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Effect of lubricant ageing on lubricant physical and chemical properties and tribological performance.
Part I: effect of lubricant chemistry

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Key words: Ageing; Wear; Tribofilm; Tribochemistry

1. Introduction

In the past decades, the ageing of the lubricants have been shown to significantly affect the performance of lubricants. Generally, this was found to be related to the ageing stability of the lubricant at different test conditions. The ageing stability of a lubricant is highly dependent on its chemical composition, the related additives and stabilizing agents [1]. The latest researches (e.g. De Feo et al.[2], Amat et al. [3]) in this area explored the ageing effect on lubricants through the surface analysis techniques to explain the tribochemistry involved within the tribological process. There is a wealth of literatures about the effect of ageing on the lubricants and the related tribological performance. In the late 1980s, Ofunne *et al.* [4] showed that ageing of lubricants was affected by temperature, the rate of air circulation, metal and water content, the type of base oil as well as the additives.

Kreuz *et al.* [5] showed that the high engine temperature is the characteristic of tropical conditions significantly affected the ageing process of the lubricant. Zhang *et al.* [6] showed that the increase of temperature could accelerate the ageing of the tested oil which resulted in an increase of the formation of decomposition products. Qian *et al.* [7] showed that the increase of temperature accelerated the bearing failure, which resulted from the thick layers formed on the running surface of the bearing's cylindrical bore and these layers were believed to be related to the organic reaction products within the lubrication system.

Ageing stability is always related to the oxidative stability of the lubricants. The majority of the modern hydrocarbon base fluids used in diesel and gasoline engines is prone to oxidative degradation [8-12].

Wear metals could act as a catalyst in the oxidation process of the lubricants [10, 12, 13]. Perryman et al. [13] stated that the wear metal-catalyzed oxidation of the lubricants could be responsible for the formation of sludge deposits in the used oils during which metals act as radical scavengers at the initial stage of the reaction but would catalyze the oxidation for the rest of the ageing process. Bondi [14] pointed out that the mechanism of catalytic oxidation of mineral oils at high temperatures is based on peroxide formation which is catalysed by free radical chain reactions shown as: chain initiation (Eq. 1), chain propagation (Eq. 2) and chain termination (Eq. 3).

$$M + O_2 \xrightarrow{K_1} M \cdots O_2 \qquad\qquad M \cdots O_2 + {*RH} \longrightarrow M + {*R} + O_2 - H \qquad \textbf{Eq. 1}$$

$$*R + O_2 \xrightarrow{K_2} *RO_2 \qquad *RO_2 + *RH \xrightarrow{K_3} *RO_2H + *R \qquad \textbf{Eq. 2}$$

$$*RO_2 + M \xrightarrow{K_3} M \cdots * RO_2 \qquad *R + *R \longrightarrow *R_2 \qquad \textbf{Eq. 3}$$

where M refers to metal catalyst and*R refers to free radical.

Naga *et al.* [15] showed the effectiveness as oxidation catalysts of several metals in the order as Cu>Fe>Ni-Cr>Al and that the harmful effect of the single metals would be decreased with the presence of other types of metals simultaneously.

Lu[16] indicated that the lubrication behaviour of steel bearings could be significantly improved by ageing the lubricant which contains Tricresyl Phosphate (TCP). However, the polarity of the base oil or contaminants within the oil could have a different effect on the formation of the reaction layer [17]. Several published works [18-22] have also studied the anti-wear performance of the degraded ZDDP. Willermet *et al.* [23-25] found that the by-products of degradation of ZDDP, especially the disulphide were less effective than ZDDP itself in anti-wear abilities. Zhang *et al.* [26] found that the anti-wear ability of ZDDP is mainly coming from its degradation product from the hydrolytic decomposition of ZDDP which are alkyl sulphides and zinc polyphosphates. Uy *et al.* [27] showed in their results that lower wear was observed with aged oils compared to fresh oils in valve-train experiments and suggested that the film formed from aged oil would provide superior wear performance than the film formed from fresh oil. The reason for this is still unclear.

In part I of this research, the main objective is to evaluate the effect of lubricant ageing on the viscosity, TAN and FTIR spectra, which are commonly-used parameters for condition monitoring of lubricants in industrial applications. In this paper, the ageing effect is evaluated through 4 steps: firstly, several types of oil will be aged with a fresh roller in a temperature controlled oven; secondly, sample oils and rollers will be taken out to check the effect of ageing on viscosity, TAN and FTIR spectra as well as roller surface; thirdly, selected aged oils will be tested in a ball-on-disc rig to evaluate the effect of ageing on friction and wear performance; the last step is to apply XPS technique to evaluated the tribochemistry change caused by ageing. Also, the results will be discussed and compared with the previous research done by Cen *et al.* [28].

2. Experimental

The ageing method applied in this paper was developed according to ASTM D943, ASTM D2893 and ASTM D7528-09 to assess different lubricating oils regarding their stability in service together with rolling bearing steel in the 100Cr6 grade. This ageing method descibes how lubricating oils can be tested for stability, oxidation and etching (corrosive attack) when subjected to elevated temperatures. The ageing temperature and duration applied in this paper were set to 80°C and 2 months (about 1000hours), while ASTM D943 states the ageing temperature should be 95°C and ageing duration should be much longer than that applied in this study. The reasons of settings of the ageing temperature and duration can be as follows:

(1) In part I of this study, only lubricant chemistry was concerned. But in part II of this study, water would be added into the oil to see the effect of water on the ageing of lubricants. If the temperature was set to 95 °C, the authors were worried that the water would be evaporated quickly and limit the effect of water on the ageing of lubricants.

(2) The ageing tests done in this paper were to address the impact of ageing on the lubricants used in motor bearings, while TOST (ASTM D943) is widely used in addressing the effect of ageing on turbine oils. The working temperature of motor bearing lubricants is much lower than that of turbine oils. The best working temperature of most common seen motor bearings (at which temperature the motor bearings can work stably) is between 20-80 °C. This is another reason of ageing temperature settled to 80 °C.

(3) About the duration of the ageing tests. TOST (ASTM D943) sets the ageing duration to about 10000 hours, which is ten times of the ageing duration applied in this paper. The ageing in this paper was applied in a heating cabinet, 1000 hours (2 months) was already a long duration for the cabinet to work stably. The cabinet cannot work stably for 10000 hours(20 months). Most turbine aged oils were taken out from an engine worked after 20 months. This is the limitation of the heating cabinet applied in this paper. Again, the aim of this paper is to address the effect of ageing on the motor bearing lubricants rather than the turbine oils.

The materials applied in the ageing process are shown in Table 1.The ageing procedure and inspection process is explained in Figure 1. During every inspection, the surface photographed and a written comment is made, such as ‘Yes’ which means sludge was found and varnish like coatings were formed on the roller surface, and ‘No’ which means hardly any sludge was found nor was any deposit formed on the roller surface. After ageing, selected lubricants were tested in the ball-on-disc test apparatus to address the effect on their tribological performance. XPS analysis was followed to study the tribofilm formed on the wear scar of the tested discs. All the test rigs and test conditions were shown in a previous paper [28].

Table 1. Information of the materials applied in the ageing process

Oil Container	Steel	Cleaning fluid	Heating apparatus	Tool for taking samples	Surface examing technique
PTFE bottles (1000ml volume) with screwcaps	Spherical rollers from small SRB(Spherical Roller Bearing)	Acetone	Heating cabinets	Tweezers	Stereo microscope

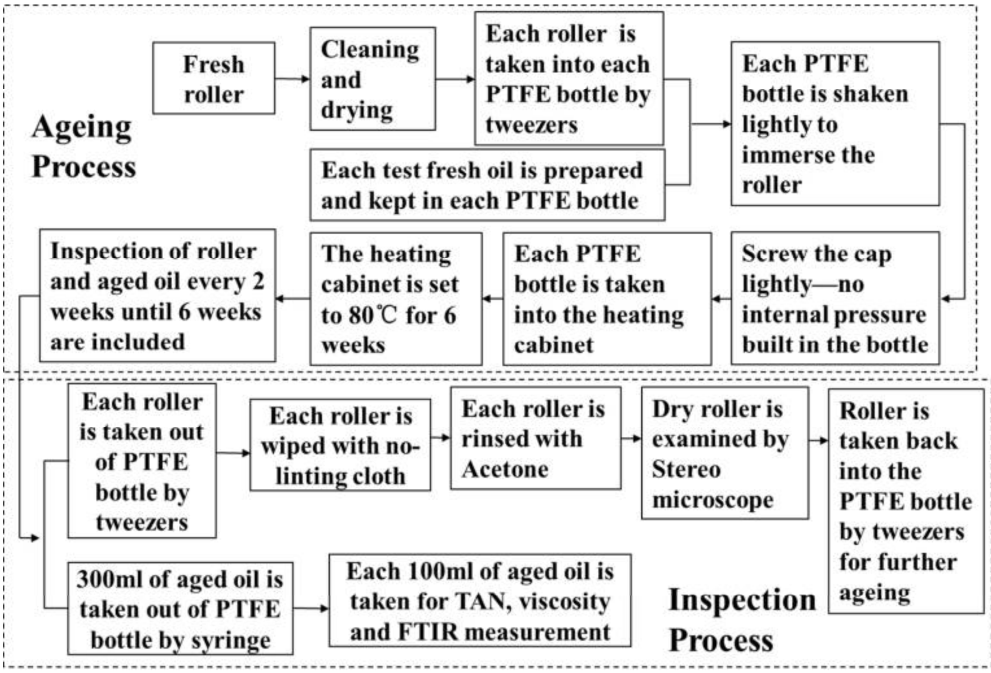


Figure 1. Lubricant ageing and inspection process

The viscosity of the lubricant was measured at 100°C using a test kit applying ASTM D7042. From the test result, the viscometer automatically calculates the kinematic viscosity and delivers measurement results which are equivalent to ISO 3104 or ASTM D445. It also has a high-precision thermostat with stability of 0.005 °C [28].

The total acid number (TAN) was tested using a test kit applying IP177/ASTM D664 which measures the change in electrical conductivity as the KOH is added. The accuracy for TAN test is ±0.2 [28].

Fourier Transform InfraRed (FTIR) Spectroscopy was used to analyse the aged lubricants to obtain the chemical changes due to ageing process. The absorption wave-numbers of most common seen chemical bonds, such as -OH, C=O, N-H and CH-, are all laying within the range of 4000-1500 cm^{-1}. The vibrational excitation is achieved by radiating the sample with a broad-band source of light in the infrared region [28]. In this research, internal reflectance sampling technique was used in the FTIR tests and all the data were normalized to the 2900 cm^{-1} band.

A ball-on-disc test rig was used in this study, which provides a unidirectional sliding point loaded contact and was used to simulate boundary lubricated contacts, to evaluate the tribological performance of the aged lubricants. The schematic representation of the contact in the rig is shown in Figure 2. The ball, which was fixed, contacted with the rotating disc and the static load was such that the system was in the boundary lubrication regime [28].

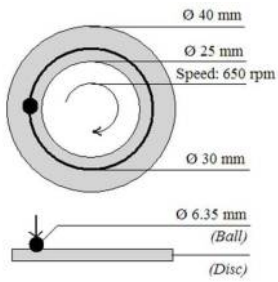


Figure 2. Ball-on-disc test setup

In the *post-test* phase, the impact of ageing on the chemical nature of tribofilms formed in tribological tests was addressed using X-ray Photoelectron Spectroscopy [28]. The X-ray photoelectron spectroscopy measurements were conducted in a PHI 5000 VersaProbe^{TM} X-ray photoelectron spectrometer (Ulvac-PHI Inc, Chanhassen, MN, US) with a monochromatized Al Kα X-ray (1486.6eV) source. The emitted electrons are collected and retarded with an Omega lens system at an emission angle of 45°. After passing a spherical capacitor energy analyzer, the electrons are collected by a 16-channel detector. The system is equipped with a high performance floating-column ion gun and an electron neutralizer for charge compensation. The residual pressure was always below 1×10^{-7} Pa. Detailed information of the base oil/additives and the lubricating oils is shown in Table 2 and

Table 3.

Table 2. Information of the base oils and additives

Details	Designation
Synthetic Group IV	PAO
Synthetic Ester	Ester
Group II Mineral B	MO
Iso-C4-ZDDP	ZDDP
Phosphoric Acid Ester Neutralized With A High Molecular Weight Amine	P

Patented Oil Based Corrosion Inhibitor	CI

Table 3. Information of the lubricating oils

Details	Designation
PAO+(2wt%)ZDDP	PAO+ZDDP
PAO+(2wt%)P	PAO+P
ester+(2wt%)ZDDP	ester+ZDDP
ester+(2wt%)P	ester+P
MO+(2wt%)ZDDP	MO+ZDDP
MO+(2wt%)P	MO+P
MO+(2wt%)ZDDP+(1wt%)CI	MO+ZDDP+CI

3. Effect of ageing on the bulk properties of lubricants

3.1 Effect of ageing on the viscosity of lubricants

Table 4 shows the viscosity values after each ageing period for all the tested lubricants. It is quite surprised to see that there is no significant change in the viscosity as a result of ageing in this study. The reason could be attributed to the ageing temperature applied in this study is 80°C which might not be high enough to initiate the chemical reactions that would affect the viscosity of the lubricants. According to ASTM D7528-09 where the ageing tests of engine oils are carried out at 170°C, the oxidation of ZDDP will be activated when the temperature is higher than 110°C and viscosity will change a lot when temperature reaches 170°C. However, the ageing tests in this paper were taken out at 80°C which is much lower than the temperature mentioned in ASTM D7528-09 tests. Furthermore, the lubricants were kept still (no churning, stirring or pumping) during ageing tests rather than circulating in ASTM D7528-09 tests, which means less prone to be exposed to oxygen to be oxidized. Therefore, it is not surprising to see that the viscosity of the aged oils in this paper did not match the change stated in ASTM D7528-09 tests.

Table 4. Viscosity change of lubricants with the increase of ageing time

Oil type	Viscosity at 100°C—(mPa·S)			
	0week	**2weeks**	**4weeks**	**6weeks**
ester+ZDDP	4.6	4.5	4.5	4.6
ester+P	4.6	4.6	4.6	4.6
PAO+ZDDP	4.0	4.0	4.0	4.0
PAO +P	4.0	4.0	4.0	4.0
MO+ZDDP	4.3	4.3	4.3	4.3
MO+P	4.3	4.3	4.2	4.3

MO+ZDDP+CI	4.4	4.4	4.4	4.4

3.2 Effect of ageing on the TAN of lubricants

Figure 3 shows the TAN changes for the ZDDP-containing P-containing lubricants. It is clear that there are no significant changes in TAN values of ZDDP-containing lubricants after ageing, while TAN values increased with ageing time for the P-containing lubricants, among which TAN of Ester+P increased dramatically. This is because ester is proved in the literature to be easily degraded[29]. It is also noticed that the TAN values of Ester+P lubricants increased much faster after two weeks ageing. The faster increase of TAN could also be a result of reducing amount of test oil after every two weeks. Less amount of test oil, which means more oxygen sealed in the bottle, could result in faster ageing compared to the 1000 mL of test oil during the first two weeks of ageing.

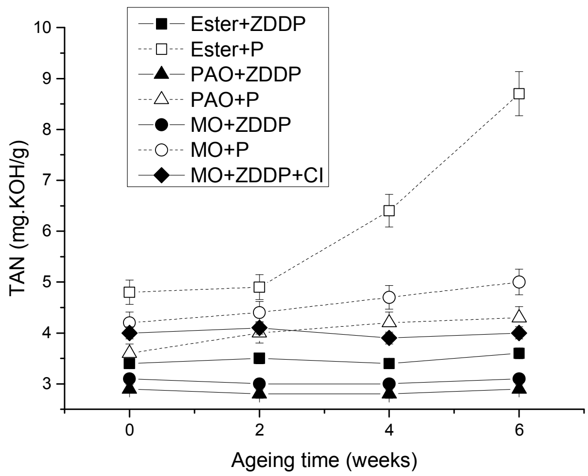


Figure 3. Effect of ageing on TAN changes of lubricants

The stable TAN values of ZDDP-containing oils after ageing indicate that the ZDDP protects base oil, especially ester from being degraded; ZDDP has been shown to be an effect anti-oxidant in several previous studies [30-32]. In addition, ZDDP is proved to be a more effective anti-oxidation additive than the P additive based on the changes of TAN values of the tested lubricants, this is because the P additive used in this study is a phosphoric acid ester itself, which can be degraded during the ageing process.

3.3 Effect of ageing on the roller surface

One obvious effect of ageing on the roller surface would be shown as the formation of deposits and sludge on the surface. Each roller has been wiped with tissue after ageing to see if any sludge (removable with tissue wiping) and deposits (irremovable with tissue wiping) forms on the roller surface. The sludge mainly comes from the by-products of the degradation (oxidation) process of the lubricants which can be accelerated by metal as shown by Hsu *et al.* [33]. The deposits formed varnish-like coatings which could not be wiped off by a tissue and appeared to be a result of corrosion [34]. Due to the limited time in the roller checking process during the ageing interval, the sludge-like deposits were not chemically examined in this research but is highly recommended to be done in the future work. As the sludge and deposit formation processes are highly dependent on additives (because additives can affect the degradation of the lubricants significantly), all the aged lubricants have been separated into ZDDP- containing and P-containing ones. Table 5 and

Table 6 show the images of the roller after wiping with tissue after ageing. The data under the lubricant name are the TAN values for fresh oil and the numbers under the images are the TAN values after each period of ageing. Description 'Yes' means sludge was found and varnish like coatings were formed on the roller surface. 'No' means hardly any sludge was found nor was any deposit formed on the roller surface.

Results in Table 5 and

Table 6 indicate less oxidation of the lubricants (no or nearly no sludge formed) and corrosion (from the images of the roller surfaces) when aged with ZDDP-containing lubricants than P-containing lubricants. This indicates a mechanism of ageing which affects the surface comes from the interaction (eg. oxidation, corrosion) between lubricant chemistry and steel substrate. As Klaus *et al.* [34] showed that metal corrosion and sludge formation are interrelated and the process is highly dependent on the contact with air, lubricant and metal surface. They also stated that the sludge formation is related to the oxidation within the system which can be catalysed by metal. Kuerten *et al.* [29] showed that the oxidation by-products interact with the iron surface which can catalyse the formation of a polymeric precursor of sludge and varnish, and the amount of corrosion product with iron is affected by the proximity of the primary oxidation reaction to the iron surface. Therefore, ZDDP is again proved to be a more effective anti-oxidation and anti-corrosion additive than the P additive applied in this study.

3.4 FTIR investigation of the effect of ageing on lubricants

Fourier Transform infrared spectroscopy (FTIR) is selected to investigate the changes in the chemical structure of lubricants after ageing. As the ZDDP-containing oils show no significant change in TAN as well as on the roller surface, PAO+ZDDP was selected to investigate the effect of ZDDP on the degradation of lubricants.

Table 5. Roller images for ZDDP containing lubricants after each period of ageing (numbers are the TAN of the related lubricant after ageing)

Oil type	After 2 weeks	After 4 weeks	After 6 weeks
ester+ZDDP 3.4	 (No) 3.8	 (No) 3.4	 (No) 3.7
PAO+ZDDP 2.9	 (No) 3.0	 (No) 2.7	 (No) 2.9
MO + ZDDP 3.1	 (No) 2.7	 (No) 3.0	 (No) 3.1
MO+ZDDP+CI 4.0	 (No) 3.4	 (No) 3.6	 (No) 3.7

Table 6. Roller images for P containing lubricants after each period of ageing (numbers are the TAN of the related lubricant after ageing)

Oil type	After 2 weeks ageing	After 4 weeks ageing	After 6 weeks ageing
ester+P 4.8	 (Yes) 4.7	 (Yes) 6.4	 (Yes) 8.7
PAO+P 3.9	 (Yes) 3.5	 (Yes) 3.3	 (Yes) 2.8

MO + P 4.5	 (Yes) 4.1	 (Yes) 4.1	 (Yes) 4.1

Figure 4 shows the FTIR spectra of the PAO+ZDDP fresh and aged lubricants. The peaks have been normalized with C-H at 2950 cm^{-1}.The P-O-C peak at a frequency of around 970 cm^{-1} and P=S at around 690 cm^{-1} are believed to come from the ZDDP additive [35-37]; its structure is shown in Figure 5. The chemical structure of P additive used in this paper is shown in Figure 6. All other bonds such as C-H (2900-3000 cm^{-1} and 1400-1500 cm^{-1}), S=O (around 1350 cm^{-1}) and S-O (around 1000 cm^{-1}) are identified through literature studying the FTIR spectra of different chemicals [38-39]. S=O and S-O can be from its by-product after oxidation or hydrolysis (shown in Cen *et al.* [28]) within the ageing system. The changing intensities of S=O and S-O suggest that ZDDP additive must have experienced some extent of degradation or hydrolysis but the two main bonds (P-O-C and P=S) from ZDDP are still present after each period of ageing. This indicates that there is still some ZDDP remaining in the lubricants after the whole ageing process, which can be an important evidence that ZDDP is effective in anti-oxidation and anti-corrosion. Thus, it is then not surprise to see the little change in TAN values and roller surface of ZDDP-containing lubricants after ageing.

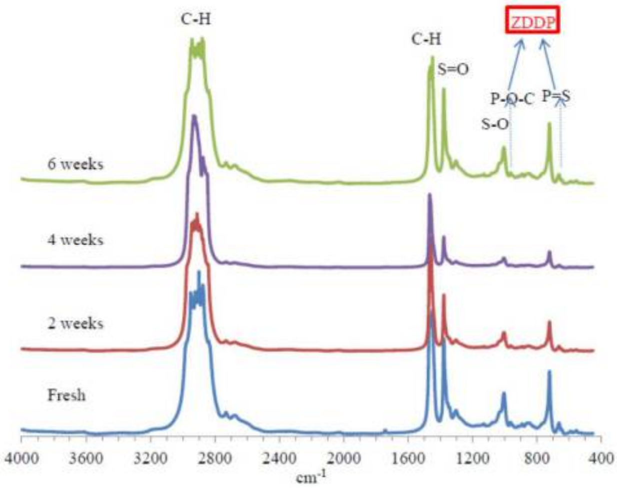


Figure 4. FTIR spectrum comparison of PAO+ZDDP fresh and aged oils

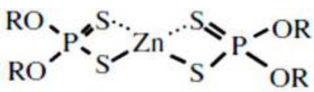


Figure 5. Molecular structure of ZDDP

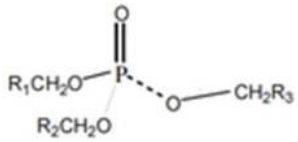
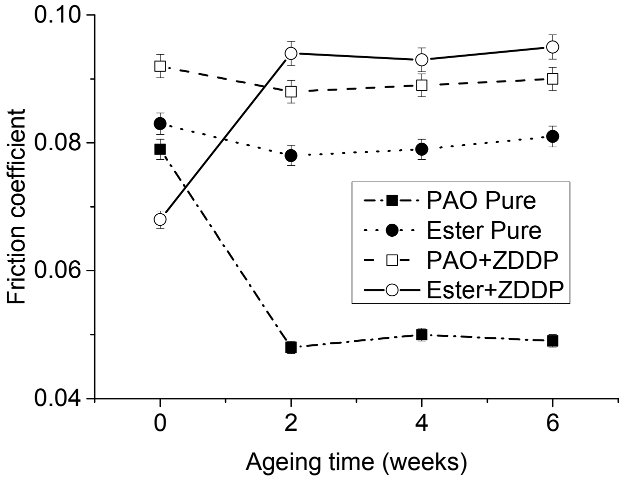


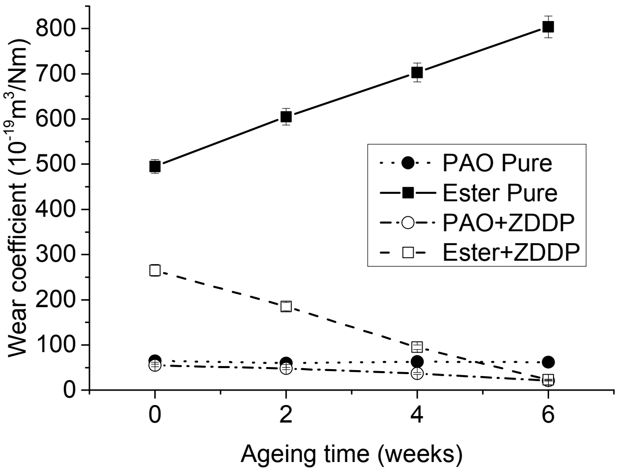
Figure 6. Molecular structure of P additive

4. Effect of ageing on the tribological performance of lubricants

As ZDDP has been confirmed to be very effective in anti-oxidation and anti-corrosion from tests on bulk properties of lubricants and roller surface investigations, its anti-wear ability is then addressed by applying ZDDP-containing lubricants as well as the base stocks in the tribological tests on a ball on disc test rig in this study. Figure 7 shows the friction and wear results from tribological tests using ester/PAO+ZDDP to study the effect of ageing on the tribological performance of lubricants. Pure ester/PAO oils were tested as well to evaluate the effect of the ZDDP additive. The wear coefficient shown in this paper represents the wear on the ball after tribological tests. The calculation process of wear coefficient has been shown in a previous paper [28].



(a)



(b)

Figure 7. Tribological performance of fresh and aged pure and ZDDP-containing lubricants; (a) friction, (b) wear (on the ball after tribological tests)

It is obvious that friction did not change much after two weeks ageing for all the tested oils. The wear performance of the fresh and aged lubricants indicates that ZDDP is an effective anti-wear additive. However, it is more effective in reducing wear in ester-based oils than PAO-based oils. This is probably as a result of the polarity of base oils as Suarez *et al.* [40] found that the polar base oil (ester) can attach to the surface to form a tribofilm which is more effective in reducing wear than no polar base oil (PAO). With the combination effect of ZDDP and polar base oil(ester), the wear reducing property would be more obvious.

The tribological results for the ester and PAO based series of lubricants (Figure 7) all show that ageing reduces the wear. However, there has been a lot of debate on the effect of ageing on the tribological performance of ZDDP-containing lubricants. Barnes and his colleagues [41] summarized that the degradation of ZDDP could either increase or decrease the wear based on different mechanisms.

The ZDDP in the lubricants in the ageing system within the oven is believed to experience only thermal degradation as there is no sliding during the ageing process. Fuller and his co-workers [17] showed in their work that the preheated ZDDP (at 150°C up to 24 hours) containing lubricants resulted in higher wear than the fresh ZDDP-containing ones. This is in contrast to our results from the aged lubricants. However, this might be resulting from the different ageing temperature and time. The ageing temperature in this study (80°C) is much lower which can result in different degradation levels of ZDDP. Coy and Jones [42] presented some results comparing the wear performance of fresh and aged oils containing ZDDP. Barber and Yamaguchi discussed the FTIR and four ball tester results done by Coy and Jones (see discussion in [42]) and conclude that: ZDDP decomposition products, which are by-products from thermal decomposition of ZDDP that are highly dependent upon temperature, provide superior anti-wear performance to that of the fresh oils.

Moreover, if the TAN values are considered together with the tribological performance, it is easy to conclude that lubricants with higher TAN values (comparing the aged ester oil series with the fresh ones) not always show higher wear, although those with higher TAN values are thought to be more corrosive to the surface. This indicates that the change in physical properties of the lubricants is not enough to explain the tribological performance of the system, thus tribochemistry within the system needs to be studied.

5. XPS analysis on the post test discs using the aged oils

X-ray Photoelectron Spectroscopy (XPS) was used to address the tribochemistry affected by ageing of lubricants. Table 7 shows the summary of the binding energies of S and P species obtained from the XPS analysis of the disc's wear scar for both fresh and aged PAO+ZDDP as well as ester+ZDDP series of lubricants. There is no obvious trend in the binding energy changes from fresh oils to aged ones (considering the accuracy of binding energy is ±0.1 eV).

Table 7. Differences of S $2p_{3/2}$ and P $2p_{3/2}$ binding energies for disc samples of both fresh and aged lubricants

Lubricants		Position of ***S*** products (eV)		Position of ***P*** $2p_{3/2}$ (eV)
		Sulphide	Sulphate	
PAO+ZDDP	Fresh	162.6	Yes	133.6
	6 weeks aged	162.8	Yes	133.6
ester+ZDDP	Fresh	162.2	Yes	133.6
	6 weeks aged	162.3	Yes	133.5

However, there is an obvious decrease from fresh to aged lubricants in the concentration of oxygen (oxide) among all elements detected after ageing, as shown in **Error! Not a valid bookmark self-reference.**. Moreover, the binding energy of this oxygen as oxide is always located around 530.0 ±0.5 eV. Within this region, the oxide is found to be iron oxide from previously published works [30-32]. Fuller and his co-workers [17] proposed in their work that ZDDP needs to be chemically adsorbed onto the substrate first and then be decomposed to yield anti-wear products. As the aged lubricants containing decomposed ZDDP products need much less running-in time than ZDDP in fresh oils to perform the anti-wear performance because of the omission of chemical adsorption of ZDDP, which then save the contacting time of oxygen and the substrate, the rate of oxidation is then reduced and less oxide exists on the disc wear scar. Combine this finding with the lower wear on the ball when tested with aged oils, it can be concluded that more iron oxide on the disc wear scar can increase the wear of ball. This might be a result that the iron oxide increased the hardness of the disc surface which results in more asperity contacts.

Table 8. Summary of oxygen element scan information on the disc wear scar

Element concentration		BO(Bridging Oxygen)(eV)	NBO(Non-Bridging Oxygen) (eV)	O (Oxide) (eV)
PAO+ ZDDP	Fresh	533.0 (8.2%)	530.0 (17.9%)	531.6 (19.4%)
Series	6 weeks aged	533.4 (12.5%)	530.0 (9.6%)	531.6 (13.2%)
ester+ ZDDP	Fresh	533.1 (7.2%)	530.0 (17.9%)	531.5 (16.9%)
Series	6 weeks aged	533.7 (8.2%)	529.8 (11.4%)	531.7 (6.4%)

6. Conclusions

The main findings of this research can be summarized as:

1) No significant change in viscosity was observed for all the lubricants aged in the conditions performed in this study. As the ageing tests done in this paper is a steady process without any churning, stirring or pumping of the oil during the ageing process and not the same ways that true application oils experience.

2) ester+P lubricants experienced a huge change in TAN which can be a result of poor thermal stability of ester as well as P additive. Also, the huge increase of TAN after two weeks of ageing can be a result of the reduction of test oil after each two weeks of ageing time.

3) ZDDP was found to be a good anti-oxidation and anti-corrosion additive from the ageing and tribological test results. This is because the main chemical chain survives from the ageing process which is proved in the FTIR results..

4) Ageing of the ZDDP-containing lubricants helps to reduce wear in this paper. This is true after the steady ageing process of the tested oil but contradictory results might occur when the ageing process and tribological test conditions are changed.

5) Oxygen concentration as oxide in the XPS detected tribofilm on the disc wear scar when using aged lubricants is lower than that when using fresh ones.

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