a longer chain polyphosphate on the surface of the tribofilm. With further increase to 150 °C, the thickness of the long-chain polyphosphate was shown to increase.

The link between long-chain polyphosphates and low wear can be explained using the Martin et al. [35] mechanism for ZDDP tribofilm formation. According to this mechanism, the short-chain polyphosphates are

Table 9
004A lubricant's tribofilm XPS quantification as a function of temperature

004A	Etching time (min)	XPS (at%)							
		C1s	O1s	S2p	P2p	Fe2p	Zn2p3/2	MO3d	N1s
30 °C	0.5	51.8	18.9	4.7	7.8	1.1	2.8	4	4.5
	5	25.8	20.8	6.3	7.7	8	4.9	7.7	4.9
	20	23.2	16.3	3.2	4	31.1	2.2	4.9	8.9
100 °C	0.5	91.1	4.1	1.6	2.2	0	0.3	0.8	0
	5	54.7	15.6	4	5.4	1.8	4.3	3.3	5.1
	20	31.8	17.1	3.2	4.2	18.5	3.7	4.7	8.7
150 °C	0.5	47.1	30.7	4.2	11.2	0	6.1	0.8	0
	5	21.9	36.7	5.7	12.7	2.6	12	1.9	4.2
	20	12.9	31.9	4.6	7.3	25.4	8.4	1.8	6.8

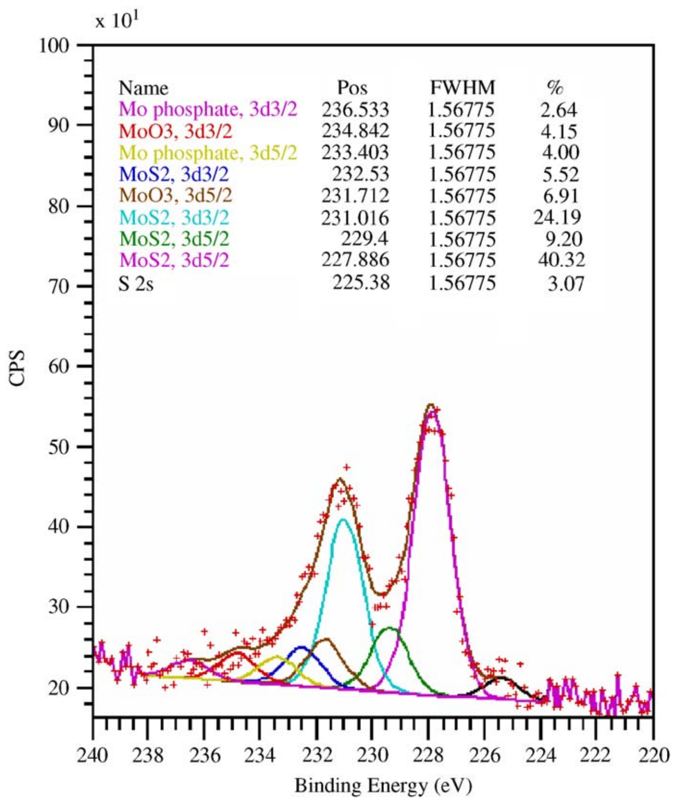

Fig. 11. Mo 3d deconvoluted XPS peak from 004A tribofilm formed at 150 °C, after 20 min Ar+ etching.

produced as a reaction of long-chain polyphosphates with the iron oxide from the substrate. Exchange of Zn^{2+} with Fe^{3+} needs more negative charge to balance the reaction, requiring shortening of the chain length. A lack of short-chain polyphosphates suggests that no iron oxide was produced with rubbing. However, the formation of the short-chain and long-chain polyphosphates could not be a function of just wear process as suggested in [35–37]. Fig. 7 shows no long-chain polyphosphate formation at 30 °C in contrast with 100 °C tests while the wear is comparable, suggesting an effect of temperature on long-chain polyphosphate formation. Willermet et al. [38], in contrast with Martin et al. [35], suggested that first short-chain polyphosphates form which then polymerise to long-chain polyphosphates. The data shown in this study show evidence of both mechanisms proposed for ZDDP film formation, suggesting that ZDDP tribofilm formation is both a function of temperature and wear process.

4.2.2. *MoDTC tribofilm*

When 003A lubricant was tested at 30 °C, the friction was not seen to reduce as low as at 100 and 150 °C. The greater effectiveness of MoDTC at high temperatures, in tests done in reciprocating mode, has been widely reported [3,11]. Increase of temperature reduces the lubricant viscosity which will result in more solid–solid contact. With rubbing the nascent Fe surface will be revealed and the S in N-containing organic group from MoDTC molecule will react with iron to form a tribofim. This process explains the detection of N and a high amount of C at the near surface detected by XPS. The role of S- and N-containing species from the MoDTC additive in formation of MoS_2 is shown in our previous work [7].

Analysing the Mo 3d XPS peaks, it can be seen that a higher amount of Mo oxides has been formed in the 30 °C tribofilm. Table 11 shows the Mo sulphide/Mo oxide ratio which is actually the ratio between low- and high-friction tribofilm formed from MoDTC.

It can be suggested that high presence of oxides in the tribofilm reduces the effectiveness of the Mo sulphide in reducing friction. This is also supported by the findings of Muraki et al. [30] that friction coefficient from a MoDTC-containing lubricant cannot be explained from Mo intensity and the friction is determined as a function of the proportion of MoS_2 in the tribofilm.

4.2.3. *ZDDP/MoDTC interaction as a function of temperature*

The effectiveness of MoDTC in reducing friction at low temperatures was seen to increase when the ZDDP was present in the lubricant. The friction was seen to reduce to the lowest values observed when MoDTC is effective in friction reduction ($\mu = 0.05$) when the 004A lubricant was

Table 10
Curve fitting Mo 3D XPS spectra recorded in tribofilm formed when 004A lubricant was tested at three temperatures

Etching time (min)	Mo 3D—004A Binding energy (in eV) at			Species
	30 °C	100 °C	150 °C	
0.5	228.4 (61.6%)	228.2 (55%)	228 (48.4%)	MoS_2
	229.6 (19.1%)	229.6 (19.8%)	229.4 (13.7%)	MoS_2
	231.8 (9.1%)	231.8 (7%)	232.7 (25%)	Mo oxide
		233.3 (2%)		Mo phosphate
5	228.1 (62%)	228 (64.8%)	228 (44.6%)	MoS_2
	229.6 (14.5%)	229.4 (13.6%)	229.6 (18.3%)	MoS_2
	231.9 (13.2%)	231.7 (11.6%)	232.4 (13.6%)	Mo oxide
	233.6 (4.5%)	233.2 (5.5%)	233.6 (10.8%)	Mo phosphate
20	228.2 (67.1%)	228 (64.4%)	228 (49.1%)	MoS_2
	229.6 (12%)	229.4 (14.7%)	229.6 (12%)	MoS_2
	231.7 (12%)	231.7 (13%)	232.3 (11.5%)	Mo oxide
	233.5 (5.3%)	233.4 (6.6%)	233.7 (15.3%)	Mo phosphate

Table 11
Calculation of the ratio between low-friction tribofilm and high-friction tribofilm formed as a result of MoDTC decomposition in the 003A lubricant

003A	MoS_2 amount—low-friction tribofilm	MoO_3 amount—high-friction tribofilm	Low-friction/high-friction tribofilm ratio
30 °C	60%	36%	1.7
100 °C	74%	21%	3.5

tested at 30 °C, showing a synergistic effect of ZDDP on friction reduction from MoDTC. These results are in agreement with Muraki et al. [17], from tests using lubricants with MoDTC and ZDDP/MoDTC additives at 25 °C. However, the test performed at 150 °C showed an antagonistic effect of ZDDP on friction reduction from MoDTC. With increasing temperature, the formation rate of species formed from both additives will increase but the extent is likely not to be the same for all species. Friction will be determined according to which tribofilm dominates the contact area.

The quantification of the tribofilms formed, shown in Tables 8 and 9, shows an increase of ZDDP elements, Zn and P, and reduction of Mo when the tests are performed at 150 °C. Observing the friction as a function of P and Zn amount (Fig. 10), it can be suggested that more ZDDP tribofilm, formed as a result of temperature increase from 100 to 150 °C, gives higher friction. This is in agreement with the results obtained analysing the tribofilms formed from lubricant containing only the ZDDP additive. The synergistic and antagonistic effect of ZDDP on MoDTC effectiveness on friction reduction was also observed by Muraki et al. [30]. The difference in their work is that they have seen this effect by increasing the ZDDP amount in the lubricant. The amount of Mo was seen to decrease with ZDDP increase in the lubricant.

The friction change cannot be explained only from the Mo amount in the tribofilm since the formation of other Mo species (besides MoS_2) which have different frictional properties is paramount. Similar to 003A tribofilm, the ratio between *low-friction tribofilm* (MoS_2) and *high-friction tribofilm* (Mo oxide and Mo phosphate) for the tribofilms formed using 004A lubricant at three temperatures is obtained (Table 12) and the link with friction is studied.

Fig. 12 shows the friction coefficient as a function of the ratio between low-friction tribofilm and high-friction tribofilm formed in the wear scar when 003A and 004A lubricants are tested.

Fig. 12 shows that an important factor that governs the friction reduction when MoDTC-containing lubricant has been used is the ratio of MoS_2 with the other high-friction species such as MoO_3 formed in the contact area. As can be seen from Table 12, this ratio for the 004A tribofilm formed at 30 °C is 8.9, which is much higher than the one obtained from 003A tribofilm tested at the same temperature. This means that MoS_2, known to be the low-friction material, dominates the tribofilm. From the deconvolution of Mo 3d XPS peaks from 003A and 004A tribofilms formed at 30 °C, shown in Fig. 8 and Table 10, respectively, and the Mo peak quantification, Tables 7 and 9, respectively, the peaks corresponding to MoS_2 are quantified. It could be seen that 4.7 and 3.2 at% of Mo corresponds to MoS_2 in the 003A and 004A tribofilm, respectively. So, the presence of ZDDP did not result in more MoS_2 formed but, as shown in previous analysis, it resulted in a higher MoS_2/MoO_3 ratio.

Table 12
Low-friction/high-friction material ratio obtained from Mo 3D XPS peak deconvolution of the 004A tribofilms

004A	Friction coefficient	Low-friction/high-friction material ratio
30 °C	0.055	8.9
100 °C	0.055	8.3
150 °C	0.062	2.5

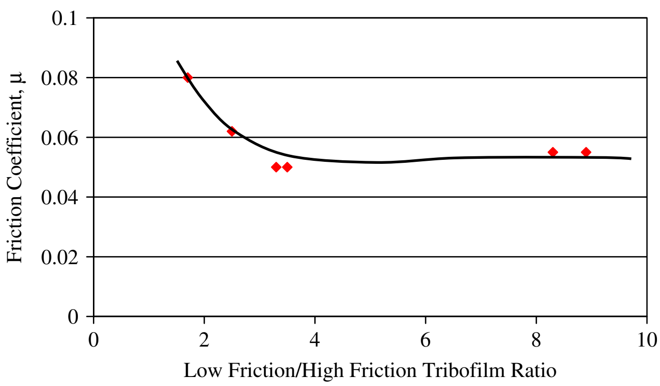

Fig. 12. Friction coefficient as a function of ratio between low-friction (MoS_2) and high-friction (remaining Mo-species) tribofilm formed in the wear scar.

The elimination of MoO_3 by the ZDDP tribofilm has been suggested before by Martin et al. [39]. The reaction between ZDDP and MoDTC tribofilm is thought to occur according to the hard and soft acids and bases principle [39]. According to this principle, phosphate (PO_4^{3-}) anion as a hard base prefers to react strongly with the molybdenum cation (Mo^{6+}) as a hard acid. As a result of this chemical process, the Zn/Mo phosphate is suggested to form. This is supported by Mo 3d curve fitting results shown in Table 10, where it can be seen that with further etching a peak which corresponds to Mo phosphate is detected.

Increase of temperature to 150 °C shows an increase of high-friction material formed in the tribofilm, MoO_3 and Mo phosphate, explaining the higher friction obtained in this temperature. Analysing the peaks obtained deconvoluting the Mo 3d XPS peaks, Table 10, it can be seen that the interactions are seen only in the formation of Mo phosphates.

It should be acknowledged that these results are obtained analysing tribofilms formed in bench tribometer. This study is continued by analysing tribofilms formed in conditions closer to in-service conditions using motored cylinder head, results of which will be published in near future.

5. Conclusions

The effect of temperature and MoDTC percentage in a ZDDP-containing lubricant on tribological performance and tribofilm characteristics has been investigated in a bench tribometer. The following conclusions can be made:

- Increase of MoDTC concentration in the ZDDP-containing lubricant from 50 to 250 ppm Mo level caused an increase in MoS_2 formation in the wear scar, resulting in further reduction of friction.
- In the case of ZDDP-containing lubricant alone, increase in temperature causes an increase in phosphate glass tribofilm formed in the wear scar. Higher phosphate chain length at the top layers of the tribofilms is shown to be related with friction increase and at the same time lower wear.
- At 30 °C, MoDTC effectiveness on friction reduction is retarded due to the Mo oxides formed in the wear scar. At this temperature, the presence of ZDDP in the MoDTC-containing lubricant resulted in improved frictional performance. This is due to the interaction between ZDDP tribofilm and Mo oxides formed from MoDTC, resulting in less Mo oxides.
- At 150 °C, ZDDP presence in the MoDTC-containing lubricant caused a slight increase in friction which is shown to be due to the increase of Zn phosphate and Mo phosphate formation at this temperature. At this temperature, a larger ratio of normal load is carried by the phosphate film formed from ZDDP and ZDDP/MoDTC interaction rather than by the MoS_2 formed from MoDTC.
- Presence of MoDTC in the ZDDP-containing lubricant caused just a marginal increase of wear when compared to the ZDDP alone. This wear was still lower than the wear obtained by base oil and lubricant containing MoDTC alone.
- An important factor that governs the friction reduction when MoDTC-containing lubricant is used is the ratio of low-friction MoS_2 with the high-friction species such as MoO_3 formed in the contact area. This ratio is shown to depend on the temperature and the ZDDP present in the lubricant.

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