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23 **An Analytical Study of Tribofilms Generated by the Interaction of Ashless Anti-**
24 **wear Additives with ZDDP using XANES and Nano-indentation**
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53 **Keywords:** Anti-wear additives, wear, ashless antiwear additives, XANES, nanoindentation
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Abstract

Mixtures of zinc dialkyl dithiophosphates (ZDDP) and ashless fluorothiophosphates and thiophosphates were examined under tribological conditions. The tribofilms were studied using nanoindentation, electron microscopy and XANES spectroscopy. With the addition of ashless fluorothiophosphates and thiophosphates there is significant reductions in wear at identical phosphorous levels. Tribofilms formed with mixtures of ZDDP and ashless antiwear additives had stable pad like structures while those from ZDDP alone were more heterogeneous. When ZDDP alone is used P L-edge indicates a preponderance of sulfates at the surface of the tribofilms while in the presence of a mixture of anti-wear additives a mixture of sulfates and sulfides was observed. In all cases the phosphates formed were short chain polyphosphates of Zn.

Introduction

Use of oil additives dates back to almost a century ago wherein lubricity enhancers were first used in 1918[1] as it was evident that for automotive applications where severe mechano-thermo-oxidative conditions are prevalent and hence additional additives are needed to maintain the desired performance characteristics of the lubricant over broad ranges of application temperatures as well as over long periods of time. Since these earlier activities, much more significant efforts have been devoted in a number of comprehensive studies throughout the 2nd half of last century to develop more effective lubricants and lubricant additives as well as in fundamental understanding the underlying mechanism by which these additives perform their tasks individually as well as in a synergistic fashion with other additives in the lubricant mix [2-13].

About 80 years ago, the discovery of zinc dialkyl dithiophosphates (ZDDP) was a major breakthrough. ZDDP has since been extensively used in the industries as an anti-wear (AW), anti-oxidant (AO) and Extreme Pressure (EP) additive [1,14-19]. Such multi-functional properties of ZDDP additive were attributed to the formation of a tribofilm due to the decomposition of the ZDDP molecules, which are well summarized by H. Spikes [1]. Jones and Coy [20] proposed the mechanism of thermal degradation of the ZDDP. In this study ³¹P and ¹H NMR spectroscopy was used to identify the decomposition products of thermally heated ZDDP under static conditions (?). It was observed that the intermolecular transfer had occurred as well as the migration of the alkyl functions from oxygen to sulfur atoms also took place (i.e. P-O-R to P-S-R). Dialkyl sulfides, alkyl mercaptan and dialkyl disulfide were found in their studies as well as a range of soluble phosphates combined with sulfur and insoluble phosphorous bound to oxygen were confirmed. Taylor et al [21] studied the friction behavior of ZDDP in a rolling/sliding rig type of wear test. The topographical measurement of the tribofilms was done using a space layer imaging method (SLIM). The results showed that the antiwear film formed during the rubbing was unevenly distributed and roughness was oriented in the sliding direction which, consequently result in the high friction values. Willermet et al [15] reported that the antiwear films was formed due to the oxidative decomposition of ZDTP and was largely composed of inorganic amorphous phosphates. In a study involving the reaction of inorganic fluorides with ZDDP it was shown that replacing sulfur with fluorine in the structure resulted in a fluorinated version of ZDDP that had improved wear behavior that could be attributed to a more tenacious tribofilm formed on the surface [22]. Additional studies on the Fluorinated ZDDP indicated improved wear performance under high load conditions that could be attributed to the formation of more durable tribofilms [23]. Warren et al [24] further explored the tribofilm surfaces and introduced two salient features “ridges and troughs” of tribofilms using an interfacial force microscopy (IFM). The nano-mechanical measurements showed that the ridges regions are harder and stiffer than the trough region thus it was concluded that ridge region carried most of the load during the wear test as they are aligned to the direction of sliding. In a recent study examining the role of contact load on wear behavior Mourhatch and Aswath have shown that increasing contract load results in tribofilms that are harder than at smaller contact loads [25] complementing the finding of Warren et. al. [24].

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4 Since, ZDDP has several advantages as a lubricant additive in term of its multi-functionality as antiwear,
5 extreme pressure, antioxidant and corrosion inhibitor, it has been used in engine oils for decades
6 [1,15,26]. However, ZDDP has demerits as it is the main source of P, S and metallic residues of Zn in the
7 surface of the catalytic convertor. The presence of these deposits results in the degradation of the
8 efficiency of the catalytic convertor in engines resulting in higher emissions [1,27,28]. It is also one of the
9 main sources of SAPS. There is a need to develop environmental friendly additives and has been
10 recently addressed with the research focus shifting towards the development of ashless i.e. metal free
11 lubricant additives [28-30].
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16 Metal-free ashless lubricant additives have been synthesized and proposed as a promising replacement
17 of ZDDP with better or comparable antifriction, antiwear, antioxidant and extreme pressure properties
18 in several studies [28,31-41]. Commonly recognized ashless chemistries as lubricant additive are
19 phosphorous and sulfur based compounds i.e. phosphate esters [38], thiophosphates and
20 dithiophosphates [27,29,39,42], alkyl/aryl mono and/or di-hydrocarbyl phosphates, amine salts of
21 aryl/alkyl-aryl or aliphatic di-hydrocarbyl thiophosphates [34], dieter polysulfide's [36], dithiocarbamic
22 [33], amidothiophosphates [42], Benzotriazole-thiadiazol [35] and most recently
23 alkylthioperoxydiphosphates and alkylphosphorofluoridithioates [31,32].
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28 In recent years, several ashless lubricant additives have been shown to possess comparable or even
29 better AW, AO, AF and EP properties than ZDDP [28-30,32,43-46]. However, developing a
30 comprehensive understanding of the mechanism of wear protection is still a challenge. Najman et al
31 [26,39] studied the mechanism of film formation and spatial distribution of chemical species in thermal
32 and tribofilms derived from ashless antiwear chemistries using X-ray absorption near edge structure
33 spectroscopy (XANES), Photo-emission electron microscopy (PEEM) and X-ray photoelectron
34 spectroscopy (XPS) and concluded that the films contain short or long chain iron polyphosphates and
35 Iron sulfates. Topographic study using Atomic force microscopy (AFM) showed that the films were
36 composed of elongated short and large antiwear pads oriented in the sliding direction. In a similar study,
37 Kim et al [29] compared the tribofilms derived from ashless dithiodiphosphates (ADDPs) and ZDDP using
38 XANES and reported the similar kind of structure of the tribofilms with ashless dialkyl dithiophosphate
39 (ADDPS) as of ZDDP with harder near surface region and a more compliant bulk to give good antiwear
40 performance. In addition, Kim et al. [27,29] also characterized the wear debris harvested from the wear
41 test (i.e. ball on cylinder) run under extreme pressure conditions of several ashless dithiophosphates
42 based additives and reported Fe_3O_4 nanoparticles embedded in the amorphous structure of tribofilms.
43 The wear performance was correlated to the number of nanocrystalline oxide particles with the one
44 with smaller number of oxide particles exhibiting the best wear performance. They also compared the
45 thickness of the films derived from the ashless dialkyl dithiophosphates and ZDDP and reported that the
46 tribofilms formed using ashless additives were significantly thicker than the one formed by ZDDP.
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54 In this study, the tribological behavior of new ashless antiwear chemistries were studied in blends with
55 ZDDP with varying ratios of ZDDP and ashless chemistries. The coefficient of friction was measured using
56 a high frequency reciprocating cylinder on flat test set up under different load conditions i.e. 54N and
57 350N. The electric contact resistance (ECR) data was also collected simultaneously which indicates the
58 incubation time for the formation of tribofilms as the test proceeded. Wear volume was calculated on
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the wear scar of the pin of each tests using optical microscopy and optical 3D interferometry. Wear data shows significant reduction in wear when ashless anti-wear additives were blended with ZDDP when compared to ZDDP at both at low and high load conditions. In an effort to understand the mechanism of wear morphology of the tribofilms was studied using scanning electron microscopy (SEM). High magnification images indicate a small pad like structure over the wear surface of the test samples at lower test load. These small patchy films tend to expand and merge into large patchy film at higher test loads. The film formation mechanism of these lubricant additives was further scrutinized using x-rays absorption near edge structure (XANES), and nano-indentation and nano-scratch were performed to measure the nano-mechanical properties of the film as a function of the film depth. A comprehensive understanding of the chemistry, structure and properties of tribofilms were developed to explain the observed wear behavior.

Experimental Details

Chemistry of Antiwear Additives:

Neutral -100 base oil and zinc dialkyl dithiophosphate (ZDDP) were purchased from commercial vendors. The ZDDP used in this study is a secondary alcohol derived ZDDP with approximately 70% neutral and 30% basic characteristic. The Ashless additives chemistry used in this study were synthesized in the lab. For that purpose, all of the reagents were purchased from commercial suppliers and used without purification unless otherwise specified. The synthesis of the phosphorofluoridithioate and thioperoxydiphosphate is shown in the earlier publications {3741; 3739}. Table 1 details the structure of the ZDDP and the ashless antiwear additives alkylphosphorofluoridithioates and alkylthioperoxydiphosphate.

Tribological Test Procedure:

Two different ashless antiwear additives i.e. PFC18 (octadecylphosphorofluoridithioate) & SSC18 (octadecylthioperoxydiphosphate) along with ZDDP (Zinc dialkyl dithiophosphate) were tested in boundary lubrication conditions to evaluate their tribological properties. Four different lubricant oil formulations were prepared in base oil i.e. (i) 100% ZDDP, (ii) 80%ZDDP+20%PFC18, (iii) 80%ZDDP+20%SSC18 & (iv) 80%ZDDP_10%PFC18+10%SSC18. Phosphorous level was kept constant at 1000 ppm in all the formulations. The tribological tests were performed on a home built high frequency cylinder on flat test set-up at Argonne National Lab, Energy System division. Load was applied using a pneumatic pressure unit and friction forces were measured using a strain gauge motion sensor. The lubricant oils were run under this set up at two different loading conditions i.e. (i) 54N & (ii) 350N that results in a maximum contact pressure (P_{max}) of 320 MPa & 800 MPa respectively. All the test were run at 300 RPM (5 Hz) reciprocation speed for the duration of an hour at 100°C temperature. Data was acquired at 5Hz rate using the DasyLab software. The stroke length was 6 mm. Tests were performed on 52100 hardened steel flat using a 52100 hardened steel bearing cylinder from RBC bearings. Both flat and pin were cleaned before each tests using standard solution followed by Isopropanol and Acetone to completely remove any oil and dust present on the initial surfaces. The rubbed surfaces after the tests were cleaned with Hexane and Isopropanol and then saved by submerging in base oil.

Analysis of the Rubbed Surfaces and Characterization of the Tribofilms:

After each test, the cylinders were cleaned using hexane followed by isopropanol and then they were examined under the optical microscope and 3D optical interferometry for the assessment of the wear track and calculation of the wear volume. The nature of the wear occurring at the surface was studied by examining the surface of the wear tracks. A Hitachi S-3000N Scanning Electron Microscope (SEM) was used to get secondary electron images of the wear track.

Nano-mechanical properties (i.e. hardness and elastic modulus) of the tribofilms generated on the flat were measured using a nano-indenter from Hysitron Triboscope^{TM}. The Nano-indentation were carried out using a Berkovich type tip geometry with a total included angle of 142.3 degrees and a half angle of 65.35 degrees. Nano-indentation were performed at nine different locations in a single sample. A cyclic loading profile with partial unload load was run for each indentation point to study the nano-mechanical properties of the tribofilms as a function of the film thickness. A scanning probe microscope mode in the tribo-indenter was also used to obtain topographical information as well as the 3D image of the tribofilms on the rubbed surfaces.

In order to understand the chemical nature of the tribofilms, XANES (X-Ray Absorption Near Edge Structure) spectra were obtained. XANES is a very robust technique to study the local co-ordination of the elements present on and in the tribofilms. It provides chemical information from 5nm of the surface to 400 nm in depth of the sample. XANES spectra were obtained at Canadian Light Source synchrotron facility at Saskatoon Canada. The phosphorous and sulfur L edge data were collected at VLS-PGM (variable line spacing plane grating monochromator) beam station which operates at the energy range of 5.5ev-250ev with a photon resolution of more than 10,000 E/ Δ E. All the spectra were collected using a 100 μ mX100 μ m photon beam spot size. Oxygen K edge, iron L edge and zinc L edge spectra were obtained at SGM (spherical grating monochromator) beam line which operates between 200ev-2500ev energy range with a photon resolution of more than 5000 E/ Δ E. Here, a spot size of 50 μ mX50 μ m was chosen to obtain high resolution spectra. Finally, phosphorous K edge and sulfur K edge spectra were obtained a SXRMB (Soft X-ray Micro characterization Beam line) beam station which operates a high energy ranging from 1.7 – 10 keV which a photon resolution of 3.3×10^{-4} Insb (111). A 1mm X 2mm spot size was chosen to collect the spectra at the SXRMB beam line.

Results and Discussion

Evaluation of Coefficient of friction and Wear Volume Loss

Coefficient of Friction (CoF) was acquired during the high frequency cylinder on flat test. Four different oil formulations were tested at two different load i.e. 54N (mixed boundary lubrication) and 350N (boundary lubrication). Figure 1 (a) is a plot of CoF over the duration of the test. All the tests were run for an hour and the friction force data was acquired at the rate of 5Hz. The coefficient of friction at 54N is higher for all the formulations than the CoF at 350N. This is because at higher loads the surface asperities get crushed, which results in smoother surface to the rubbing motion and also stable (and

perhaps thicker) tribofilm formation on the rubbing surface. Thus, the CoF curves for 350N load are lower and show good stability during the entire tests. However, the CoF doesn't vary much with the addition of ashless fluorothiophosphates anti-wear chemistry to the ZDDP. At 54N, the friction data show high fluctuations during the test which is due to the formation of unstable tribofilms during the test that break down periodically as the test proceeds. The coefficient of friction is comparable when ZDDP is used with and without the ashless fluorothiophosphates additives.

Wear assessment was done by measuring an average wear width from the different pins (52100 steel) rubbed against the flat surfaces (flat surface) using an optical microscope and 3D optical interferometry. Figure 1(b) shows the comparison of wear volume loss for the different lubricant oil formulations at different loads, error bars in the figure indicate the deviation in the wear volume calculations. The addition of ashless fluorothiophosphates to ZDDP shows significant improvement in wear reduction under both 54N and 350N loads. On comparing the wear volume from the blends of ZDDP with ashless additives with oils that contain only ZDDP, a maximum wear reduction, i.e., $\approx 80\%$, was observed from the blend with 80%ZDDP+20%SSC18 formulation at 54N. However, the other formulations of ashless fluorothiophosphates with ZDDP also showed significant wear volume reductions when compared to formulations that only contained ZDDP. At 350N load, the wear volume increase to much higher values than it was at 54N for all the formulations. Here also, comparing to the wear volume from formulations that only contain ZDDP, the addition of ashless fluorothiophosphates to the ZDDP improves the anti-wear properties significantly.

Incubation time for the tribofilms formation

Most ZDDP derived tribofilms formed at tribological contacts are generally amorphous glasses and known to have very high electrical resistivity. At the initial stage of the test when tribofilms are not formed yet, direct contact of asperities of two surfaces in tribological contact result in very low contact resistance, however, as the test progresses with the formation of protective tribofilms, the resistance between the contacting surfaces increases and can be used as a way of determining effectiveness of tribofilm formation. The voltage drop across the tribocontact ranges from 0 to 1200 mV which is normalized from 0 to 1. The 0 corresponds to no tribofilm present and 1 corresponds to when an effective tribofilm is present on the surface. The voltage drop was integrated over time to illustrate the overall effectiveness of tribofilm formation over time, larger values correspond to more net coverage of tribofilm over the duration of the test. In addition the slope of the curve indicates the effectiveness of tribofilm formation with larger slopes having better tribofilm formation. Figure 2(a) shows the voltage drop data for all the four formulations run under the load of 54N. The graph shows potential drop between the pin and the surface as a function of time. At 54N, the incubation time for the tribofilms formation for the oil that only contains ZDDP is relatively higher than the mixes of ZDDP with ashless fluorothiophosphates, as the graphs show higher potential drop from the beginning of the test. However, the tribofilms are not stable and they break down periodically during the test as evidenced by the sharp drop in normalized voltage to 0. This also explains the large fluctuations in the friction curves at 54N load tests. Figure 2(b) is the plot of electrical contact resistance for the four lubricant oil formulations used at 350N load tests. As the data indicates the tribofilms form very early in the test and stay stable for the duration of the test in the cases of ZDDP with the addition of ashless fluorothiophosphates. On the other hand in formulations that

only contain ZDDP, even though the tribofilm forms in the early stages of the test they are not stable and there is constant breakdown and reformation of the tribofilms.

Topographical study of the tribofilms using Scanning Electron Microscopy (SEM)

SEM images of the tribofilms formed on the flat were imaged using S-3000N variable pressure SEM. Figure 3 is the secondary emission SEM images of the rubbed surfaces for the four different oil formulations at 54N and at 350N. At 54N load test, SEM images show less coverage of tribofilms on the wear surfaces. At higher magnification i.e. 4000X, small patches (darker contrasting areas) of tribofilms are observed. Whereas at 350N load test, the wear surfaces show features of patchy tribofilms all over the sample which also have grown larger into size than the patches of tribofilms in 54N test. This indicates that at higher load the tribofilms tend to grow into larger pads along the sliding directions.

Nano-mechanical measurements and 3D imaging of the tribofilms using Nano-indentation

Nano-Indentation

Nine nano-indentation tests were performed for each of the tribofilms using a cyclic loading with partial unloading load function (2 seconds for linear loading segment, 2 seconds for holding segment and 2 seconds for linear unloading segment) with a peak load ranging from 100 μ N to 1000 μ N. Figure 4(a) is a typical load profile as a function of time for the nano-indentation tests. Figure 4 (b) and (c) shows the plot of hardness as a function of the indentation depth into the tribofilms generated from all the different lubricant formulations as well as the 3D images of the wear surfaces (30 μ mX30 μ m) obtained via scanning probe microscope (SPM). SPM images were obtained before and after the nano-indentation. Images taken before the indentation were used to locate the best possible flat region in order to make sure a smoother surface is provided to the nano-indentation probe for proper indentations. However, on wear surfaces obtained at 54N load test, finding a flat region was a challenge since (as shown in fig 4(a) SPM images) the surfaces consist of a large number of small rounded pad like features of tribofilms with very little flat areas (caused large fluctuation in the friction data at 54N load test shown earlier). This resulted in a wider range of the nano-hardness measurements at different location of measurement. The SPM images taken on the wear surfaces generated at 350N load tests show larger pad like structure of the tribofilms. This confirms the topographical information obtained from the SEM images that at higher loads the patches of tribofilms grow larger in size resulting in a much smoother surfaces resulting in lower friction. As shown in figure 4(b), hardness data obtained for the formulations containing ashless fluorothiophosphate additives with ZDDP in the mixtures of base oil show high consistency and doesn't vary much with different location of indentations whereas the hardness obtained from the formulation containing ZDDP falls into a broader range, the SPM images of the tribofilms from ZDDP formulations indicate a much smaller pad size and uneven tribofilm formation explaining the broader range of hardness data derived from the tribofilms. This indicates that the wear surfaces generated with the blends of ashless thiophosphates with ZDDP are smoother with larger tribofilm pad sizes than the wear surface obtained using only ZDDP. It was observed that the hardness of the tribofilms generated from these tests does not vary much with penetration depth as the hardness curve drawn for the 54N load test and 350N load test gives similar outcome and also follow the same

1 trend. In addition, the nano-mechanical properties of the tribofilms generated from the formulation
2 using only ZDDP and formulations that contain a mixture of ZDDP with ashless fluorothiophosphate
3 additives can be differentiated easily. As can be seen from figure 4 (b) and (c), the tribofilms formed
4 from ZDDP at a load of 350N has a hardness of about ~14 GPa near the surface which eventually
5 decreases to 6-7 GPa with film depth of 50-60 nm. Several studies in the past [2621] have indicated that
6 typical tribofilms range in thickness from 80-200 nm. Whereas, tribofilms obtained with the addition of
7 ashless fluorothiophosphate additives with ZDDP show uniform hardness at different location of
8 indentations and also does not vary much as a function of the film depth. The hardness near the surface
9 of the tribofilms (< 20 nm) is about 8 GPa that decreases to 4-5 GPa as the indentation depth increases
10 to 60nm. Similar results were found by Kim et al [2621], where they reported the hardness of tribofilms
11 generated using ZDDP as additive in base oils starts from higher values which eventually decreases to
12 around 8GPa as the indentation depth increases while the hardness of ashless DDP remains close to
13 5GPa throughout the test. However, they found the tribofilms to be much thicker than the values
14 reported in this paper, this could possibly due to the different nature of the test used where they ran
15 the test at very high contact pressure. In another study by Bec et al [4680], they reported the nano-
16 hardness measurements of the tribofilms generated at 360MPa mean contact pressure (close to the
17 P_{mean} used in this paper). They found that the wear surfaces consists of multilayer tribofilms. The nano-
18 indentation measurements showed that the mechanical properties of the tribofilms are heterogeneous
19 spatially as well as with thickness also. This explains the broader hardness data obtained using ZDDP
20 additive only (figure 4 (c)). It can be hypothesized that the tribofilms generated from ZDDP only are non-
21 uniform and heterogeneous in nature with varying film thickness, whereas, the tribofilms generated
22 from ZDDP plus FTPs additives formulations are more uniform and homogeneous in nature.

23 XANES Analysis

24 XANES analysis has been used extensively in tribology to examine the chemical nature of the tribofilms
25 derived using various anti-wear additives [26,29,32,39,47-53]. It provides chemical information for total
26 electron yield (TEY) and fluorescence yield (FLY) for the P L-edge of 5 and 60 nm respectively and
27 sampling depths for TEY and FLY at the P K-edge are 50nm and >800nm, respectively [41,54]. Both TEY
28 and FLY spectra were acquired from the tribofilms formed using the four different formulations studied
29 here.

30 Phosphorous Characterization by XANES

31 Phosphorous L edge XANES spectra provides a wealth of chemical information as the depth of sampling
32 is close to the average thickness of the anti-wear tribofilms which is 50-100nm in most cases. The
33 phosphorous L edge TEY and FLY spectra of the tribofilms generated from ZDDP and combinations of
34 ZDDP with ashless PFC18 & SSC18 compounds along with the model compounds $Zn_3(PO_4)_2$ and $FePO_4$
35 are shown in the Figure 5(a), (b) and (c). Here, different peak positions of the model compounds are
36 assigned as a, c, c' and d. Peak labelled as **a** corresponds to the spin orbital splitting of the phosphorous
37 2p electrons present in $Zn_3(PO_4)_2$ whereas peaks labelled as **c** and **c'** are attributed to the transition of
38 the phosphorous 2p electrons to the t^*_2 molecular orbital in $Zn_3(PO_4)_2$ and $FePO_4$ compounds
39 respectively, and peak **d**, located ~146.0ev is a shape resonance peak, is characteristic of all phosphates

regardless of the structure, whether crystalline or glassy [50,55,56]. From the graphs, it can be deduced that for the tribofilms generated at 350N, phosphorous is primarily present in the form of zinc phosphate rather than iron phosphate as the peak position **c** is well aligned to the tribofilms spectra both in TEY and FLY modes. Moreover, the pre-peak shoulder for the tribofilms also matches with peak position **a**, corresponding to the zinc phosphate. However, clear differences between the chemistry of the tribofilms formed from different formulations cannot be observed here. In case of tribofilms derived from 54N load tests, a mere presence of FePO_4 can be observed in the case of 100ZDDP and 80ZDDP_20SSC18 additives formulations. This can be explained as at lower loads there is a competition between the Zn^{+2} cation and Fe^{+2} cation to form an anti-wear films but at higher loads decomposition of ZDDP increases and thicker pads of anti-wear films formed that reduces the availability of Fe^{+2} cation and leads to the formation of zinc phosphate on the rubbing surfaces.

Phosphorous L edge spectra also used for the determination of the chain length of the polyphosphates present in the tribofilms using peak intensity ratio of peaks **a** and **c**. Chain lengths of polyphosphates are characterized on the basis of peak height of **a** relative to peak **c** where ratio a/c up to 0.3-0.4 represents short-chain polyphosphates and $a/c > 0.6$ indicates long-chain polyphosphates [26,50,57]. Tribofilms studied in this work show very small pre-peak intensity of **a** in TEY mode which becomes less evident or starts to disappear in FLY mode, suggesting presence of short-chain polyphosphates and mono phosphates at the surface (≈ 5 nm) of the tribofilms whereas the bulk (≈ 30 -40 nm) is largely made up of mono phosphates.

Phosphorous K edge spectra are shown in Figure 6 (a), (b). Only TEY spectra of phosphorous K edge are considered as the depth of sampling for P K-edge at FLY mode (1 - $2\ \mu\text{m}$) is much higher than the thickness of the tribofilms thus can be disregarded for the purpose of this study. On the other hand, the TEY spectra provides cumulative chemical information in the tribofilms from 50 - 75 nm. P K-edge spectra from the tribofilms are plotted with the model compounds for the comparison. Two peak position are shown in the graphs labelled as **c** and **c'** which corresponds to the transition of the core phosphorous $1s$ electron to unoccupied p-like valence state [29] for $\text{Zn}_3(\text{PO}_4)_2$ and FePO_4 respectively. Two main difference between the model compounds, zinc phosphate and iron phosphate are first, main peak position for FePO_4 , **c'** (2151.5eV), has slightly higher energy than the main peak position, **c** (2150eV), for $\text{Zn}_3(\text{PO}_4)_2$ and second, P K-edge spectra for iron phosphate show small pre-edge that is more evident in FLY graph. The spectra for ZDDP and the mix between ZDDP and ashless chemistries indicates that in the bulk of the tribofilms, phosphorous is primarily present in the form on $\text{Zn}_3(\text{PO}_4)_2$ which is similar to the findings in P L-edge FLY.

Sulfur Characterization by XANES

Sulfur L-edge spectra provides a useful information regarding the local co-ordination/oxidation state of sulfur near the surface of the tribofilms [23,53,58-60]. The S L-edge spectra are plotted for the tribofilms derived from ZDDP and combinations of ZDDP with ashless PFC18 & SSC18 compounds and compared with the spectra of several model compounds in figure 7 (a) and (b). Differences in the spectra of the model compounds and their relative peak energies are detailed by Kim et al in an earlier study [29]. At the outset it is important to note that the S L-edge spectra are much weaker than the spectra for the P

L-edge indicating a preponderance of phosphates species near the surface of the tribofilm. The TEY spectra of the S L-edge suggests that the sulfur is present primarily in the form of sulfides rather than sulfates in the tribofilms. Presence of sulfates is more noticeable in the case of tribofilms generated at 54N load tests. A broad peak at position **f** indicates that sulfur is present in a mixture of different sulfate (Zn and Fe) species and is the primary species of sulfur present near the surface, the presence of small amounts of ZnS and FeS cannot be ruled out. On the other hand, TEY spectra of the tribofilms generated at 350N tests resemble the ZnS and to a lesser extent the presence of FeS. Figures 7 (b) are showing the FLY data of the tribofilms formed at 350N and model compounds. The sampling depth at S L-edge FLY is about 40-50 nm while the sampling depth at S L-edge TEY spectra is about 4-5nm. Here, interestingly, the spectra of the tribofilms resemble closely to the spectra of the ZnS as the peak positions **a**, **b**, **c**, **d** and **e** from ZnS aligns to the tribofilms spectra for the 350N load tests but still the broad shoulder after peak position **b** and also broadened peak **c** suggest that more than one type of sulfide species are present i.e. ZnS as well as FeS in the bulk of the tribofilms. Nicholls et al [48] explained the mechanism for the sulfide formation in the tribofilms using the principle of hard acids and soft bases which suggests that soft bases as S^{2-} prefers to react with the borderline soft acid Zn^{+2} over the harder acid Fe^{+2} and Fe^{+3} . They also expressed thermodynamically that the free energy of the ZnS formation is more negative than FeS. However, thermodynamically zinc prefer to form zinc polyphosphates instead of zinc sulfides thus most zinc gets consumed in the form of polyphosphates and becomes less available to form zinc sulfide while available iron can react with sulfur to form iron sulfides.

Figure 8 (a) (b) and (c) are plots of sulfur K edge spectra in TEY and FLY mode for model compounds and tribofilms respectively. Figure 8(d) is the deconvoluted plot of S K-edge of 80ZDDP+20PFC18 detailing the contribution of the different sulfur species in the overall spectra from the tribofilm. Only TEY spectra for the model compounds are shown for the comparison as there is no significant difference in the spectra for the two modes, since the chemistry of the model compounds does not change with the sampling depth in XANES. Sulfur can exist in different valence states ranging from -2 to +6 with -2 being the reduced states and the +6 being the oxidized states. The absorption edge of the different valence states can be easily distinguished by XANES spectra. In addition, the spectra from the model compounds indicate that the K-edge is ideally suited to distinguish between the different sulfides of Fe and Zn and between sulfides and sulfates. The peak identified as **a'** is unique to FeS while the peak labeled **a** is present in ZnS. On the other hand peak **c** is primarily present in sulfates and is common to both $FeSO_4$ and $ZnSO_4$. From the plots, S K-edge TEY spectra of the tribofilms indicate that a mixture of sulfide and sulfate species are present in the tribofilms, interestingly, the intensity of the sulfate peaks are less pronounced in the case of the tribofilms formed under 350N load tests than the tribofilms formed under 54N load tests. Moreover, sulfate peaks tend to diminish in FLY mode in all the cases as plenty of oxygen is available in the surface region rather than in bulk thus sulfur gets oxidized to form sulfates on the surfaces but not in the bulk of the tribofilms. S K-edge spectra of the tribofilms both in TEY (Figure 8(b)) and FLY (Figure 8(c)) mode indicate that besides sulfate, sulfur is also present in the form of ZnS as the peak position **a** (i.e. 2473ev) from the ZnS model compound spectra aligns to the spectra of the tribofilms. This confirms the earlier information from the S L-edge FLY data that in the bulk of the tribofilms sulfur is dominantly present in the form of ZnS with a small presence of FeS. A ratio of peak area ratio (**a/c**) under peaks **a** and **c** provide additional insight into the relative proportion of ZnS and

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4 sulfates are measured by deconvoluting the spectra as detailed in Figure 8(d) and provided in detailed in
5 Table 2. It is evident from the data using both measures that in comparison to ZDDP by itself,
6 formulations that contain a mix of ZDDP with ashless additives PFC18 and SSC18 have higher ratio of ZnS
7 in the tribofilms that are generally more beneficial from a tribological point of view.
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10 *Oxygen characterization by XANES*

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12 Even though oxygen is present in only one valence state, it can be bound directly with different cation's
13 such as Zn and Fe as well present in different anions such as sulfate and phosphates that can
14 subsequently be bound with cation's such as Fe and Zn. The resulting O K-edge XANES absorption
15 spectra of such compounds are distinctively different when viewed as pure model compounds as shown
16 in Figure 9(a). It is clearly evident that Fe_2O_3 can be distinguished from ZnSO_4 , $\text{Zn}_3(\text{PO}_4)_2$, ZnO , FeSO_4 and
17 FePO_4 by the nature of the pre-edge peaks present at 530-532 eV. However, in a tribofilm O is present
18 in multiple anions and is bound to different cation's making it difficult to uniquely identify the local
19 environment for oxygen. However, some distinctive differences can be ascertained by an examination of
20 the spectra. Oxygen K-edge spectra were recorded in both TEY and FLY mode for the tribofilms
21 generated from all the four formulation ran at 54N and 350N load tests, the TEY and FLY spectra being
22 very similar, only the TEY spectra are shown for reference while the discussion pertains to both TEY and
23 FY spectra. O K-edge TEY spectra of the tribofilms shown in Figure 9(b). We can eliminate the possibility
24 of the oxidation of zinc and iron as the spectra of the tribofilms do not show the presence of these
25 compounds. Other than that, results are quite complicated and hard to distinguish as the earlier
26 companion P, S, Zn and Fe spectra showed more or less the presence of all the ZnSO_4 , $\text{Zn}_3(\text{PO}_4)_2$, FeSO_4
27 and FePO_4 model compounds in the tribofilms. However, for the tribofilms generated under 350N load
28 tests presence of peak at 538.6eV is matching with the primary peak of $\text{Zn}_3(\text{PO}_4)_2$ model compound and
29 also the pre-peak bump at 531.9 eV is less pronounced, therefore, we can say that $\text{Zn}_3(\text{PO}_4)_2$ is present
30 as the major constituent of tribofilms formed at 350N load tests. Whereas, at 54N load tests, pre-peak
31 bump at 531.9eV becomes more noticeable in the spectra suggesting some sulfates (ZnSO_4) is present.
32 In two of the compositions that contain SSC18. This may arise from the fact that the compositions with
33 SSC18 have loosely bound sulfur that is readily available under tribological conditions to form sulfates of
34 Zn.
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45 *Zinc characterization by XANES*

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47 The Zn L-edge may be used to characterize the coordination of Zn with other elements such as O, S, F as
48 well as anions such as phosphates and sulfates. The model compounds shown in Figure 10(a) indicate
49 that the absorption spectra of Zn L-edge for the different compounds are distinctively different and may
50 be used to distinguish between the different species. The spectra were acquired for all the tribofilms
51 tested at 54 and 350 N in both TEY and FY mode and the spectra in TEY and FY are very similar and only
52 the TEY spectra (Figure 10 (b)) are shown for discussion. It is evident from a comparison of the spectra of
53 the tribofilms with that of the model compounds that the preferred compound present is $\text{Zn}_3(\text{PO}_4)_2$ in all
54 cases. The S K-edge spectra has indicated the presence of ZnS as the primary S containing compound in
55 the tribofilm, however the Zn L edge clearly indicates that the primary Zn containing compound is
56 $\text{Zn}_3(\text{PO}_4)_2$. This suggests that while ZnS is present in the tribofilm the phosphates of Zn are the
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predominant species. This is also self evident from the P and S L edge spectra that indicated that the relative intensity of the P L-edge spectra was much stronger than the S L-edge indicating a preponderance to the formation of phosphates. This can be correlated to the study by Nicholls et al [48], where they reported that zinc phosphate is the thermodynamically more stable form of zinc.

Discussion of XANES Data

The complementary XANES spectra at different edges and different elements provide a detailed way by which chemistry of tribofilms may be analyzed. A comparison of the P and S L-edge spectra of the tribofilms indicate that phosphorous spectra are much stronger than the sulfur spectra suggesting that phosphates of Zn are the dominant species in the tribofilms. The sulfur present in the tribofilms is largely sulfates at lower loads and transition to ZnS at higher loads. When tribofilms from ZDDP are compared to those formed from mixtures of ZDDP and ashless fluoro thiophosphates and ashless thiophosphates it is evident that sulfide species are more dominant in the mixtures when compared to when ZDDP is used by itself. The O K-edge clearly indicates that oxides of Fe are not present in any significant quantity in the tribofilm and the most likely candidates are phosphates of zinc and some sulfates of Zn and Fe. The P K-edge spectra indicate the presence of phosphates of Zn and when the S K-edge spectra is considered it is evident that from the TEY spectra that at lower loads (54N) there is a larger proportion of sulfates when compared to the higher loads (350N). It is also evident from the S K-edge spectra that tribofilms from ZDDP have a higher proportion of sulfates relative to sulfides when compared to blends that contain ZDDP and ashless PFC18 and SSC18 that have a larger proportion of sulfides of Zn. The presence of the ashless fluoro thiophosphates and/or ashless thiophosphates appears to assist in the formation of Zn phosphates and ZnS in the tribofilm. This is also confirmed by the Zn L-edge spectra that indicate the primary presence of Zn phosphate in the tribofilm. Fluorine K edge analysis (not shown here) indicated very little presence of any fluorine at the surface of the tribofilm indicating that while the presence of fluorine certainly helps in the formation of the tribofilm and its stability very little of it is left behind on the wear surfaces.

Conclusions:

- (i) The frictional behavior of lubricant formulation with ZDDP and ZDDP blended with ashless fluoro thiophosphate and/or ashless thiophosphates are essentially identical indicating no mechanistic change tribologically with the addition of the ashless antiwear additives to the mix.
- (ii) The wear behavior both at low (54N) and high (350N) loads indicate that mixtures with ZDDP and ashless antiwear additives have significantly superior wear behavior when compared to ZDDP by itself. The incubation time to form tribofilms is shorter when mixtures of ZDDP and ashless antiwear additives are used in comparison to ZDDP by itself.
- (iii) Morphology of the wear surface using scanning electron microscopy indicates that at lower loads (54N) tribofilms are not well developed and largely heterogeneous while at higher loads (350 N) the tribofilms develop a larger pad like structure that is interconnected and aligned in the direction of rubbing. Formulations with a mixture of ZDDP and ashless

- additives yielded stable pad like tribofilms while the ones from ZDDP alone were more heterogeneous.
- (iv) Scanning probe microscopy and nano-mechanical testing of the tribofilms indicate that properties at 54N in all cases have a large degree of scatter due to the heterogeneous nature of the tribofilms while at 350N the hardness data in the formulation with ZDDP and ashless additives is uniform and independent of depth while those from ZDDP alone exhibit a large amount of scatter, a consequence of their heterogeneous nature.
- (v) The P and S Ledge XANES Data indicate the preponderance of phosphates (short chain or monophosphates) of Zn in the tribofilm while the S that is present is largely in the form of ZnS. When only ZDDP is present the surface of the tribofilms contains sulfates of Zn while in the case of ZDDP with ashless antiwear additives a mixture of sulfates and sulfides of Zn are present.
- (vi) The O K-edge XANES spectra indicates very little presence of oxides of Fe or Zn in the tribofilm and complement the P L-edge spectra that indicate the primary presence of phosphates of Zn.
- (vii) The P and S L edge XANES spectra indicate the presence of Zn Phosphates and in the case of S, primarily the presence of ZnS. The S K-edge spectra complement the L-edge spectra wherein the S is present more as a sulfate when only ZDDP is used where as when mix of ZDDP and ashless antiwear additives are used the reduced form of S is more likely to be present.
- (viii) The Zn L-edge spectra complements all the other XANES data confirming that the coordination of Zn is largely in the form of Zn phosphates.

Acknowledgements: Support provided by the Materials Science and Engineering Department and use of the characterization facilities at the Center for Characterization of Materials and Biology at The University of Texas at Arlington is gratefully acknowledged. The XANES experiments were performed at Canadian Light Source, which is supported by NSERC, NRC, CIHR and the University of Saskatchewan. Tribology experiments were performed at Argonne National Laboratory, which is a U.S. Department of Energy Office of Science laboratory, and operated under Contract No. DE-AC02-06CH11357.

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List of Figures and Tables

Table 1: Structure of the Anti-wear Additive Compounds.

Table 2: Details peak fitting for the S K-edge spectra and ratio of sulfides to sulfates.

Figure1: Tribological behavior of formulations with ZDDP and mixtures of ZDDP and ashless thiophosphates in base oil mixtures. Fig. 1(a) shows the coefficient of friction as a function of time at two different load i.e. 54N and 350N. Fig. 1(b) shows the comparison of wear volume for the different oil formulations at two different loads.

Figure 2: Electrical contact resistance for all the tribological tests with ZDDP and ZDDP with ashless thiophosphates conducted at 54N and 350N.

Figure 3: Showing the secondary emission SEM images of the rubbed surfaces for the four different oil formulations at 54N at 350N.

Figure 4: Nano-mechanical properties of tribofilms obtained from nano-indentation using cyclic loading with partial unloading load function (shown in Fig. 4(a)). Fig. 4(b) & (c) show a comparison of nano-hardness profile of tribofilms using ZDDP and 80%ZDDP+20% PFC as a function of indentation depth at 54N and 350N respectively as well the corresponding 3-D SPM images.

Figure 5: (a) Phosphorous L-edge XANES TEY spectra of tribofilms generated at 54N and model compounds (b) Phosphorous L-edge XANES TEY spectra of tribofilms generated at 350 N and model compounds (c) Phosphorous L-edge XANES FLY spectra of tribofilms generated at 350N and model compounds.

Figure 6 (a) Phosphorous K-edge XANES spectra of tribofilms generated at 54N and model compounds (b) Phosphorous K-edge XANES spectra of tribofilms generated at 350N and model compounds.

Figure 7: (a) Sulfur L-edge XANES TEY spectra of the tribofilms generated at 54 N. (b) Sulfur L-edge XANES TEY spectra for tribofilms generated at 350 N as well as the model compounds.

Figure 8: (a) Sulfur K-edge XANES spectra of the model compounds of sulfur. (b) Sulfur K-edge XANES TEY spectra of the tribofilms obtained at 54N. (c) Sulfur K-edge XANES TEY spectra of the tribofilms obtained at 350N. (d) Representative deconvolution process used to determine the contribution from the different valence states of sulfur in the tribofilm from a formulation that contains 80% ZDDP + 20%PFC18.

Figure 9: (a) Oxygen K-edge XANES spectra of model compounds containing oxygen. (b) Oxygen K-edge TEY spectra of tribofilms generated at loads of 54 and 350N.

Figure 10: (a) Zinc L-edge XANES spectra of model compounds that contain zinc (b) Zinc L-edge TEY spectra of tribofilms generated at loads of 54 and 350N.

Figure 1(a)

Figure 1(b)

Figure 2(a)

Figure 2(b)

Figure 3

Figure 4(a)

Figure 4(b)

Figure 4(c)

Figure 5(a)

Figure 5(b)

Figure 5(c)

Figure 6

Figure 6(b)

Figure 7(a)

Figure 7(b)

Figure 8(a)

Figure 8(b)

Figure 8(c)

Figure 8(d)

Figure 9(a)

Figure 9(b)

Figure 10(a)

Figure 10(b)

Table-1

Coded Name	Chemical Name	Chemical Structure
ZDDP	Zinc Dialkyldithiophosphate (R = C4,C6 and C8)	
PFC18	Octadecylphosphorofluoridothioate	
SSC18	Octadecylthioperoxydiphosphate	

Table-2

Sample	S K-edge TEY Photon Energy (ev)					a/c Ratio (area)
	a'	a	b	c	d	
FeS	2470.03	x	2475.82	2481.40	x	
ZnS	x	2472.72	2475.94	x	2484.71	
100% ZDDP @ 54N	x	2472.86	2476.33	2481.60	2484.79	0.43
80% ZDDP + 20% PFC18 @54N	x	2472.88	2476.04	2481.36	2485.07	0.73
80% ZDDP + 20% SSC18 @54N	x	2472.38	2475.99	2480.67	2484.92	0.83
80% ZDDP + 10% SSC18 + 10% PFC18 @54N	x	2472.78	2476.15	2481.30	x	0.47
100% ZDDP @350N	x	2473.10	2476.04	2481.00	x	0.41
80% ZDDP + 20% PFC18 @350N	x	2473.51	2476.67	2481.52	2485.86	0.96
80% ZDDP + 20% SSC18 @350N	x	2472.90	2475.84	2481.11	2485.12	0.75
80% ZDDP + 10% SSC18 + 10% PFC18 @350N	x	2472.93	2475.78	2481.15	2485.34	0.66