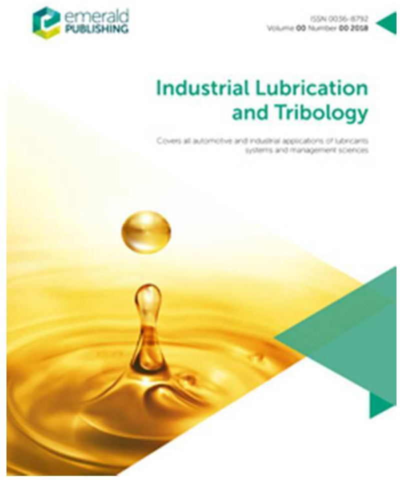
Article:

Cen, H, Morina, A orcid.org/0000-0001-8868-2664 and Neville, A orcid.org/0000-0002-6479-1871 (2019) Effect of ageing on lubricants' physical and chemical properties and tribological performance: Part II: effect of water contamination on lubricant. Industrial Lubrication and Tribology, 71 (1). pp. 48-53. ISSN 0036-8792

https://doi.org/10.1108/ILT-01-2018-0025



Effect of ageing on lubricant physical and chemical properties and tribological performance. Part II: Effect of water contamination on lubricant

Journal:	*Industrial Lubrication and Tribology*
Manuscript ID	ilt-01-2018-0025.R4
Manuscript Type:	Original Article
Keywords:	ageing, Wear, Water, tribofilm, Tribochemistry

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Abstract

Purpose-The main objective of this study is to evaluate the effect of water contamination ageing of lubricants.

Design/methodology/approach-The viscosity, TAN(Total Acid Number) and FTIR (Fourier Transform infrared spectroscopy) spectrum of a series of lubricants after ageing with water were studied. The tribological performance (friction and wear) of the aged lubricants was also analysed, followed by XPS(X-ray Photoelectron Spectroscopy) analysis on the selected post test samples to study the tribochemical features of the tribofilm.

Findings –The results were also compared with part I of this study and found that ageing has different impact on lubricants and tribological performances based on the physical and chemical properties when water is present in the lubricants.

Originality/value – This paper is a continuation of part I of this study and gives an understanding on the impact of water on the lubricants as well as related tribological and tribochemical performance.

Key words: Ageing; Wear; Water; Tribofilm; Tribochemistry

1. Introduction

Ageing of the lubricants has been shown to significantly affect the performance of lubricants. De Feo *et al.* (2015) and Amat *et al.* (2013) explored the ageing effect on lubricants and tried to explain the tribochemistry involved within the tribological process. Ofunne *et al.* (1989) summarized 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. In part I of this study (Cen *et al.* 2018), the effect of lubricant chemistry during the ageing process on the physical and chemical properties and tribological performance has been studied. However, in the industrial applications, water contamination can also participate in the degradation of the lubricants, especially in some lubrication systems working in a humid environment (e.g. wind turbines, paper mills and marine cargos).

A change of the lubricant bulk property could result in different effects on their tribological performance. Although the tribological test itself (done in research by Cen *et al.* (2012)) could be regarded as a short dynamic ageing process of the lubricants, it is important for industrial applications to evaluate the lubricants' ageing sensitivity at much longer time. In this research, the main objective is to evaluate the effect of water contamination on the lubricant ageing. The results will be compared with part I of this study as well as the previous research done by Cen *et al.* (2012).

2. Experimental

Lubricants with different types of base oils and additives contaminated with water have been aged with an identical roller from a roller element bearing in an oven for 6 weeks. 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. 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 is 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.

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 (Cen *et al.* 2018).

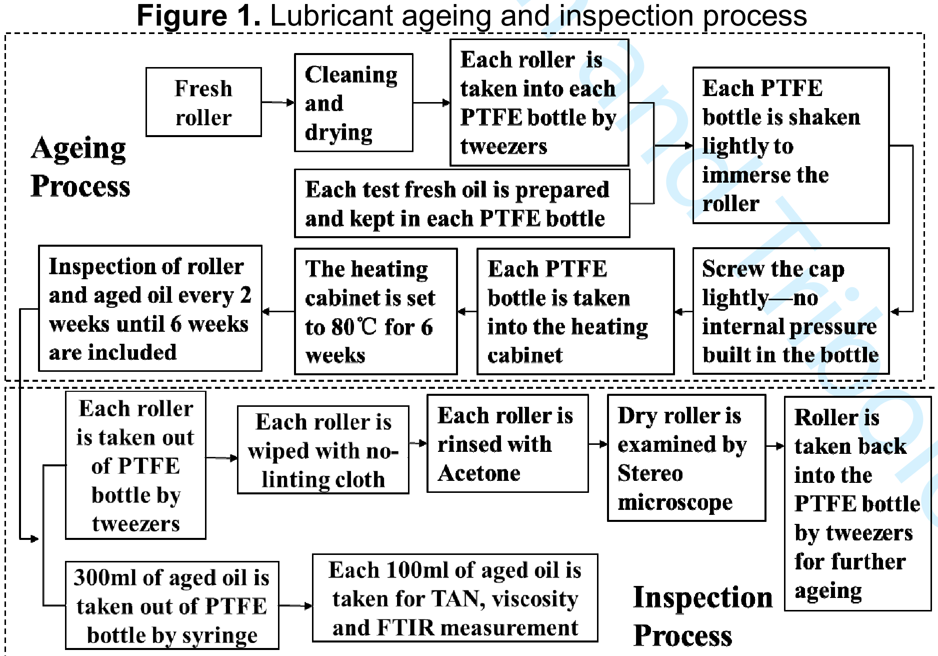
The total acid number (TAN) was tested using a test kit applying IP177/ASTM D664 which measures the change in electrical conductivity as the KOH is added. The accuracy for TAN test is ±0.2 (Cen *et al.* 2018).

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(Cen *et al.* 2018). 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.

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

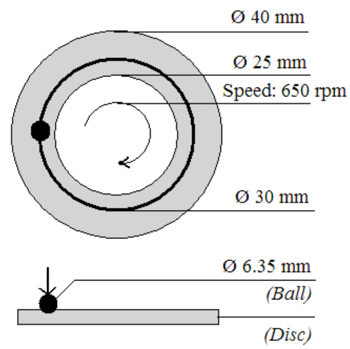
Oil Container	Steel	Cleaning fluid	Heating apparatus	Tool for taking samples	Surface examing technique
PTFE bottles (1000ml volume) with screwcaps	Spherical rollers from small SRB(Spherical Roller Bearing)	Acetone	Heating cabinets	Tweezers	Stereo microscope

Figure 1. Lubricant ageing and inspection process



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 [(Cen *et al.* 2018).

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 (Cen *et al.* 2018). 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.Table 3 shows the information of the lubricating oils (PAO, ester and Mineral oils) used in this part of the research and details of the base oil and additive have been shown in part I of this study (Cen *et al.* 2018).

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+(1wt%) Distilled water	PAO+ZDDP+Water
PAO +(2wt%)P+(1wt%) Distilled water	PAO+P+Water
ester+(2wt%)ZDDP+(1wt%) Distilled water	ester+ZDDP+Water
ester+(2wt%)P+(1wt%) Distilled water	ester+P+Water
MO+(2wt%)ZDDP+(1wt%) Distilled water	MO+ZDDP+Water
MO+(2wt%)P+(1wt%) Distilled water	MO+P+Water
MO+(2wt%)ZDDP+(1wt%)Corrosion Inhibitor+(1wt%) Distilled water	MO+ZDDP+CI+Water

3. Effect of water on bulk properties of lubricants after ageing

3.1 Effect of ageing on water concentration of lubricants

Figure 3 shows the water concentration in the lubricants after ageing. It is clear that the water concentration decreases with ageing. This might be due to evaporation of water during the ageing process. Moreover, water can also be consumed in some hydrolysis processes. P-containing lubricants always show higher water concentration than those ZDDP-containing ones, and ester based oils always “hold” more water than PAO based oils. This can be explained by the polarity of base oil and additives. P additive might have higher polarity than the ZDDP additive used in this paper, and ester is more polar than PAO base oil which has been shown in the literature (Fitch and Jaggernauth, 1994; Fall *et al.*, 2001). Thus, the higher polarity of P additive and ester base oil makes them easier to attract more water molecules to form reverse micelles of which the mechanism has been shown by Pawlak *et al.* (2005).

3.2 Effect of water on viscosity of lubricants during ageing process

Table 4 shows the viscosity values after each ageing period for all the tested lubricants. It is quite obvious that there is no significant change in the viscosity as a result of ageing, which was also found in part I of this study. Although water was involved in the ageing process, which was a steady process without any churning, stirring or pumping of the oil during the ageing process, it was not the same way as shown in turbine oxidation stability test (ASTM D943-TOST). Furthermore, the lubricants were aged at 80°C in this paper which is lower than 95°C as mentioned in ASTM D943 test, which resulted in less oxidation of lubricants than that shown in such test. Thus, it was not surprising to see that the viscosity of the lubricants did not change much after ageing in this paper.

3.3 Effect of water on the TAN of lubricants during ageing process

Figure 4 shows the TAN changes for the tested oils. All ester-based lubricants experienced a large TAN increase throughout the whole ageing process. TAN of the lubricants with addition of water/saltwater are much higher and experienced much bigger changes than the dry ageing results shown in part I of this study. This indicates that water accelerates the degradation of the ester-based lubricants during the ageing process. In addition, ester+P lubricants always show higher TAN than ester+ZDDP lubricants which is in line with the dry ageing results shown in part I of this study. This is because ester is proved in the literature to be easily degraded, especially much more prone to be hydrolysed when water is present and yields acid as a by-product (Wolfe, 1980).

Figure 3. Water concentration of tested lubricants

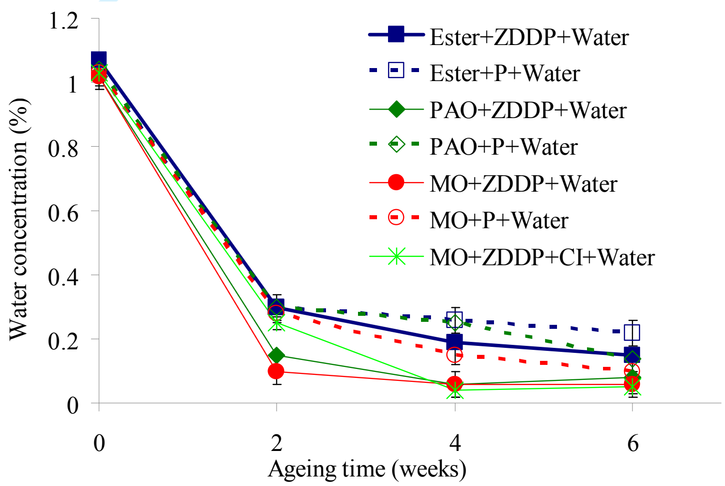
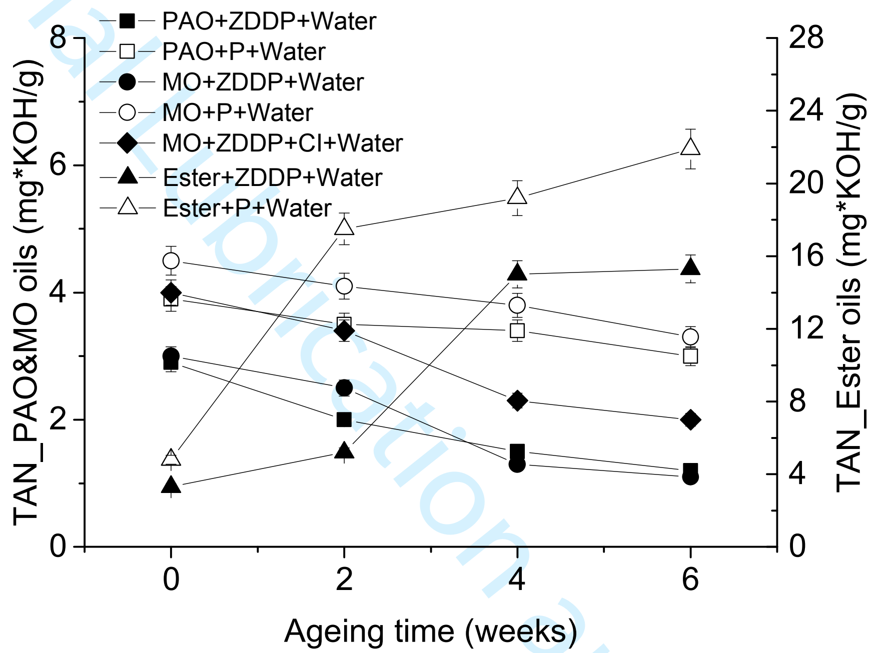


Table 4. Viscosity change of tested lubricants

Oil type	Viscosity—(mPa·S)			
	0week	2weeks	4weeks	6weeks
ester+ZDDP+Water	4.6	4.4	4.4	4.4
ester+P+Water	4.6	4.4	4.4	4.5
PAO+ZDDP+Water	4.0	4.0	4.0	4.0
PAO+P+Water	4.0	3.8	3.8	3.8
MO+ZDDP+Water	4.3	4.2	4.2	4.3
MO+P+Water	4.3	4.2	4.2	4.2
MO+ZDDP+CI+Water	4.4	4.4	4.4	4.4

It is quite surprising that TAN of both PAO+ZDDP and PAO+P lubricants decreased with ageing time. The hydrolysis of ZDDP additive can form phosphate acid as shown by Spedding and Watkins (1982). Meanwhile, the hydrolysis of the P additive used in this paper can also yield acid as a by-product as shown by Wolfe (1980). Then, it can be postulated that the TAN decrease of PAO+ZDDP and PAO+P oils after ageing could be resulting from the higher acidity of the original ZDDP and P additive than the by-product acid. TAN of tested MO lubricants also decreased during the whole 6 weeks' ageing, of which the reason is similar to that of PAO+ZDDP and PAO+P lubricants. Another observation from Figure 4 is that P containing lubricants always show higher TAN than ZDDP containing lubricants. This gives an indication that the acidity of P additive used in this paper is higher than that of ZDDP additive.

Figure 4. Effect of ageing on TAN changes

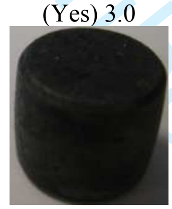


3.4 Effect of water on the roller surface during ageing process

Table 5 shows the roller images for ZDDP-containing and P-containing lubricants after each period of ageing, respectively. The data in the table are the TAN values. Description 'Yes' means sludge was found, while 'No' means hardly any sludge was found.

Sludge is found after ageing for all the ZDDP- and P-containing lubricants and different types of deposit were found on the surface as well. In part I of this study , it has been found from the dry ageing results that ZDDP has a very good anti-oxidation ability which keeps the base oils from being degraded during the ageing process. However, it loses this ability once 1% of water is added into the oil which might result from the hydrolysis of ZDDP (Nicholls *et al.*, 2005). This indicates that water plays a role in etching the surface through either interaction directly with steel substrate or chemical reactions with additives/base stocks first and then the by-products etch the surface.

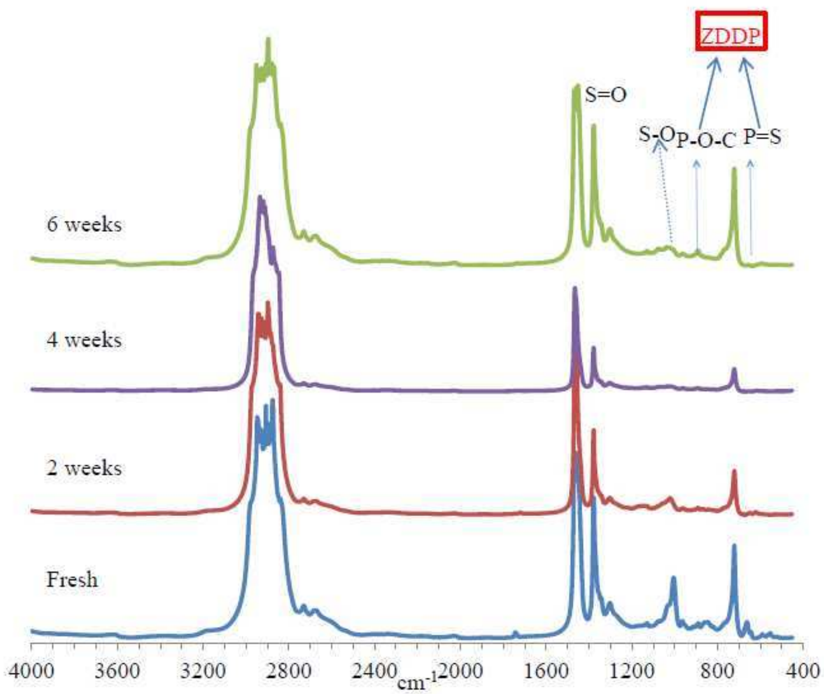
Table 5. Roller images after ageing

Oil type	After 2 weeks	After 4 weeks	After 6 weeks
ester+ZDDP+Water 3.4	 (Yes) 5.2	 (Yes) 15.0	 (Yes) 15.3
PAO+ ZDDP+Water 2.9	 (Yes) 2.0	 (Yes) 1.5	 (Yes) 1.2
MO+ ZDDP+Water 3.0	 (Yes) 2.5	 (Yes) 1.3	 (Yes) 1.1
MO+ZDDP+CI+Water 4.0	 (Yes) 3.4	 (Yes) 2.3	 (Yes) 2.0
ester+P+Water 4.8	 (Yes) 17.5	 (Yes) 19.2	 (Yes) 21.9
PAO+P+Water 3.9	 (Yes) 3.5	 (Yes) 3.4	 (Yes) 3.0
MO+P+Water 4.5	 (Yes) 4.1	 (Yes) 3.8	 (Yes) 3.3
New Roller			

3.5 FTIR investigation of the effect of ageing on lubricants

To reduce the amount of work and due to the limitation of the research, only PAO+ZDDP+ Water was chosen to be studied to evaluate the effect of water on the degradation of ZDDP. Figure 5 shows the FTIR spectra comparison of the tested lubricants. It is quite obvious that P=S and P-O-C from ZDDP presented in the fresh oil became very weak or even disappeared in the spectrum after ageing. This indicates that the remaining ZDDP amount became less and disappeared finally through the ageing process. Compared to the FTIR results of the dry aged oils shown in part I of this study , where the intensities of P=S and P-O-C peaks are higher than the lubricants aged with water in this paper, it can be concluded that water speeds up the degradation process of ZDDP. Thus, it is not surprising to see sludge formed and etching of the roller surface shown in Table 5.

Figure 5. FTIR spectrum comparison of PAO+ZDDP+Water fresh and aged oils



4. Effect of the water on the tribological performance of aged lubricants

As ZDDP has been confirmed to be very effective in anti-wear shown in part I of this study, the tribological performance of PAO/Ester+ZDDP+ Water was studied. Figure 6 shows the friction and wear performance of the tested lubricants, also these results were compared with the dry aged lubricants shown in part I of this study. The calculation process of friction and wear coefficient has been shown in a previous paper (Cen *et al.* 2012). It is obvious that friction did not change much after two weeks ageing for all the tested oils (the results of the dry aged oils are from part I of this study). Moreover, the friction coefficient of oils aged with water after two weeks is quite similar to that of dry aged oils. This gives an indication that ageing with water has limit effect on the friction performance of lubricants in this paper.

Figure 6. Tribological performance comparison of tested oils

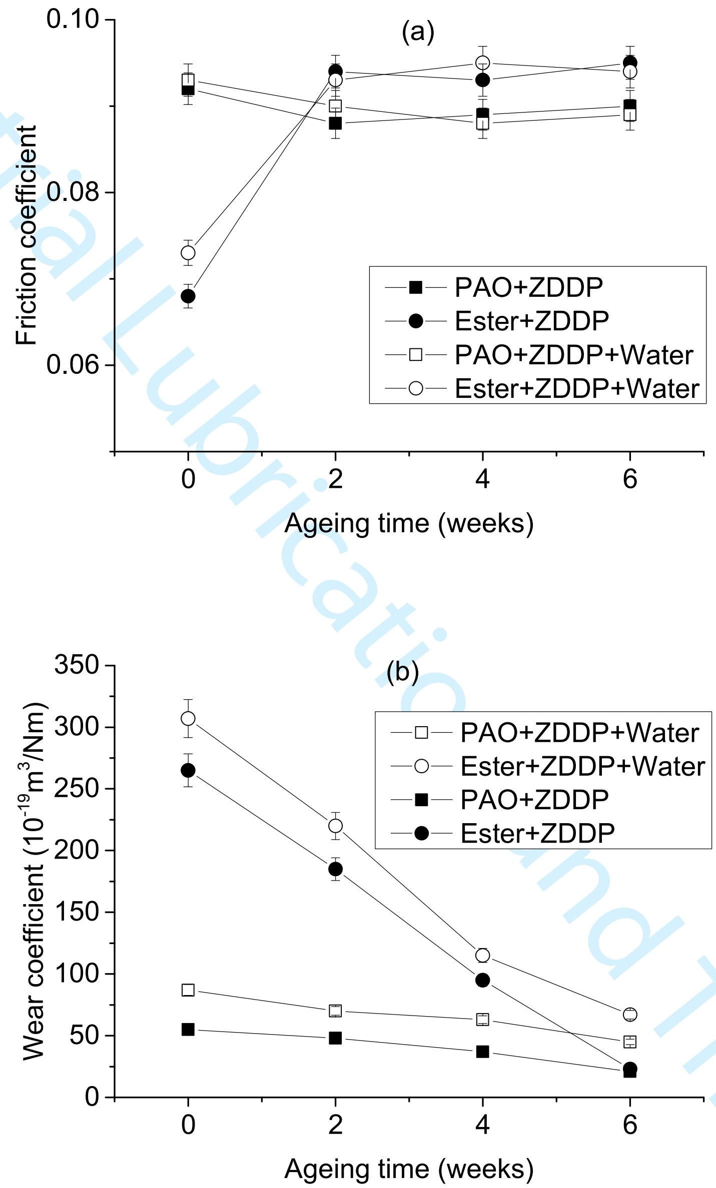


Figure 6 (b) shows that wear decreases with ageing for both PAO and Ester oils. This is also found in part I of this study, which confirms that ZDDP is an effective anti-wear additive even with ageing with water. Furthermore, lubricants aged with water always show higher wear than those dry aged oils. This is because water can speed up the degradation process of ZDDP as shown in Figure 5. Meanwhile, polar water molecule can compete with ZDDP during the tribofilm formation process, which can also limit the anti-wear effect of ZDDP.

Furthermore, ZDDP is more effective in reducing wear in ester-based oils than in PAO-based oils. Although polar water molecule and ester molecule can compete with each other on the substrate, the limit amount of water after ageing compared to the base stock is not enough to show the impact of water on the wear performance. Considering the TAN results shown in Figure 4, it can be concluded that higher TAN values of lubricants do not always lead to higher wear (refer to the aged ester oil series). Therefore, it is not enough to explain the tribological performance of the system only based on the change in physical properties of the lubricants, tribochemistry within the system also needs to be studied.

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

X-ray Photoelectron Spectroscopy (XPS) was applied to study the tribochemistry affected by ageing of lubricants with water. Selected aged lubricants were studied due to the limitation of the research. Curve fitting details of XPS data have been shown in a previous paper (Cen *et al.* 2012). Also, results from part I of this study were also compared. Table 6 shows the summary of the binding energies of element scan results obtained from the XPS analysis. There is no obvious trend in the binding energy changes of $P2p_{3/2}$ with ageing, neither with the change from dry oils to water added oils (considering the accuracy of binding energy is ±0.1 eV). However, there is an obvious trend in the concentration of oxygen (oxide) among all elements detected from fresh oils to aged ones as well as from dry oils to oils aged with water (shown in Figure 7). As discussed in part I of this study, 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. Moreover, water molecule in the lubricants can reduce the rate of oxidation (Spedding and Watkins, 1982; Lancaster, 1990) in the running in period of ZDDP. In consequence, the surface was provided with less protection of oxide which results in higher wear as shown in Figure 6 (b). The higher wear of water added lubricants can also result from the increase of contact asperity provided by the high hardness of iron oxide.

6. Summary

The main findings of this research could be summarized as follows:

- No significant change in viscosity was observed for all the lubricants aged in the conditions performed in this study.

- Ester-based lubricants experienced a huge change in TAN because of their poor hydrolytic stability.
- Water concentration decreases with ageing.
- The good anti-oxidation ability of ZDDP is lost and even corrosion inhibitor is not effective in anti-corrosion when water is present.
- Wear increases with the addition of water into the lubricants.

Oxygen concentration as oxide decreases with the addition of water into the lubricants in the XPS detected tribofilm on the disc wear scar, which provides less protection of the surface in the running-in period thus increases the wear on ball.

Table 6. Differences of S 2p3/2 and P 2p3/2 binding energies for disc samples of both fresh and aged lubricants

Lubricants		Position of ***S*** products (eV)		Position of ***P*** $2p_{3/2}$ (eV)	Position of BO (eV)	Position of NBO (eV)	Position of Oxide (eV)
		Sulphide	Sulphate		Bridging Oxygen	Non-Bridging Oxygen	Oxygen as Oxide
PAO+ZDDP	Fresh	162.6	Yes	133.6	533.0	530.0	531.6
	6 weeks aged	162.8	Yes	133.6	533.4	530.0	531.6
PAO+ZDDP+Water	Fresh	162.8	Yes	133.6	533.1	531.7	530.1
	6 weeks aged	162.7	Yes	133.5	533.4	531.9	530.1
ester+ZDDP	Fresh	162.2	Yes	133.6	533.1	530.0	531.5
	6 weeks aged	162.3	Yes	133.5	533.7	529.8	531.7
ester+ZDDP+Water	Fresh	162.5	Yes	133.6	533.0	531.5	529.8
	6 weeks aged	162.4	Yes	133.5	533.2	531.7	530.1

Figure 7. Element concentration of oxygen as oxide curve fitted from O1s element

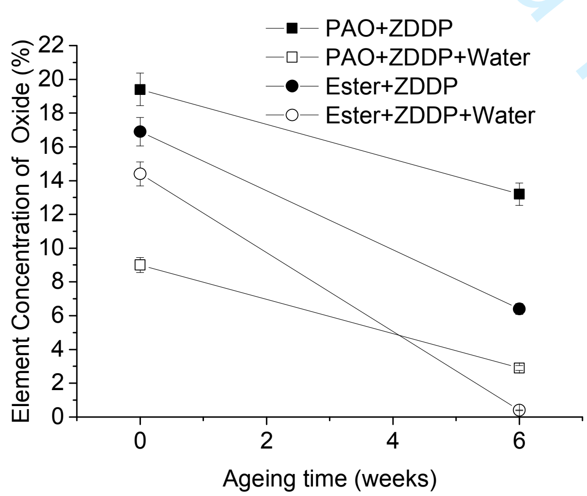


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Figure 1. Lubricant ageing and inspection process

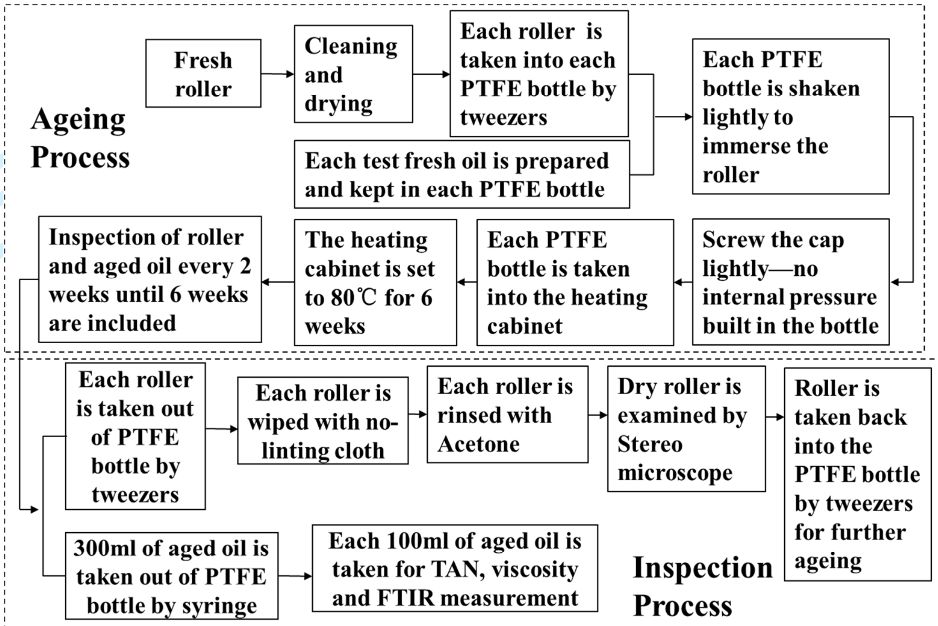

Figure 2. Ball-on-disc test setup

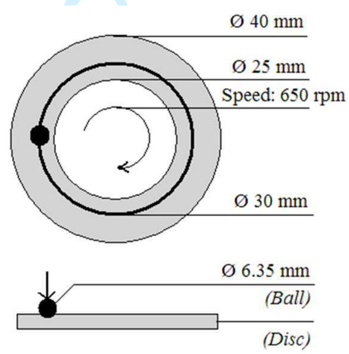

Figure 3. Water concentration of tested lubricants

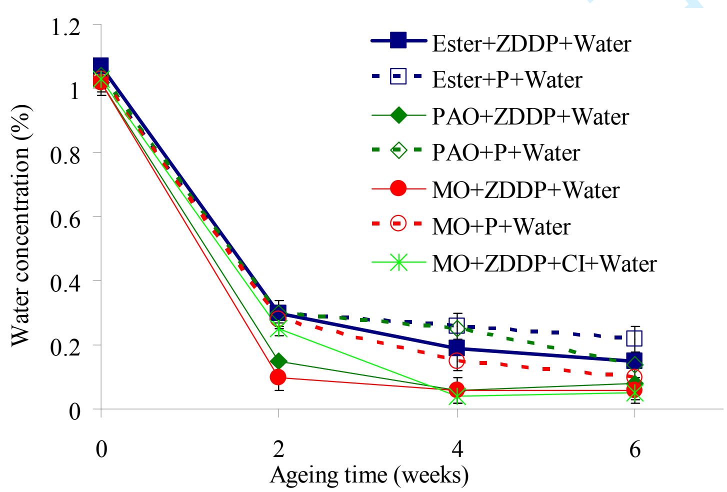

Figure 4. Effect of ageing on TAN changes

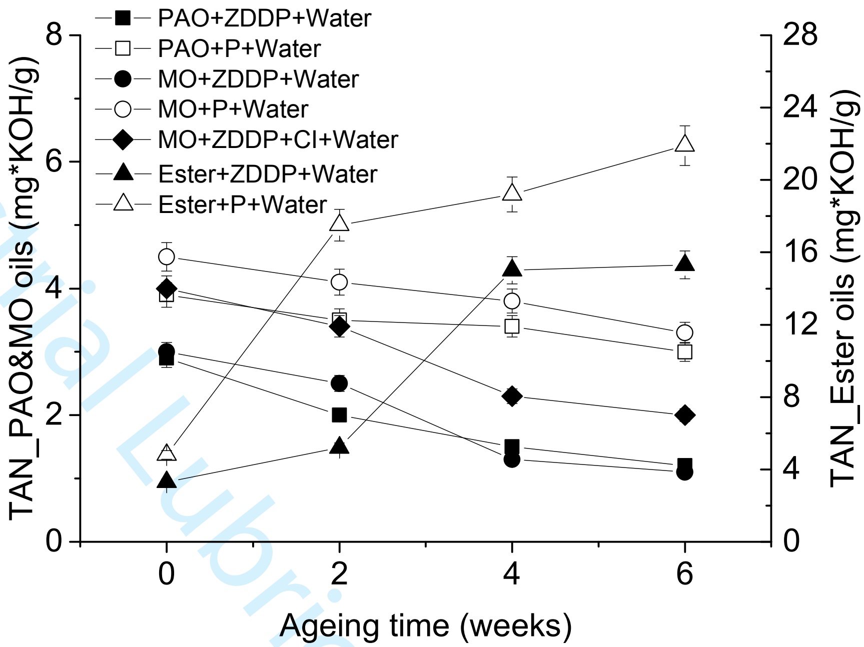

Figure 5. FTIR spectrum comparison of PAO+ZDDP+Water fresh and aged oils

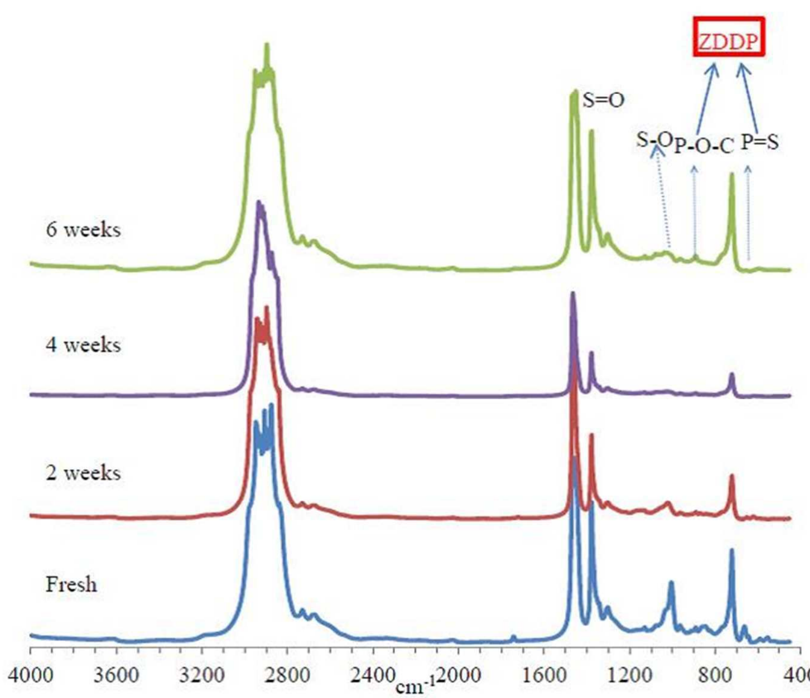

Figure 6. Tribological performance comparison of fresh and aged oils; (a) friction, (b) wear

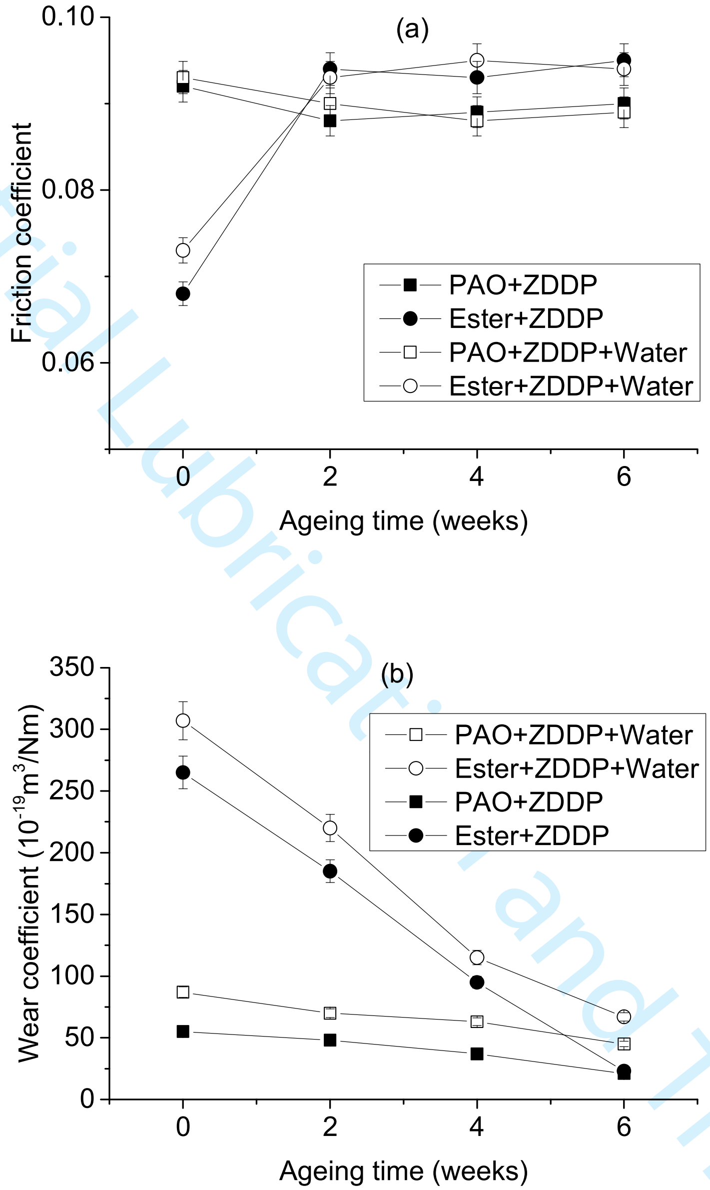

Figure 7. Element concentration of oxygen as oxide curve fitted from O1s element