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Tribofilms: aspects of formation, stability and removal

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Abstract
There has been much attention paid to the lubricant additives zinc dialkyldithiphosphate and molybdenum dialkyldithiocarbamate as the most commonly used antiwear/antioxidant and friction modifiers. The mechanism by which they function has been the subject of much research work. As a result of these efforts the tribofilms formed from the above additives are fully chemically characterized but understanding the physical properties and the dynamics of their formation, stability and removal is still not satisfactory and needs more research. This paper reviews the general characteristics of tribofilms formed from these additives in single component systems and also on their interactions as well as the current understanding of the dynamics of their formation. Experimental work is then presented alongside discussion of the literature to present a current status of understanding of the stability and the removal of tribofilms. The effect of temperature and additive interactions on the thickness of the steady state tribofilms, and consequently the effect on friction performance, is evaluated. The results of this study show that temperature and additive interactions play a significant role on the dynamic process of tribofilm formation as well as its chemical properties. This study also highlights the areas in which further development is needed to ensure progress in understanding of the tribofilm's formation and removal processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Effective lubrication of boundary lubricated systems such as the valve train in the internal combustion engine is ensured by the formation of very thin films in the contact as a result of interaction between chemical components of the oil with the lubricated surface. These films are known as tribofilms. There are different mechanisms by which the tribofilms ensure low wear and friction. In terms of tribofilms which protect component surfaces from excessive wear, the most common is the tribofilm formed from the zinc dialkyldithiphosphate (ZDDP) additive. Friction reduction is achieved by tribofilms formed from the friction modifiers; these are commonly organometallic species such as molybdenum dialkyldithiocarbamate (MoDTC). In the literature, a range of theories are given for the mechanisms by which tribofilms form and provide their functionality.

Formation of ZDDP tribofilms has been the subject of several review papers which have summarized the knowledge obtained from research going back to the 1950s [1–3]. Also the formation of low friction tribofilms from MoDTC-containing lubricants has been the subject of several research works [4–6]. Despite this not much is known about the tribofilms' kinetics of formation and removal. Tribofilm formation is a dynamic process which involves creation, removal and replenishment [7], and so in order to understand the formation of stable tribofilms it is very important to understand the kinetics of these processes. This study focuses only on the tribofilms formed from model lubricants that contain only ZDDP, MoDTC and ZDDP/MoDTC. The authors acknowledge that the tribofilm formation, stability and removal processes will also be affected by other additives in the lubricant, other than ZDDP and MoDTC, but consider that understanding these processes in model tribofilms will facilitate the understanding of the more complex processes related with the tribofilm formed from fully formulated lubricants.

The current study focuses on understanding the effects of temperature and additive interactions on the thickness of the steady state tribofilms and making the link to the friction properties. It also reviews the current state of knowledge of the *kinetics* of tribofilm formation, removal and replenishment from ZDDP and MoDTC additives as part of an engine oil lubricating conventional iron materials and the factors which influence it. This study highlights several issues related to the dynamic process of tribofilm formation which are still not fully exploited because of the lack of technology to make truly *in situ* measurements which would enable a more detailed understanding.

The paper initially reviews the literature related to aspects of tribofilm formation from ZDDP and MoDTC additives and its thickness then progresses to consider the effect of temperature on tribofilm thickness and tribological performance.

1.1. General aspects of the ZDDP tribofilm and its thickness

The initial phase of ZDDP tribofilm formation is thought to be the formation of phosphate precursors and the organic sulfur species in the bulk oil [8–10]. During running-in, an iron sulfide film forms from the sulfide products. This film prevents localized adhesion and metal transfer between contacting asperities [11]. As the severity of the asperity contact is diminished by plastic deformation, sulfidation and oxidation, deposition of the polyphosphate decomposition product begins. This creates a barrier against access of sulfur and oxygen, thus reducing the rate of the chemical wear caused by uncontrolled sulfide and oxide growth, as the amorphous phosphate film structure develops.

There are several theories on the antiwear mechanisms of the ZDDP tribofilm: formation of a softer than substrate tribofilm which reduces the number of asperities in contact exceeding the shakedown limit [12], reduction of three-body abrasive wear by the digestion of the iron oxide particles [13], by the ZDDP tribofilm debris re-entering the contact [14] and by the formation of a phosphate glass structure which in contact conditions will behave as a viscous lubricant [8]. Another mechanism of wear protection from ZDDP antiwear film is the effect of glassy phosphates in passivation of the surface against further thermo-oxidative reactions such as corrosive wear. All the theories agree that the tribofilm formed from ZDDP is the source of the antiwear performance and this study focuses on the dynamics of its formation. The other aspects of the ZDDP tribofilm characteristics, such as mechanisms of its formation and effect of the testing environment on its formation, have been the subject of several comprehensive reviews [1–3].

The steady state thickness of engine oil additive tribofilms is determined by the balance between the rate of film formation/replenishment and the rate of film removal. Measurement of tribofilm thickness, in particular of the tribofilms formed from ZDDP, has been the subject of several studies. One of the main drawbacks of the existing techniques used for film measurements is that they do not truly measure the film thickness *in situ*. *In situ* assessment of additive film formation processes has been possible only by *qualitative* means where electrical contact resistance (ECR) is correlated with film formation. This technique has been shown to be very useful in monitoring the formation of ZDDP tribofilms, since this additive forms a non-conducting film. This technique

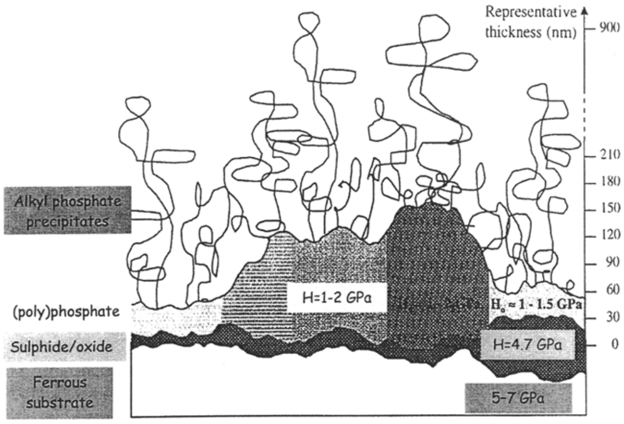

Figure 1. Schematic picture of the structure and mechanical properties of ZDDP tribofilm layers [30].

is not very useful in the case of the tribofilm derived from MoDTC which has conducting properties [15]. ECR is a qualitative method of showing the formation of non-conductive film but there is no link between the contact resistance and the actual film thickness. As such, the ECR is limited to giving information primarily on the rate of film formation at the start of the rubbing which can be useful in terms of monitoring the initial growth in thickness [16–19].

Tribofilm thickness has been quantitatively estimated indirectly by using the x-ray absorption near edge structure (XANES) spectroscopy combined with the particle induced x-ray emission (PIXE) technique [20], from energy dispersive x-ray (EDX) intensity [21, 22], from the Auger electron spectroscopy (AES) depth profiling [9, 23], ellipsometry [24, 25], atomic force microscopy (AFM) [26] and optical interferometry based techniques such as the spacer layer interferometry method (SLIM) [27, 28]. All techniques show the ZDDP film thickness to be in the range 50–150 nm, although what is considered as thickness is still unclear. Each of the methods above has its drawbacks which ultimately affect the accuracy of the measured film thickness. In the case of the film thickness obtained by the surface analytical techniques such as XANES and EDX, because the analyses are performed in high vacuum the samples should be free of any residual oil. In the case of the ZDDP tribofilm, shown schematically in figure 1, it is documented to consist of three layers: the inner chemically reacted film, the chemisorbed layer and the physisorbed gel-like layer [17, 29, 30]. It is believed that after the cleaning the physisorbed layer (the alkyl phosphate precipitates) is removed implying that the film thickness measured by vacuum based techniques is less than it is in the real contact. The thickness of the full ZDDP tribofilm, including the viscous overlayer of alkyl phosphate precipitates, is suggested to be up to 1000 nm thick [11, 30]. Most of the above techniques estimate the thickness of the tribofilm formed on *one* of the surfaces of the tribocouple. If the same tribofilm is formed on the counterbody surface the overall layer in between the contacting surfaces will be greater than 1000 nm.

The ability to get information on the tribofilm thickness and ultimately chemical composition while in contact is of paramount importance to be able to understand the exact antiwear mechanism of this tribofilm. At this stage, the technique which has shown the greatest potential for accurately measuring the tribofilm thickness is the SLIM method. The interference of the tribofilm is minimized using the SLIM technique although the major drawback is having to stop the tribological process during measurement.

1.2. General aspects of the MoDTC tribofilm and its thickness

The MoDTC additive reduces friction by forming a MoS_2-containing tribofilm on the tribological contact [5, 31–35]. The layer-lattice structure of the molybdenum disulfide facilitates the low friction between the tribocouple components [36]. In the MoS_2 molecule, figure 2, there is powerful covalent bonding between atomic species, but between lattice layers there is only a 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.

Chemical characterization of MoDTC tribofilms has shown the tribofilm to be carbon-based containing a few per cent of highly dispersed MoS_2 in the form of individual sheets of length less than 10 nm [5]. The ability of the MoDTC additive to form a low friction tribofilm depends on many factors such as the MoDTC type and concentration, operational temperature, type of contact, load and surface roughness [34].

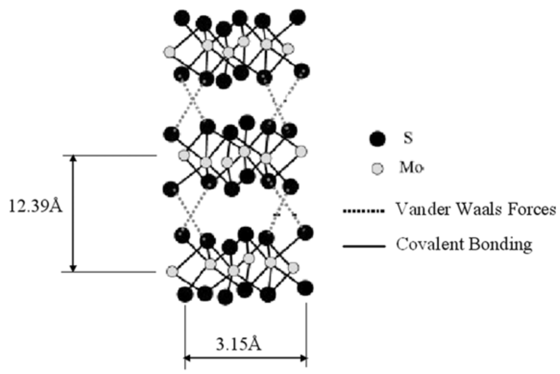

Figure 2. MoS_2 solid state structure.

A typical friction trace for a MoDTC-containing lubricant shows two distinct regions, the initial one with high friction, called the induction phase, and subsequent reduced friction phase. During the induction phase no Mo-containing tribofilm is formed [6, 34] and recent work by the authors demonstrated the formation of a N and S-containing tribofilm [6]. Yamamoto and Gondo [31] claimed that the concentration of the MoDTC affects only the first region of the friction response; the increase in MoDTC concentration reduces the time required to reduce friction. All concentrations reached the same friction at the end of the test. The minimum concentration of the MoDTC in the oil which enables the formation of low friction tribofilm was found to be approximately 180 ppm Mo [35] but this changes at different temperatures and contact conditions explaining the conclusions of the Sorab *et al* study [37] that a Mo percentage higher than 500 ppm is needed for the formation of low friction tribofilm.

It was observed that MoDTCs are most effective in forming a low friction tribofilm and hence in reducing friction at a combination of high additive concentration and high temperature [34]. The schematic model of the evolution of the MoDTC tribofilm, deduced from the chemical analyses of the tribofilm published by the authors [6], is given in figure 3. Formation of the N and S-containing radical group from the MoDTC additive also explains the high amount of C associated with these tribofilms.

In general, the effectiveness of the MoDTC additive in forming the low friction tribofilm depends on the reaction rate which is a function of the MoDTC percentage, temperature and contact conditions.

There are a few studies addressing thickness measurement of the MoDTC tribofilm. In a study by Bec *et al* [38] the MoDTC tribofilm thickness has been estimated from

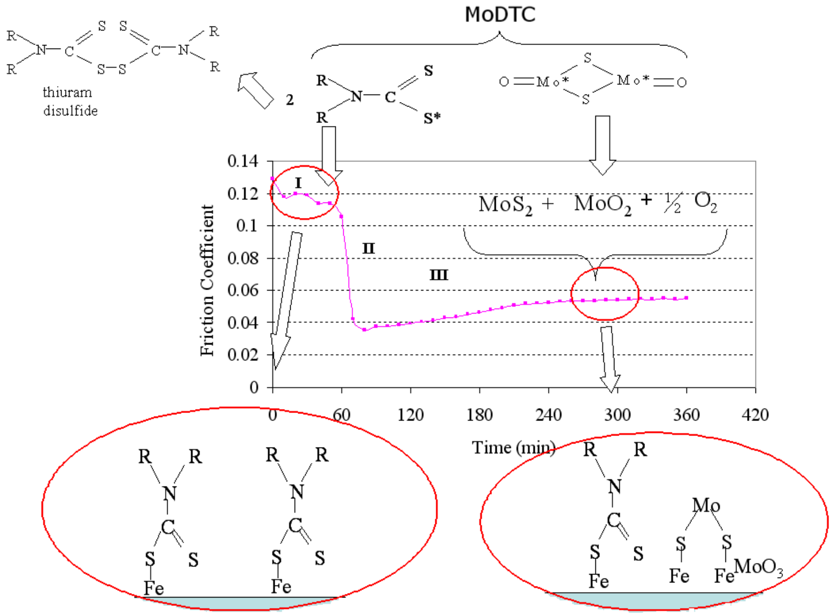

Figure 3. Schematic model and the formation processes of MoDTC tribofilm during the induction phase and at the end of the test. I—formation of N-containing species resulting in protecting the surface from wear. II—formation of Mo oxide beside formation of species from process I. III—formation of MoS_2 and Mo oxide.

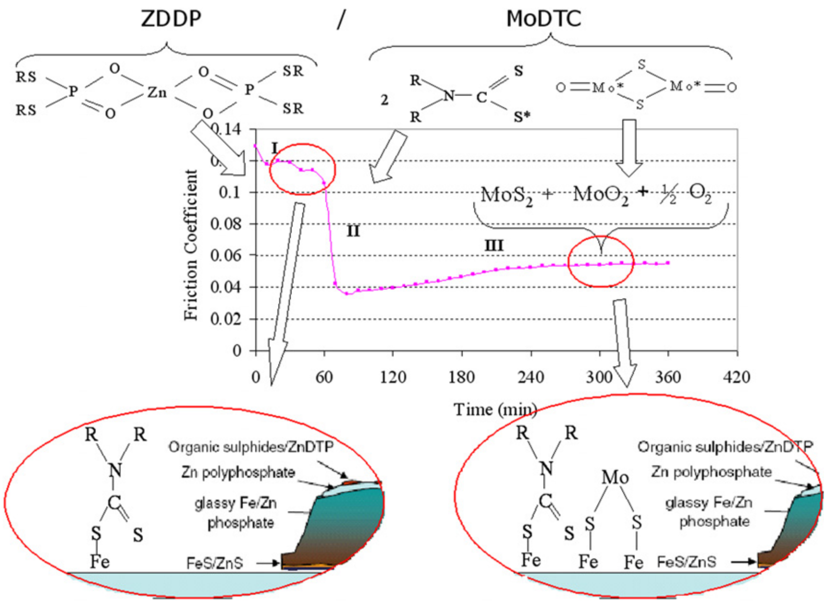

Figure 4. Schematic model and formation processes of the ZDDP/MoDTC tribofilm during the induction phase and at the end of the test. I—formation of N-containing species and ZDDP tribofilm resulting in wear reduction. ZDDP tribofilm with its roughness will increase solid–solid contact promoting the MoS_2 formation. II—adsorption of Mo oxide beside formation of species from process I. III—adsorption of MoS_2 and Mo oxide beside ZDDP tribofilm.

the tribofilm stiffness measurements performed during the experiments using the rheological film model. The film appears to be homogeneous in its thickness, with constant elastic behaviour as a function of depth. The thickness of the film was found to be between 30 and 75 nm. Several studies that have used a combination of surface analysis with etching [6, 39, 40] have given the depth profile of the MoDTC tribofilm formed in the boundary lubrication showing that even after 1000 s etching there is still a Mo-containing tribofilm in the surface analysed.

1.3. General aspects of the ZDDP/MoDTC tribofilm and its thickness

Interactions between ZDDP and MoDTC additives in tribofilm formation and subsequently in tribological performance are shown to occur in the bulk oil [41] and in the tribofilm [42]. In general, it is accepted in the literature that the ZDDP/MoDTC tribofilm is a two phase composition: Zn/Mo phosphate glass and a carbon-rich amorphous phase with MoS_2 sheets embedded in the phosphate glass [6, 43–47].

ZDDP is thought to promote formation of the MoS_2 from MoDTC additive [39, 48] and the mechanism by which this is done could be by providing sulfur [47, 49] or by preserving the pure MoS_2 from oxidation [42] to MoO_3. Sogawa *et al* [49] investigated the origin of sulfur in the MoS_2 tribofilm formed from a ZDDP/MoDTC lubricant. They investigated whether sulfur comes from MoDTC molecule or from some other sulfur-containing additives in lubricant, such as ZDDP. They found that the percentage of sulfur derived from ZDDP in MoS_2 is around 40%. It was found that in the presence of mixture MoDTC/ZDDP, a two-step reaction occurs: first, a reaction between phosphate and iron oxide, and second, a reaction between the nascent iron surface and a sulfide species. These reactions are found to be well explained by the hard and soft acids and bases (HSAB) principle according to which the hard acid reacts with hard base and soft acid reacts with soft base. It is suggested that the wear is reduced because of the elimination of MoO_3 and possible iron oxides when they react with zinc polyphosphate which in the same time preserves pure MoS_2 from oxidation [42]. As a result of the interactions between ZDDP and MoDTC in the lubricant solution [7, 41], MoDDP is being formed in the bulk lubricant and then the reaction products are being detected at the surface. In a similar manner to ZDDP, MoDDP forms a Mo phosphate as a result of thermal decomposition of this additive.

Figure 4 gives the schematic model of the evolution of the ZDDP/MoDTC tribofilm with time, deduced from the chemical analyses of the tribofilm published by the authors [6]. MoS_2 will form following the formation of a ZDDP and N-containing film [6] during the induction time. The interaction between ZDDP and MoDTC additives in friction performance is also likely to be as an interaction between the tribofilms formed from ZDDP and MoDTC in the contact area [6, 50]. An initial study on the effect of ZDDP tribofilm on friction reduction from the MoDTC lubricant [51] done by applying a ‘changing lubricants’ procedure showed clearly that when a tribofilm formed from a ZDDP-containing lubricant was further rubbed in a MoDTC-containing lubricant, the induction time prior to friction drop is significantly reduced, giving useful information about the interaction between ZDDP and MoDTC in low friction tribofilm formation.

The tribofilms formed from ZDDP/MoDTC lubricants have been found to have functionally graded structures with different mechanical properties [52, 53] and different friction properties [54]. ZDDP/MoDTC tribofilms have also been shown to have a lower shearing yield stress than the ZDDP tribofilm [52]. When the ZDDP/MoDTC tribofilm was analysed, nanostrips oriented in the sliding direction were found [53] at a depth of around 10 nm from the surface. It is suggested that these nanostrips, characterized as MoS_2 sheets, act as a solid lubricant to reduce friction coefficient. A sufficiently high contact pressure is needed to reach a favourable orientation of MoS_2 sheets and obtain a low friction coefficient [45].

The ZDDP/MoDTC lubricant forms a tribofilm 60–120 nm thick with very heterogeneous properties [45]. Indentation tests have shown the formation of three different tribofilms from the ZDDP/MoDTC lubricant, with different thickness and mechanical properties [45].

The previous sections give an overview of the current understanding of chemical and thickness aspects of the ZDDP and MoDTC steady state tribofilms. In the following sections the factors that influence the rate of tribofilm formation and its steady state thickness as well as tribofilm durability will be reviewed through presentation of data to illustrate the effect of lubricant temperature on the tribofilm thickness and friction and wear performance. In this work the tribofilms are formed in boundary lubrication conditions in a pin-on-plate tribometer while the rate of tribofilm formation and steady state tribofilm thickness is deduced through the friction performance and the EDX spectra obtained from the tribofilms.

2. Experimental

2.1. Tribological experiments

A reciprocating pin-on-plate tribometer was used to test the additive containing oils in boundary lubrication conditions. Detailed information on the tribometer is given in the authors previous work [6]. From these tests the friction coefficient is obtained which is then plotted as a function of time for the duration of the test. The material for both 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 60-64HRC 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. The wear factors are calculated from the wear scar diameter *on the pin*. Wear in plates was found to be very low and difficult to measure with high accuracy. The wear calculated from pins' wear scar indicates the lubricant effectiveness in wear reduction in the overall lubricating system.

A load of 188 N was applied 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 $0.1\,m\,s^{-1}$. The tests were performed at three temperatures: 30, 100 and 150°C.

The lubricants used are defined in table 1. The base oil (BO) was synthetic oil polyalphaolefin (PAO6) of viscosity 31 cSt ($mm^2\,s^{-1}$) at 40 °C and 5.8 cSt ($mm^2\,s^{-1}$) at 100 °C. Incorporating the additives did not result in a significant change in BO viscosity.

Table 1. Lubricant composition and designation.

Designation	Lubricant
ZDDP	PAO6 + 1.2 wt% secondary ZDDP
MoDTC	PAO6 + 250 ppm MoDTC
ZDDP/MoDTC	PAO6 + 1.2 wt% secondary ZDDP + 250 ppm MoDTC

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

2.2. Post-test surface analysis—EDX

The tribofilms formed on the plate were chemically analysed using EDX analysis. The EDX technique has a probing depth in excess of 1 μm and 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 and is useful to give the overall concentration of the main additive elements in the tribofilm. The EDX analyses were taken from an area of $500\,\mu m \times 400\,\mu m$ at three different positions in the middle of the wear scar and the quantification shown is the representative one. Prior to the analysis, the plate was left to drain the lubricant and then immersed in heptane for about 2 s, in order to eliminate the residual lubricant.

3. Results and discussion

3.1. ZDDP film formation/replenishment

There are a range of factors that influence film formation from additives, affecting the species formed in the lubricant bulk and at the contacting surface. Lubricant temperature and interactions between additives determine the species formed in the bulk [7] while the contact conditions will determine the rate and nature of the tribofilm formed in the component surface.

One important factor which influences the film formation from the ZDDP additive is the lubricant temperature. The temperature and contact conditions will affect the reaction kinetics of the film formation [55]. The analyses of the ZDDP film thickness at different temperatures [25, 56] have shown that higher temperature results in thicker ZDDP tribofilm although Fujita *et al* [27] and Gao *et al* [57] claim that the effect of temperature is in increasing the tribofilm formation rate and not much on the overall steady state film thickness. These observations are also influenced by the ZDDP type. The type of ZDDP is defined by the organic alcohol used to synthesize it: alkylphenols for aryl ZDDP, primary alcohols for primary ZDDP ($CH_3CH_2CH_2CH_2O$–), and secondary alcohols for secondary ZDDP ($CH_3CH_2CH(CH_3)O$–). Primary and secondary alkyl ZDDPs have different thermal stabilities, primary ZDDP being more thermally stable than secondary ZDDP. Their different thermal stabilities affect the rate of film formation [58–60] and in turn the antiwear performance [61]. In general, the primary ZDDPs are preferred for use in diesel engines while the secondary ZDDPs are preferred for use in gasoline engines [62].

Achieving steady film thickness with higher temperatures can be assumed to occur if the chemical quantification of the tribofilms formed at 30, 100 and 150 °C lubricant temperature tests is considered (figure 5). P and Zn quantifications, which are the main constituents of the ZDDP tribofilm, rise

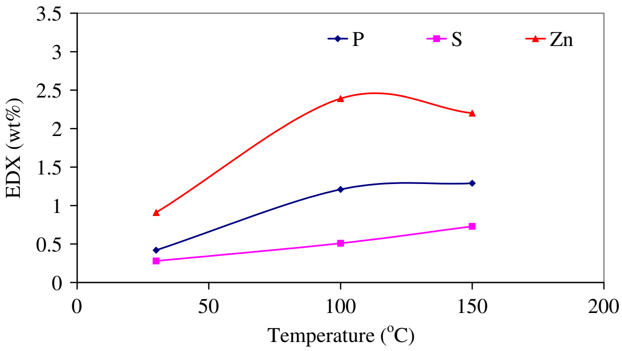

Figure 5. ZDDP tribofilm EDX quantification as a function of temperature.

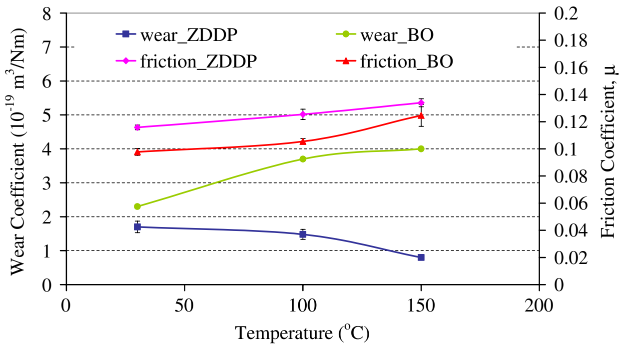

Figure 6. Friction and wear as a function of temperature for the ZDDP-containing lubricant and BO tested with a load of 188 N and a sliding speed of 0.1 m s^{-1} for 6 h.

at temperature of 100 °C but seem to level out with further increase in temperature to 150 °C. Higher concentration of ZDDP main elements in the wear scar with higher temperature was also observed by Lin *et al* [29].

Figure 6 shows that ZDDP lubricant, as expected, gives lower wear than BO but higher friction at three temperatures tested. Higher temperature will increase the chemical reactivity of the additives and, depending on the species formed in the wear scar, a change in tribofilm topographical and mechanical properties will occur. At the same time the lubricant viscosity will reduce forming a thinner elasto-hydrodynamic film (EHL) at increased temperatures. The wear at 150 °C (figure 6) reduced to about 50% of the value at 30 and 100 °C and the friction coefficient increased at higher temperature. Depending on the oil temperature tribofilms with different physical properties will form. So *et al* [58] have shown in their work that above 80 °C lubricant temperature a chemisorbed ZDDP film is formed. In the case of a ZDDP tribofilm, the components that contribute to the growth rate of the effective film thickness, h_{effect}, can be expressed as [29]

$$h_{\text{effect}} = h_{\text{phy}} + h_{\text{chem}} + h_{\text{react}}, \qquad (1)$$

where h_{phy} is the physisorbed film growth rate, h_{chem} the chemisorbed film growth rate and h_{react} the chemically reacting film growth rate.

Viscosity reduction at higher temperatures will also promote the process of the chemically reacted tribofilm formation since more solid–solid contact will occur, providing the nascent iron surface for the additive to react with. From this

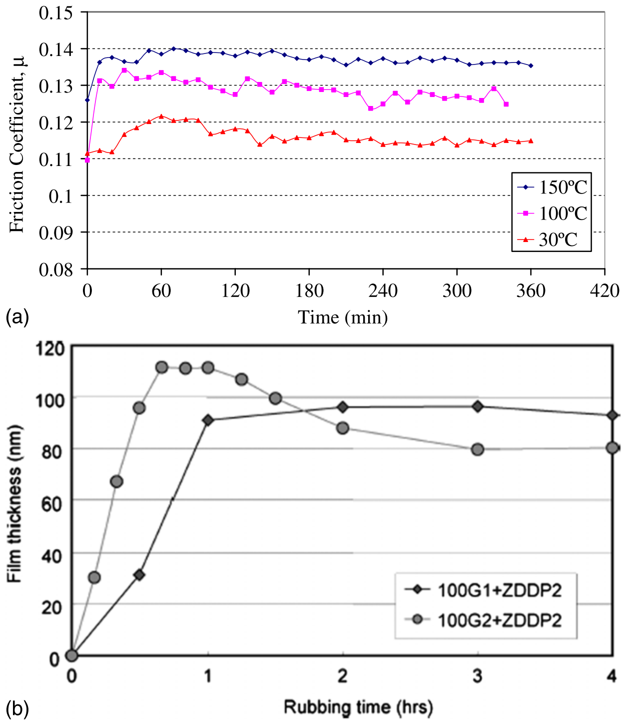

Figure 7. (*a*) Friction as a function of time for the ZDDP-containing oil tested with a load of 188 N and a sliding speed of 0.1 m s^{-1} for 6 h. (*b*) Evolution of the ZDDP tribofilm thickness obtained using the SLIM technique, taken from [60].

it can be deduced that the higher temperature, which in terms of film thickness does not have a significant effect, increases the formation rate of the *chemisorbed* and *chemically reacted* ZDDP film, which results in overall lower wear and higher friction.

Depending on the temperature, the rate of the tribofilm formation components and also the removal rate of these films will change, affecting the total film thickness as well as the intrinsic properties of the tribofilm. Results in this study demonstrate that the formation of thicker ZDDP tribofilms at higher temperatures results in lower wear, which is in agreement with the data shown by Lin *et al* [29], although the contact conditions are different. In contrast Choa *et al* [25] observed increase in wear at higher temperatures, and this is suggested to be related to a decrease in the tribofilm durability and reduction in lubricant viscosity. What is evident is that the lubricant temperature increases the rate of the ZDDP tribofilm formation in the wear scar which, depending on the removal rate, may result in thicker tribofilms.

The friction trace as a function of time (figure 7(*a*)) has been shown to correlate well with the build up of ZDDP tribofilm with rubbing measured indirectly using ECR [57] and SLIM [60] techniques. Results obtained with the SLIM technique [60], figure 7(*b*), illustrate that the ZDDP tribofilm starts to form during the initial rubbing, it reaches maximum film thickness after 1 h of rubbing and then the film thickness levels out to a steady state. This correlates with initial increase in friction at the start of the rubbing and then a slight drop of friction in the steady state regime shown in figure 7(*a*).

Formation of the ZDDP film is seen to be increased in more severe rubbing conditions, thicker films are observed when the sliding frequency is decreased and the contact pressure is increased [63]. Formation of the ZDDP tribofilm is seen even after short rubbing [6, 64], which supports the theory that ZDDP works as an antiwear additive from the first stroke, reducing excessive wear of the running-in phase.

3.2. ZDDP film stability/removal

The ZDDP tribofilm, once formed, is very stable. Its stability has been studied by several research groups, mainly by obtaining chemical and physical information from the ZDDP tribofilm after being rubbed in oil with no additive replenishment [20, 28, 51]. Increased sliding distances have shown to result in a reduction of the ZDDP tribofilm thickness [20, 28], suggesting that species which contribute to the film formation can also act as abrasives in the contact region, stimulating the film removal. This is only for a certain time after which a film with steady thickness forms. Figure 8 shows that stability of the ZDDP tribofilm reduces when rubbing in lubricant which contained dispersants [60].

Dispersants are chemical compounds that disperse or suspend in the lubricant potential sludge- or varnish-forming materials, particularly those formed during low temperature operation when condensation and partially burned fuel find their way into the lubricant. Typical dispersants are polymeric succinimides, succinic esters of polyols and Manich base [65–67]. They function by forming micelles which trap deposit precursors. The most commonly used dispersant agent used in engine oils is the polyisobutylene succinimide (PIBS). Although dispersants perform their principal function in the bulk oil, they are also surface active. They interfere with the formation of metaphosphates in the surface from the ZDDP additive [23, 68]. The study by Fujita *et al* [60] shows another antagonistic effect between dispersants and the ZDDP in tribofilm formation but the exact mechanisms of how dispersants increase the removal rate of the ZDDP tribofilms is still unknown.

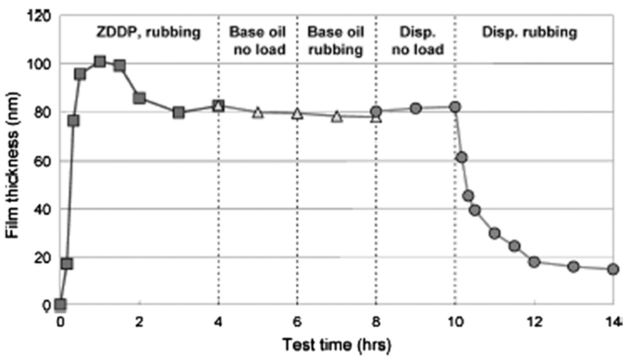

Figure 8. ZDDP tribofilm stability reduction when rubbed in dispersant-containing lubricant [28].

For good antiwear performance, the rate of tribofilm removal should always be lower or equal to the rate of the tribofilm formation. This is expressed by Lin *et al* [29] using equation (2):

$$h_{\mathrm{effect}} \geqslant h_{\mathrm{scrape}}, \tag{2}$$

where h_{scrape} defines the tribofilm removal rate.

The rate of ZDDP tribofilm removal will depend on the contact conditions and the environment and needs more focused research to be quantified. In any case, its high durability is obvious in explaining the superior antiwear performance of this tribofilm.

3.3. MoDTC film formation/replenishment

Figure 9 shows the friction trace as a function of time for the tests where MoDTC lubricant is tested at three temperatures. The rate of friction reduction increases with higher temperature, suggesting a higher formation rate of the low friction tribofilm. Friction reduction below 0.1 is taken as an indication that the low friction tribofilm is formed.

The EDX spectra of the tribofilms, given in figure 10, show a bigger Mo peak for tribofilms formed at higher temperatures suggesting higher Mo concentration. Friction trace as a function of time and the end of test chemical analyses show that higher temperature increases the rate of film formation, which results in shorter induction time, and overall Mo-containing tribofilm thickness.

Temperature has been shown to have a different effect on the formation of low friction tribofilm depending on the contact conditions. In reciprocating tests an increase in temperature above 100 °C required longer rubbing for the friction to drop but once the friction dropped the values were lower than for the low temperatures tests [69]. In the case of rubbing in a linear sliding mode, higher temperature was found to decrease the induction time prior to the friction drop [35] but the effectiveness of MoDTC to reduce friction was lost later during

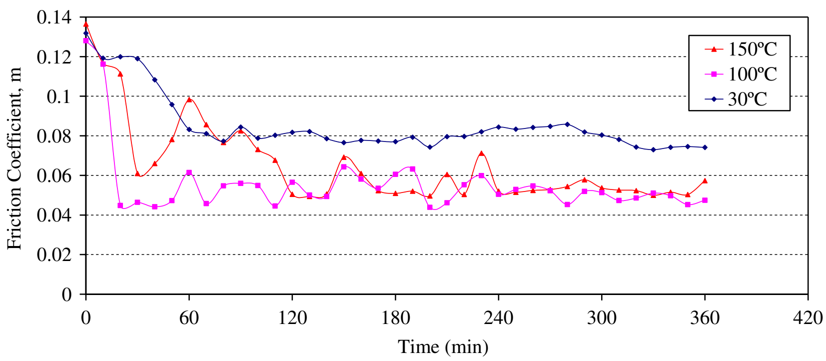

Figure 9. Friction coefficient as a function of temperature for MoDTC-containing lubricant tested with load of 188 N, sliding speed of 0.1 m s^{-1} for 6 h.

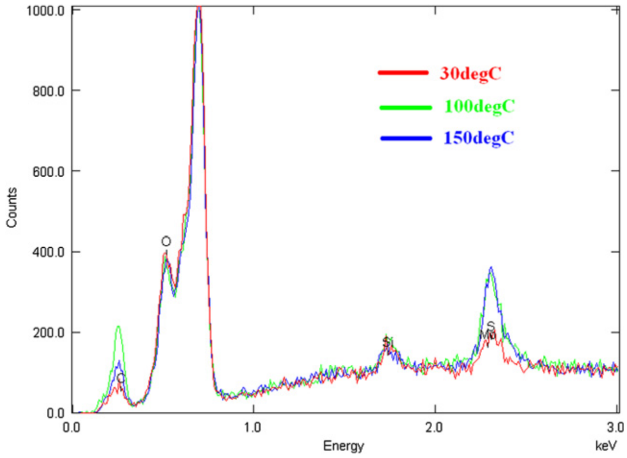

Figure 10. MoDTC lubricant's tribofilm EDX spectra as a function of temperature.

the test resulting in increase in friction. This is suggested to be due to the conditioning of the surfaces during rubbing, which reduces their reactivity towards MoDTC rather than depletion of the additive. The sliding distances before the friction drop, around 140 m for tests in [35] and around 10 m for tests in [69], are completely different. These differences in effectiveness of MoDTC could be due to the rubbing mode, the reciprocating mode was shown to promote the formation of MoS_2. The more severe rubbing reciprocating mode will result in more solid–solid contact, which is seen to promote the formation of low friction tribofilm from MoDTC additive [34]. One possible mechanism that could explain this is that with solid–solid contact the oxide layer is removed resulting in nascent iron surface in which S in the N-containing radical, formed from breakdown of MoDTC, will react according to the HSAB principle, since S^{2-} and metal atoms are known to be soft base and acid, respectively, forming FeS_x and leaving the N part to deposit on the surface. In this case the formation of FeS_x will act as a protective layer reducing wear [70–72] and by that allowing the formation of a friction-reducing layer of MoS_2 from the other radical of the MoDTC molecule. The formation of FeS from MoDTC has been previously observed [71, 72]. Formation of an initial durable tribofilm reduces wear and by that promotes formation of the MoS_2 tribofilm from MoDTC additive [51].

3.4. Low friction MoDTC film stability/removal

Stability/removal of the low friction MoDTC tribofilms has been reported by the authors in a previous study through recording the friction performance. Figure 11 shows that once the low friction MoDTC tribofilm is formed from the MoDTC lubricant at 100 °C and the low friction is reached (at 240 min), the replenishment of MoS_2 in the tribofilm is essential to maintain the low friction. The authors' previous work has shown an instantaneous change in low friction obtained from the MoDTC once the additive is removed from the lubricant [73]. Compared with the ZDDP tribofilm, the MoS_2 tribofilm formed from MoDTC is much less stable and is easily removed from the contact.

The need for continuous replenishment of the low friction tribofilm in order to maintain low friction from the MoDTC

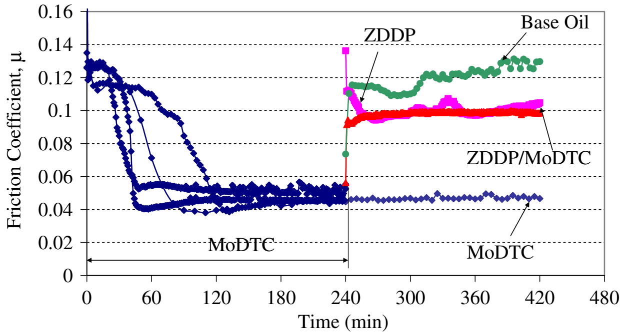

Figure 11. Friction coefficient obtained from rubbing further the wear scar produced with the MoDTC lubricant in BO, ZDDP, MoDTC and ZDDP/MoDTC lubricants [73].

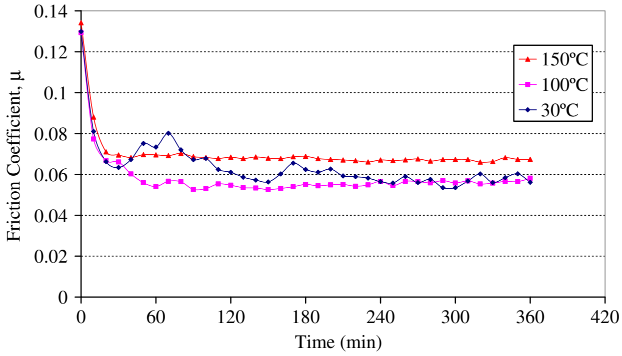

Figure 12. Friction coefficient as a function of temperature for ZDDP/MoDTC lubricant tested with load of 188 N, sliding speed of 0.1 m s^{-1} for 6 h.

additive was also observed by Graham *et al* [35]. In their work they showed that oxidative degradation of the MoDTC additive reduced the bulk concentration of the additive and by that reduced replenishment of the low friction tribofilm.

To the authors' knowledge no other work has studied the stability of the low friction tribofilm formed from the MoDTC lubricant.

3.5. ZDDP/MoDTC film formation/replenishment

Figure 12 shows the friction trace as a function of time for tests where ZDDP/MoDTC lubricant is tested at three temperatures. What can be observed is that there is no change in the rate of friction drop at the start of the test but the temperature affected the level of friction reduction in the steady state tribofilm, giving a slightly higher friction coefficient at 150 °C.

Compared with the friction response of MoDTC lubricant, there is a significant reduction in the induction phase prior to the friction drop and the mechanism of this is discussed in previous studies by the authors [51, 73]. The higher rate of the low friction tribofilm formation is suggested to be linked to the evolution of the ZDDP/MoDTC tribofilms, reviewed in section 1.3 of this study.

Figure 13 gives the EDX spectra of the ZDDP/MoDTC tribofilms formed at three temperatures, giving an insight into their thicknesses.

Increase in the lubricant temperature to 150 °C did not show a significantly larger peak of Mo but significantly larger

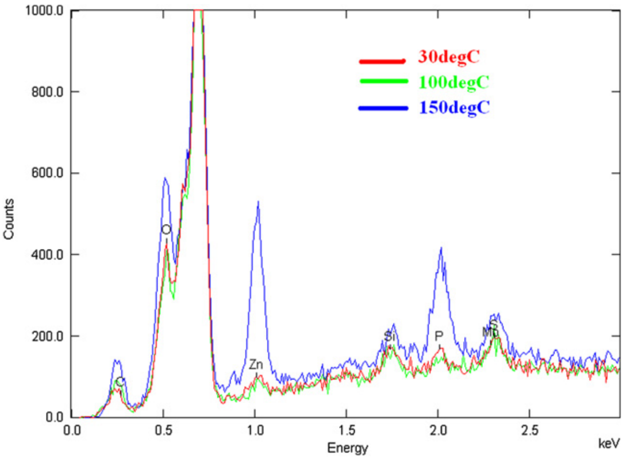

Figure 13. ZDDP/MoDTC's tribofilm EDX spectra as a function of temperature.

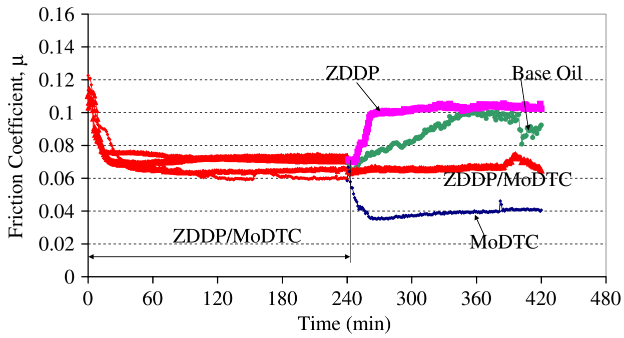

Figure 14. Friction coefficient obtained from rubbing further the wear scar produced with the ZDDP/MoDTC lubricant in BO, ZDDP, MoDTC and ZDDP/MoDTC lubricants [73].

peaks of Zn and P, the main constituents of the ZDDP tribofilm. This suggests that a thicker phosphate film formed at this temperature. Detailed analyses of the XPS molybdenum peaks showed that besides MoS_2 and MoO_3 Mo phosphate is also formed. The amount of Mo phosphates, in relation to Mo sulfide and Mo oxide, is seen to dominate in the tribofilm formed at 150 °C [50].

3.6. ZDDP/MoDTC film stability/removal

Figure 14 gives qualitative information of the stability of low friction tribofilm formed from a ZDDP/MoDTC—containing lubricant at 100 °C. Once the tribofilm is formed (at 240 min in figure 14) the lubricant is changed to one with different additives or BO.

Loss of low friction tribofilm is also evident in this case, the difference being the rate of loss of low friction performance. Increase in friction was also observed when testing BO or ZDDP lubricant in a ZDDP/MoDTC tribofilm formed initially, with a distinctive difference being the time taken for the friction to increase once the lubricant is changed. It took approximately 15 min and 40 min for friction to reach 0.08 once the lubricant is changed from ZDDP/MoDTC to ZDDP lubricant and BO, respectively [73]. In terms of sliding distance this will result in 18 m, in the case of the lubricant changed to ZDDP, and 48 m, when the lubricant is changed to BO, of low friction without any low friction tribofilm replenishment. The higher rate of friction increase when the lubricant is changed to ZDDP is a result of the formation of a high friction tribofilm from ZDDP whereas when the lubricant is changed to BO the friction increase is most likely due to local removal of the tribofilm and higher metal to metal contact. It is important to note that the mechanisms by which the friction value increases is subtly different in both cases.

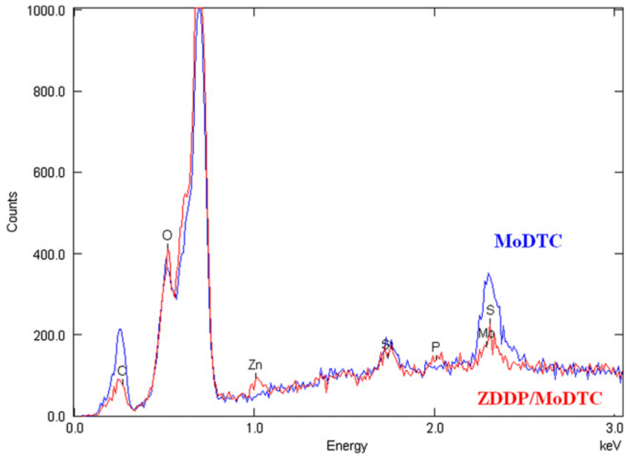

Figure 15. Comparison of typical EDX spectra obtained from MoDTC and ZDDP/MoDTC tribofilms formed at 100 °C tests.

3.7. ZDDP/MoDTC interactions effect in tribofilm thickness

The EDX quantification of tribofilms formed at 100 °C shows that thickness of the Mo-containing tribofilm is higher on the tribofilm formed from MoDTC than the one formed from ZDDP/MoDTC lubricant. Figure 15 gives the overlaid EDX spectra obtained from MoDTC and ZDDP/MoDTC tribofilms, proving the suggestion that thicker Mo film is formed in the MoDTC tribofilm.

The EDX technique probes more than 1 μm thickness of the surface analysed, hence the quantification of the tribofilms by this technique is a good indication of the amount of Mo species formed in *all* layers of the film. Considering the XPS etching results of these tribofilms, even after 1200 s etching with Ar^+ the Mo film was still detected in the contact area [6]. Similar results are also shown by Muraki *et al* [39] and Unnikrishnan *et al* [40] where the Mo element was detected in the MoDTC tribofilm even after 1000 s and 2500 s, respectively. Because the etching rate of the tribofilm is unknown, an accurate figure of film thickness is impossible to be derived from the etching results. If as an indication the etching rate of SiO_2 (0.07 nm s^{-1} [74]) is used, it can be indicated that the MoDTC tribofilm thickness is thicker than 70 nm. Although this value is not accurate since it is derived from an etching rate of a known substance and not of the MoDTC tribofilm, it is still comparable to the thickness estimated from the MoDTC tribofilm stiffness measurements performed during the experiments using the rheological film model [45]. Bec *et al* [45] estimated the thickness to be in the range 30–75 nm.

Comparing the spectra obtained from ZDDP and ZDDP/MoDTC tribofilms, figure 16, it can clearly be seen

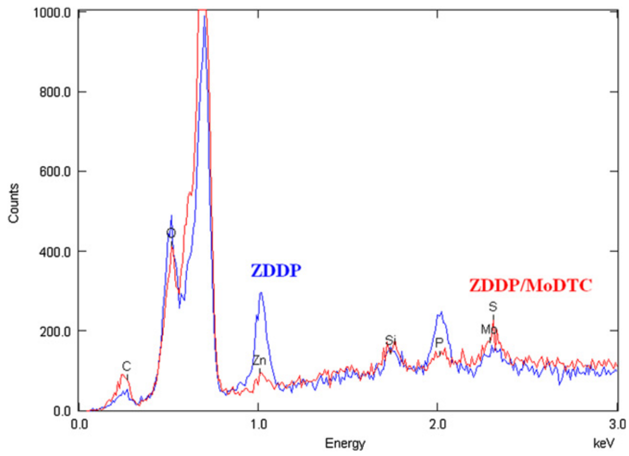

Figure 16. Comparison of typical EDX spectra obtained from ZDDP and ZDDP/MoDTC tribofilms formed at 100 °C tests.

that a thicker Zn phosphate film is formed from ZDDP rather than from ZDDP/MoDTC lubricant.

The EDX results given in figure 16 are obtained from a region of 500 × 400 μm^2 in tribofilms so the uniformity of tribofilms in the wear scar will affect the intensities of elements found. Topographical images of the ZDDP and ZDDP/MoDTC tribofilms using the atomic force microscope have shown a more uniform film is formed from ZDDP/MoDTC lubricant than from ZDDP lubricant [6, 51], indicating that the higher intensity of Zn and P is mainly because of thicker phosphate formed from the ZDDP lubricant.

Zn and P are key constituents of the ZDDP tribofilm and so lower amounts mean that the presence of MoDTC in the lubricant resulted in a thinner ZDDP tribofilm. Formation of a thinner ZDDP tribofilm when MoDTC is present in the lubricant has also been reported by Muraki *et al* [48] and is proposed to be due to the competitive adsorption between ZDDP and MoDTC. XPS quantification of the tribofilms formed from ZDDP and ZDDP/MoDTC lubricants, shown in the authors' previous work [6], proves that a thicker tribofilm is formed from ZDDP rather than from a combination of ZDDP and MoDTC additives. This stresses the point that while obtaining and testing tribofilms from model lubricants is essential for fundamentally understanding the process of tribofilm formation, chemical and physical properties of the overall tribofilms formed from fully formulated lubricants are significantly affected by interactions between the additives in the lubricant and should be taken into consideration.

4. Summary and conclusions

Understanding the mechanism of how ZDDP and MoDTC additives work is of great importance to the engine oil formulator in order to develop new additive packages compatible with the new environmental legislation requirements. This study has shown some of the authors' experimental work in terms of the effect of temperature on the steady state tribofilm thickness and the formation process as well as reviewing the existing understanding of the lubricant additive tribofilm formation and the factors which affect the dynamic process of formation, replenishment and its removal. As a consequence several conclusions can be obtained:

- Higher temperature results in the formation of thicker ZDDP tribofilms with higher friction coefficient. Rise of lubricant temperature increases the rate of film formation, shown by the increase in friction and film data in the literature.
- ZDDP tribofilm once formed is very stable and durable to the further rubbing in a BO.
- Higher temperature results in a higher rate of low friction tribofilm formation from the MoDTC-containing lubricant, and ensures the typical low friction of the MoS_2 tribofilm. Increase in the temperature above 100–150°C does not result in thicker Mo-containing tribofilm.
- Low friction tribofilm formed from the MoDTC lubricant once formed needs continuous replenishment of the MoDTC additive to maintain the low friction. The low friction MoDTC tribofilm is not stable and it is removed instantly from the contact once the additive replenishment is stopped.
- ZDDP/MoDTC lubricant in all three temperatures resulted in a higher rate of low friction tribofilm formation compared with the MoDTC lubricant, resulting in much shorter induction times. At 150 °C test significantly thicker phosphate film forms.
- Low friction tribofilm formed from ZDDP/MoDTC lubricant at 100 °C shows higher stability. Rate of tribofilm removal (rate of friction increase) is shown to be an effect of rubbing and not instantaneous as in the case of the MoDTC tribofilm.
- Thicker tribofilms were formed when single additives were used in BO rather than when used together. MoDTC lubricant gave thicker Mo-containing tribofilm in the wear scar compared with the ZDDP/MoDTC lubricant. Similarly, ZDDP lubricant gave thicker Zn and P-containing tribofilm compared with the ZDDP/MoDTC lubricant.

Difficulty in measuring the chemical and physical properties of the tribofilm *in situ* greatly limits the understanding of the phenomena related to lubrication in the boundary regime. Future research in this area should utilize the latest developments in ambient pressure surface analyses and understanding of the tribophysics to come up with innovative experimental procedures that will make possible analyses of the tribofilms while in contact.

References

[1] Barnes A M, Bartle K D and Thibon V R A 2001 A review of zinc dialkyldithiophosphates (ZDDPs): characterisation and role in the lubricating oil *Tribol. Int.* **24** 389–95

[2] Nicholls M A, Dao T, Norton P R, Kasrai M and Bancroft G M 2005 Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates. *Tribol. Int.* **38** 15–39

[3] Spikes H 2004 The history and mechanisms of ZDDP *Tribol. Lett.* **17** 469–89

[4] Grossiord C, Martin J M, Mogne T L and Palermo T 1998 In situ MoS_2 formation and selective transfer from MoDTP films *Surf. Coat. Technol.* **108–109** 352–9

[5] Grossiord C, Varlot K, Martin J M, Mogne T L, Esnouf C and Inoue K 1998 MoS_2 single sheet lubrication by molybdenum dithiocarbamate *Tribol. Int.* **31** 737–43

[6] Morina A, Neville A, Priest M and Green J H 2006 ZDDP and MoDTC interactions and their effect on tribological performance—Tribofilm characteristics and its evolution *Tribol. Lett.* **24** 243–56

[7] Korcek S, Jensen R K, Johnson M D and Sorab J 1999 Fuel efficient engine oils, additive interactions, boundary friction, and wear *Proc. 25th Leeds–Lyon Symp. on Tribology, Lubrication at the Frontier: 1999 (Lyon, France)* (Amsterdam: Elsevier) pp 13–24

[8] Martin J M 1997 Lubricant additives and the chemistry of rubbing surfaces: metal dithiophosphates triboreaction films revisited *Japan. J. Tribol.* **42** (9) 1–13

[9] Martin J M, Grossiord C, Mogne T L, Bec S abd Tonck A 2001 The two-layer structure of Zndtp tribofilms: I. AES, XPS and XANES analyses *Tribol. Int.* **34** 523–30

[10] Fuller M L S, Kasrai M, Bancroft G M, Fyfe K and Tan K H 1998 Solution decomposition of zinc dialkyl dithiophosphate and its effect on antiwear and thermal film formation studied by X-ray absorption spectroscopy *Tribol. Int.* **31** 627–44

[11] Bell J C, Delargy K M and Seeney A M 1992 The removal of substrate material through thick zinc dithiophosphate antiwear films *Wear Particles: From the Cradle to the Grave (Tribology Series vol 21)* ed D Dowson *et al* (Amsterdam: Elsevier) pp 387–96

[12] Williams J A 2004 The behaviour of sliding contacts between non-conformal rough surfaces protected by 'smart' films *Tribol. Lett.* **17** 765–78

[13] Martin J M 1999 Antiwear mechanisms of zinc dithiophosphate: a chemical hardness approach *Tribol. Lett.* **6** 1–8

[14] Belin M, Martin J M, Tourillon G, Constans B and Berlusconi C 1995 Local order in surface ZDDP reaction films generated on engine parts, using EXAFS and related techniques *Lubr. Sci.* **8** 1–14

[15] Muraki M and Wada H 2002 Influence of the alkyl group of zinc dialkyldithiophosphate on the frictional characteristics of molybdenum dialkyldithiocarbamate under sliding conditions *Tribol. Int.* **35** 857–63

[16] Georges J M, Martin J M, Mathia T, Kapsa P, Meille G and Montes H 1979 Mechanism of boundary lubrication with zinc dithiophosphate *Wear* **53** 9–34

[17] So H and Lin Y C 1994 The theory of antiwear for ZDDP at elevated temperature in boundary lubrication condition *Wear* **177** 105–15

[18] McQueen J S, Gao H, Black E D, Gangopadhyay A K and Jensen R K 2005 Friction and wear of tribofilms formed by zinc dialkyl dithiophosphate antiwear additive in low viscosity engine oils *Tribol. Int.* **38** 289–97

[19] Yamaguchi E S, Roby S H, Ryason P R and Yeh S W 2002 Electrical contact resistance bench wear testing: comparison with engine test results *SAE* 2002-01-2674

[20] Fuller M L S, Fernandez L R, Massoumi G R, Lennard W N, Kasrai M and Bancroft G M 2000 The use of X-ray absorption spectroscopy for monitoring the thickness of antiwear films from ZDDP *Tribol. Lett.* **8** 187–92

[21] Palacios J M 1986 Thickness and chemical composition of films formed by antimony dithiocarbamate and zinc dithiophosphate *Tribol. Int.* **19** 35–9

[22] Palacios J M 1987 Films formed by antiwear additives and their incidence in wear and scuffing *Wear* **114** 41–9

[23] Willermet P A, Dailey D P, III ROC, Schmitz P J, Zhu W, Bell J C and Park D 1995 The composition of lubricant-derived surface layers formed in a lubricated cam/tapped contact: II. Effects of adding overbased detergent dispersant to a simple ZDTP solution *Tribol. Int.* **28** 163–75

[24] Cavdar B and Ludema K C 1991 Dynamics of dual film formation in boundary lubrication of steels: I. Functional nature and mechanical properties *Wear* **148** 305–27

[25] Choa S H, Ludema K C, Potter G E, DeKoven B M, Morgan T A and Kar K K 1994 A model of the dynamics of boundary film formation *Wear* **177** 33–45

[26] Pidduck A J and Smith G C 1997 Scanning probe microscopy of automotive antiwear films *Wear* **212** 254–64

[27] Fujita H and Spikes H A 2004 The formation of zinc dithiophosphate antiwear films *Proc. Inst. Mech. Begin,* J **218** 265–77

[28] Fujita H, Glovnea R P and Spikes H A 2005 Study of zinc dialkyldithiophosphate antiwear film formation and removal processes: I. Experimental *Tribol. Trans.* **48** 558–66

[29] Lin Y C and So H 2004 Limitations on use of ZDDP as an antiwear additive in boundary lubrication *Tribol. Int.* **37** 25–33

[30] Bec S, Tonck A, Georges J M, Coy R C, Bell J C and Roper G W 1999 Relationship between mechanical properties and structures of zinc dithiophosphate antiwear films *Proc R Soc Lond* A **455** 4181–203

[31] Yamamoto Y and Gondo S 1989 Friction and wear characteristics of molybdenum dithiocarbamate and molybdenum dithiophosphate *Tribol. Trans.* **32** 251–7

[32] Davis F A and Eyre T S 1990 The effect of a friction modifier on piston ring and cylinder bore friction and wear *Tribol. Int.* **23** 163–71

[33] Martin J M, Mogne T L, Grossiord C and Palermo T 1996 Tribochemistry of ZDDP and MoDDP chemisorbed films *Tribol. Lett.* **2** 313–26

[34] Graham J, Spikes H and Korcek S 2001 The friction reducing properties of molybdenum dialkyldithiocarbamate additives: I. Factors influencing friction reduction *Tribol. Trans.* **44** 626–36

[35] Graham J, Spikes H and Jensen R 2001 The friction reducing properties of molybdenum dialkyldithiocarbamate additives: II. Durability of friction reducing capability *Tribol. Trans.* **44** 637–47

[36] Lansdown A R 1999 *Molybdenum Disulphide Lubrication* (Amsterdam: Elsevier)

[37] Sorab J, Korcek S and Bovington C 1998 Friction reduction in lubricated components through engine oil formulation *SAE* 982640

[38] Bec S, Tonck A, Georges J M and Roper G W 2004 Synergistic effects of MoDTC and ZDTP on frictional behaviour of tribofilms at the nanometer scale *Tribol. Lett.* **17** 797–809

[39] Muraki M, Yanagi Y and Sakaguchi K 1997 Synergistic effect on frictional characteristics under rolling-sliding condition due to a combination of molybdenum dialkyldithiocarbamate and zinc dialkyldithiophosphate *Tribol. Int.* **30** 69–75

[40] Unnikrishnan R, Jain M C, Harinarayan A K and Mehta A K 2002 Additive-additive interaction: an XPS study of the effect of ZDDP on the AW/EP characteristics of molybdenum based additives *Wear* **252** 240–9

[41] Johnson M D, Jensen R K and Korcek S 1997 Base oil effects on friction reducing capabilities of molybdenum dialkyldithiocarbamate containing engine oils *SAE* 972860 pp 37–47

[42] Martin J M, Grossiord C, Mogne T L and Igarashi J 2000 Transfer films and friction under boundary lubrication *Wear* **245** 107–15

[43] Martin J M, Crossiord C, Varlot K, Vacher B and Igarashi J 2000 Synergistic effects in binary systems of lubricant additives: a chemical hardness approach *Tribol. Lett.* **8** 193–201

[44] Grossiord C, Martin J M, Varlot K, Vacher B, Mogne T L and Yamada Y 2000 Tribochemical interactions between Zndtp, Modtc and calcium borate *Tribol. Lett.* **8** 203–12

[45] Bec S, Tonck A, Georges J M and Roper G W 2004 Synergistic effects of MoDTC and ZDTP on frictional behaviour of tribofilms at the nanometer scale *Tribol. Lett.* **17** 794–809

[46] Kasrai M, Cutler J N, Gore K, Canning G, Bancroft G M and Tan K H 1998 The chemistry of antiwear films generated by the combination of ZDDP and MoDTC examined by X-ray absorption spectroscopy *Tribol. Trans.* **41** 69–77

[47] Barros M I D, Bouchet J, Raoult I, Mogne T L, Martin J M, Kasrai M and Yamada Y 2003 Friction reduction by metal sulfides in boundary lubrication studied by XPS and XANES analyses *Wear* **254** 863–70

[48] Muraki M and Wada H 1993 Frictional properties of organo molybdenum compounds in presence of Zndtp under sliding conditions: I. Frictional properties of MoDTC and MoDTP *Japan. J. Tribol.* **38** 1347–59

[49] Sogawa Y, Yoshimura N and Iwasaki O H 2000 R&D on new friction modifier for lubricant for fuel economy improvement wwwpecjorjp/gijutu-report/e-report/00E115epdf

[50] Morina A, Neville A, Priest M and Green J H 2006 ZDDP and MoDTC interactions in boundary lubrication—the effect of Temperature and ZDDP/MoDTC ratio *Tribol. Int.* **39** 1545–57

[51] Morina A, Neville A, Green J H and Priest M 2004 Additive/additive interactions in boundary lubrication—a study of film formation and tenacity *Proc. 31st Leeds–Lyon Symposium on Tribology, Life Cycle Tribology: 2004 (Leeds, UK)* (Amsterdam: Elsevier) pp 757–66

[52] Ye J, Kano M and Yasuda Y 2002 Evaluation of local mechanical properties in depth in MoDTC/ZDDP and ZDDP thribochemical reacted films using nanoindentation *Tribol. Lett.* **13** 41–7

[53] Ye J, Kano M, Yasuda Y 2003 Determination of nanostructure and mechanical properties on the surface of molybdenum dithiocarbamate and zinc dialkyl-dithiophosphate tribochemical reacted films using atomic force microscope phase imaging technique *J. Appl. Sci.* **93** 5113–7

[54] Ye J, Kano M and Yasuda Y 2004 Evaluation of nanoscale friction depth distribution in ZDDP and MoDTC tribochemical reacted films using a nanoscratch method *Tribol. Lett.* **16** 107–12

[55] Jahanmir S 1986 Wear reduction and surface layer formation by a ZDDP additive *J. Tribol.* **109** 577–86

[56] Taylor L, Dratva A and Spikes H A 2000 Friction and wear behaviour of zinc dialkyldithioposphate *Tribol. Trans.* **43** 469–79

[57] Gao H, McQueen J S, Black E D, Gangopadhyay A K and Jense R K 2004 Reduced phosphorus concentration effects on tribological performance of passenger car engine oils *Tribol. Trans.* **47** 200–7

[58] So H, Lin Y C, Huang G G S and Chang T S T 1993 Antiwear mechanism of zinc dialkyl dithiophosphates added to a paraffinic oil in the boundary lubrication conditions *Wear* **166** 17–26

[59] Yamaguchi E S, Roby S H and Yeh S W 2005 Time-dependent film formation from ZnDTPs and nonphosphorus antiwear agents *Tribol. Trans.* **48** 57–68

[60] Fujita H, Glovnea R P and Spikes H A 2005 Study of zinc dialkydithiophosphate antiwear film formation and removal processes: I. Experimental *Tribol. Trans.* **48** 558–66

[61] Sheasby J S, Caughlin T A and Habeeb J J 1991 Observation of the antiwear activity of zinc dialkyldithiophosphate additives *Wear* **150** 247–57

[62] Khorramain B A, Iyer G R, Kodali S, Natarajan P and Tupil R 1993 Review of antiwear additives for crankcase oils *Wear* **169** 87–95

[63] Ji H, Nicholls M A, Norton P R, Kasrai M, Caperhart T W, Perry T A and Cheng Y 2005 Zinc-dialkyl-dithiophosphate antiwear films: dependence on contact pressure and sliding speed *Wear* **258** 789–99

[64] Zhang Z, Yamaguchi E S, Kasrai M and Bancroft G M 2005 Tribofilms generated from ZDDP and DDP on steel surfaces: 1. Growth, wear and morphology *Tribol. Lett.* **19** 211–20

[65] Mortier R 1999 Gasoline engine lubricants *Modern Petroleum Technology: Downstream* vol 2, ed A G Lucas (New York: Wiley)

[66] ATC 1993 Lubricant additives and the environment Document 49 at press, http://www.atc-europe.org/info_/public/pubdoc49.pdf

[67] Rudnick L 2003 *Lubricant Additives: Chemistry and Applications* (New York: Dekker)

[68] Martin J M, Grossiord C, Mogne T L and Igarashi J 2000 Role of nitrogen in tribochemical interaction between Zndtp and succinimide in boundary lubrication *Tribol. Int.* **33** 453–9

[69] Yamamoto Y and Gondo S 1991 On properties of surface films formed with molybdenum dithiocarbamate (MoDTC) under different conditions *Japan. J. Tribol.* **36** 309–21

[70] Forbes E S 1970 The load-carrying action of organo-sulphur compounds—a review *Wear* **15** 87–96

[71] Isoyama H and Sakurai T 1974 The lubricating mechanism of di-u-thio-dithio-bis (diethyldithiocarbamate) dimolybdenum during extreme pressure lubrication *Tribol. Int.* **7** 151–60

[72] Mitchell P C H 1984 Oil-soluble Mo–S compounds as lubricant additives *Wear* **100** 281–300

[73] Morina A and Neville A 2007 Understanding the composition and low friction tribofilm formation/removal in boundary lubrication, at press *Tribol. Int.* doi:10.1016/j.triboint.2007.02.001

[74] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-ray Photoelectron Spectroscopy* (Minnesota: Perkin-Elmer Corporation)