

# Tribofilms generated from ZDDP and DDP on steel surfaces: Part 1, growth, wear and morphology

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The growth and morphology of tribofilms, generated from zinc dialkyldithiophosphate (ZDDP) and an ashless dialkyldithiophosphate (DDP) over a wide range of rubbing times (10 s to 10 h) and concentrations (0.1–5 wt% ZDDP), have been examined using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) spectroscopy at the O, P and S K-edges and the P, S, and Fe L-edges. The physical aspects of the growth and morphology of the tribofilms will be presented in Part I and the chemistry of the films will be discussed in Part II. The major components of all films on 52100 steel are Zn and Fe phosphates and polyphosphates. The average thickness of these phosphate films has been measured using P K-edge XANES and XPS profiling. For ZDDP, a very significant phosphate film (about 100 Å thick) forms after 10 s, while film development for DDP is substantially slower. However, for both additives, the average film thickness increases to 600–800 Å after 30 min of rubbing, before leveling off or decreasing. The antiwear properties of pure ZDDP and in combination with DDP at different rubbing times and concentrations have also been examined. It was found that under all conditions, the performance of ZDDP as an antiwear agent is superior to that of DDP. However, DDP has no adverse effect on the performance of ZDDP when the two are mixed. The AFM results show that ZDDP forms larger and better developed “pads” than DDP at short rubbing times. At longer rubbing times, both films become more uniform. For the 1 h ZDDP films, the film thickness is surprisingly independent of the ZDDP concentration from 0.1 to 5 wt% ZDDP. The film thickness is also independent of the ratio of ZDDP/DDP concentrations.

**KEY WORDS:** ZDDP, DDP, chemistry of tribofilms, wear, AFM, XPS, XANES

## 1. Introduction

In recent years, many researchers have applied advanced spectroscopic techniques to investigate the chemistry, morphology and film thickness of tribofilms formed as a result of additive decomposition in the contact zone. In part I of this study we report on the growth, wear properties and morphological aspects of the tribofilms and in the second part we discuss the chemistry of the films.

A number of surface analytical techniques have been used to determine thickness and the morphology of the tribofilms [1–2]. Techniques such as X-ray Photoelectron Spectroscopy (XPS) [2–9], Auger Electron Spectroscopy (AES) [3,6–11] and Secondary Ion Mass Spectrometry (SIMS) [12,13] in conjunction with ion etching, have been used to determine the physical film thickness. Surface profilometry [9] may be used to measure the depth of the etched crater. Unfortunately, ion etching destroys the sample and thus the same sample cannot be used for other characterizations.

Techniques such as Electron-Probe Micro-Analysis (EPMA) [5,9], Secondary Electron Microscopy with Energy Dispersive X-ray Analysis (SEM/EDX) [1,12,13], Particle Induced X-ray Emission (PIXE) [14] and X-ray

Absorption Near Edge Structure (XANES) Spectroscopy [15–17] are more desirable in that they are non-destructive. These techniques yield a mass film thickness, and provided that the film density is known, a physical thickness can be calculated. Using AES-depth profiling, Jahanmir [10] determined that ZDDP derived antiwear films extend beyond 400 Å in thickness. Wilbermet *et al.* [9] also used AES-depth profiling, along with surface profilometry, to confirm physical film thickness estimates from SEM/EPMA measurements. The average thickness of a film formed from ZDDP alone was found to be 530 Å. Suominen Fuller *et al.* [15] using X-ray absorption spectroscopy found the tribofilm thickness to have an average thickness of ~500 Å.

ZDDP tribofilms have also been investigated using imaging techniques such as scanning electron microscopy (SEM) [18–20], atomic force microscopy (AFM) [21,22] and imaging nanoindenters [21–25]. These techniques illustrate the morphology of the film and are all in agreement that the ZDDP antiwear film is laterally and vertically heterogeneous, being composed of ridges and valley regions. The ridge regions are composed of raised patches of film that have been termed antiwear pads [21,22]. It has been suggested that these pads are responsible for bearing the load between the two rubbing surfaces and limiting the contact between the asperities, thereby reducing wear [22].

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In this two part study, using mainly AFM, XPS and XANES, we focus our attention on the differences between the morphology, wear properties, average thickness (Part 1), and chemistry (Part 2) of the ZDDP and DDP films from different concentrations of ZDDP and DDP. For the first time, we examine films formed after very short rubbing times (e.g., 10 s to 1 min).

## 2. Experimental

### 2.1. Materials

A commercial zinc dialkyldithiophosphate (ZDDP), ashless dialkyldithiophosphate (DDP) and base oil used in this paper were supplied by Imperial oil (Esso) Canada. The ZDDP consisted of the secondary butyl (85%) and *n*-octyl (15%) groups. The concentrations of ZDDP are in the range 0.1–5.0 wt%. DDP is the same as DTP-1 additive used by Najman *et al.* [26]. The circular coupons ( $\phi$  19 mm, 4 mm in thickness) and cylindrical pins ( $\phi$  6.2 mm, 11 mm in length) used in this work were of 52100 steel, hardened to Rockwell C60–64. The coupons were polished by 3  $\mu$ m diamond paste to a mirror finish, washed with detergent, distilled water and methanol, respectively, and then dried in air. The polished coupons and cylindrical pins were cleaned in an ultrasonic bath for 20 min using hexane.

The tribological films (referred to as tribofilms) were generated in a Plint tribometer on 52100 steel coupons. Experimental details for film generation have been described before [26]. The testing conditions were: temperature 100 °C; Speed 25 Hz; Load 225 N; Stroke 7 mm; rubbing time 10 s to 10 h.

Several  $(1-x)\text{Zn}-x\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$  glasses as model compounds were prepared by a procedure described in the literature [27]. The other model compounds were purchased commercially and used without purification.

### 2.2. AFM analyses

All AFM topography images of tribofilms were collected using a Nanoscope IIIa equipped with a Multimode head (Digital instruments, Santa Barbara, CA). The images of the antiwear films were recorded in contact force mode with V-shaped silicon nitride cantilevers possessing a nominal spring constant of 0.12 N/m.

### 2.3. XPS analysis

The XPS sputtering analyses were obtained at Surface Science Western, using a modified Science Laboratories SSX-100 X-ray Photoelectron Spectrometer with a monochromatized Al K $\alpha$  X-ray (1486.6 eV). Samples were argon ion sputtered using 4 KV ions over an area of  $\sim 2 \times 2$  mm<sup>2</sup>.

### 2.4. XANES data analyses

Oxygen (K-edge), phosphorus (K- and L-edge), sulfur (K- and L-edge) and Fe L-edge X-ray absorption near edge structure (XANES) spectra were collected on the three Canadian Synchrotron Radiation Facility (CSRF) beamlines situated on the 1 GeV Aladdin storage ring, University of Wisconsin, Madison. The O and Fe analyses were carried out using the high resolution Spherical Grating Monochromator (SGM) beamline, which covers the energy region of 200–600 eV. The Fe L-edge spectra at about 700 eV were acquired with second order radiation at about 350 eV. The photon resolution for SGM is about 0.1 eV for both edges. The P and S K-edge studies were carried out on the Double Crystal Monochromator (DCM) at a photon resolution of about 0.8 eV. Phosphorus and sulfur L-edge spectra were obtained on the Grasshopper soft x-ray beamline at a photon resolution of about 0.2 eV. All XANES spectra were recorded simultaneously in both the total electron yield (TEY) and fluorescence yield (FY) modes of detection to provide chemical information on both the surface/near surface and bulk of the films. The sampling depths of the TEY and FY at the P K-edge are  $\sim 50$  and  $> 800$  nm respectively. The sampling depths of the TEY and FY at the P L-edge are  $\sim 5$  and  $\sim 60$  nm respectively, and at the O K-edge and Fe L-edge are estimated to be  $\sim 10$  and 100 nm, respectively [28]. The area analyzed is about 4 mm<sup>2</sup> for the Grasshopper and Double crystal results and 3 mm<sup>2</sup> for the Spherical Grating results. For energy scale calibration at O K-edge FePO<sub>4</sub> was used at 530.8 eV. The calibration at other edges has been reported before [16,17].

## 3. Results and discussion

### 3.1. Film thickness

We have shown in previous papers that the intensity of the P K-edge XANES spectra can be used to measure the average thickness of the major phosphate component of ZDDP-derived antiwear films and thermal films [15–17]. The measured P K-edge peak heights and edge jumps from the XANES spectra measured in the FY mode were initially plotted against the particle induced X-ray emission (PIXE) results, yielding calibration curves (figure 2 in Ref. 15). The PIXE results yield absolute P “areal densities” in atoms/cm<sup>2</sup>; and the linear calibration curves were used along with the P K-edge XANES intensities to determine the average P areal density of a set of antiwear films. The areal densities are converted to film thickness using the density of Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

Representative P K-edge spectra from ZDDP antiwear films from a 1 wt% ZDDP solution after very short rubbing times are shown in figure 1(a). These spectra arise from the phosphate in the film, and not the

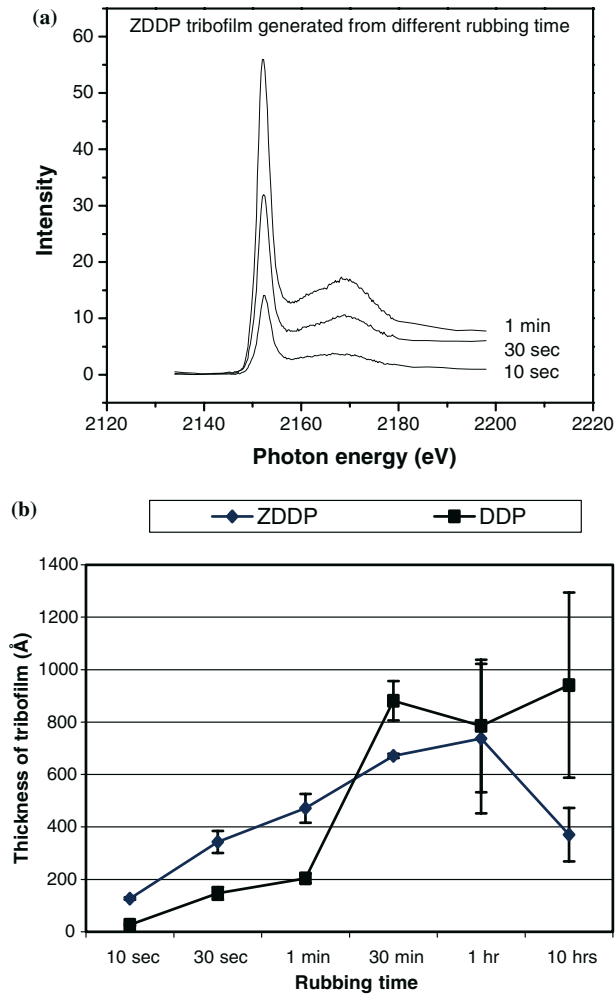


Figure 1. (a) P K-edge XANES spectra for ZDDP tribofilms from short rubbing times, (b) average thickness of tribofilms as a function of rubbing time for ZDDP and DDP.

original ZDDP, which gives a lower energy peak at  $< 2150$  eV. Qualitatively, it is rather remarkable that, even after 10 s of rubbing, a rather intense phosphate P

K-edge spectrum arises (figure 1(a)). The P K-edge intensities for the comparable DDP antiwear films (not shown) were much weaker. These P K-edge intensities for different rubbing times were converted to phosphate thickness and plotted in figure 1(b). The thickness for both ZDDP and DDP films at longer rubbing times agree semi-quantitatively with those obtained previously by our group [15,16]: both the ZDDP and DDP films increase to a maximum at 500–1000 Å thickness before leveling off or decreasing. Very recently Fujita and Spikes [29] using *in situ* spacer layer interferometry found that after 1 h rubbing the ZDDP film thickness reaches its maximum thickness of  $\sim 900$  Å which is in good agreement with the above results. It is interesting to point out that our technique measures the phosphate thickness whereas the interferometry technique measures the physical thickness comprising other entities present in the film. This indicates that the major component of the film is the phosphate constituent.

However at very short rubbing times, the ZDDP films are much thicker than the comparable DDP films: for example after 10 s rubbing, the ZDDP film is over 120 Å thick whereas the DDP film is barely detectable. After 1 min of rubbing, the ZDDP film is well over 400 Å thick, whereas the comparable DDP film is about 200 Å thick. Obviously, the very rapid film formation for ZDDP results in the generally lower wear rates for ZDDP compared to DDP as shown in the next section and suggested by Najman *et al.* [16]. Somewhat surprisingly, the DDP films are thicker at the longer rubbing times; but this observation, and the decrease or leveling off of the film thickness, confirms what we have seen previously in the two separate studies of ZDDP and DDP antiwear films [15,16].

The relative intensities of phosphorus versus sulfur in the XANES spectra for tribofilm are plotted in figure 2. It is very interesting to note that the P/S ratio for ZDDP remains practically the same for all films (10 s to 10 h rubbing); whereas for DDP tribofilms, after 1 min

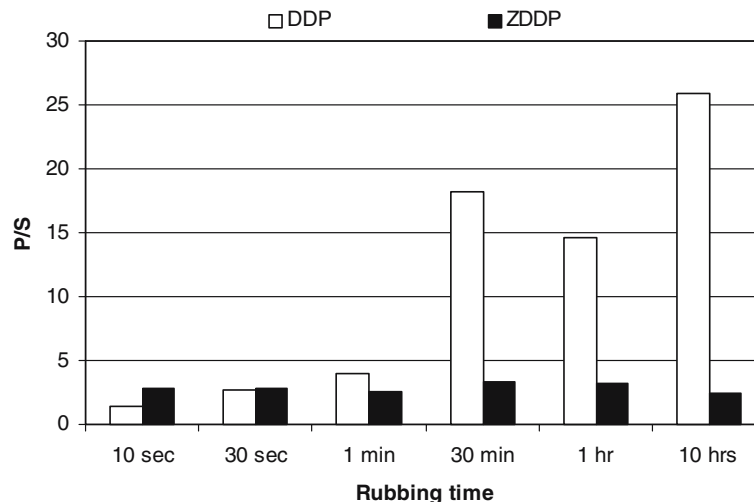


Figure 2. P/S ratio from XANES spectra for tribofilms from ZDDP and DDP.

rubbing, the proportion of sulfur in the films drops almost by an order of magnitude. This was also confirmed by the XPS measurement for 1 h film (see below, figure 5). This observation points to the important function of Zn in the ZDDP additive. Zinc functions as a sink for sulfur. As it will be shown in Part 2, in ZDDP films, sulfur is present mostly as ZnS, whereas in the DDP film sulfur appears as iron sulfide. It seems after a short rubbing time the surface is partially covered with phosphate and there is less iron available for iron sulfide formation.

Palacios [12,13] used SEM/EDX to monitor antiwear film thickness with changes in additive concentration, load and contact temperature. A limiting thickness was also observed. He concluded that film thickness arises from a balance between the rate of growth depending on the additive concentration in base oil, contact temperature, and the rate of removal determined by wear.

The tribofilm thickness generated from different concentrations measured by XANES for 1 h are listed in figure 3. Somewhat surprisingly, the very low ZDDP concentrations give, if anything, the thickest films. Obviously there is more than enough ZDDP to give a thick film even with 0.1 wt% ZDDP. It is not clear what relationship film thickness has to wear. For example, in a previous study [30], the P thicknesses showed no cor-

relation to the wear scar width obtained from calcium sulfonate in the presence of several ZDDPs. The film thicknesses after 1 h of rubbing are also very constant with different proportions of ZDDP and DDP (figure 4). This is not surprising after the results in figure 1 that show similar thicknesses for just DDP or ZDDP.

XPS profiling using  $\text{Ar}^+$  sputtering was used to investigate the thickness and elemental composition of tribofilms. The results are presented in figure 5(a) and (b) for the ZDDP and DDP films, respectively. The sputtering rate has been calibrated using a film of  $\text{SiO}_2$  and found to be  $\sim 50 \text{ \AA}/\text{min}$ . It is apparent from figure 5(a), after 800 s sputtering, the proportions of Zn, P and S approaches zero and that of Fe increases sharply and levels off. This corresponds to a thickness of  $\sim 700 \text{ \AA}$ , which is in good agreement with the non-destructive XANES analysis shown in figure 1(b).

In the initial stage of sputtering of the ZDDP film (figure 5(a), up to 60 s ( $\sim 50 \text{ \AA}$ ), the Fe proportion is very low ( $< 1\%$ ), whereas the Zn proportion is high ( $> 20\%$ ) indicating that in the top layer of the film, Zn is the main counter cation for phosphate or sulfide. The proportion of Zn remains almost constant up to  $\sim 300 \text{ \AA}$ , whereas that of the Fe increases to 25%. This sharp increase suggests that Fe from the substrate

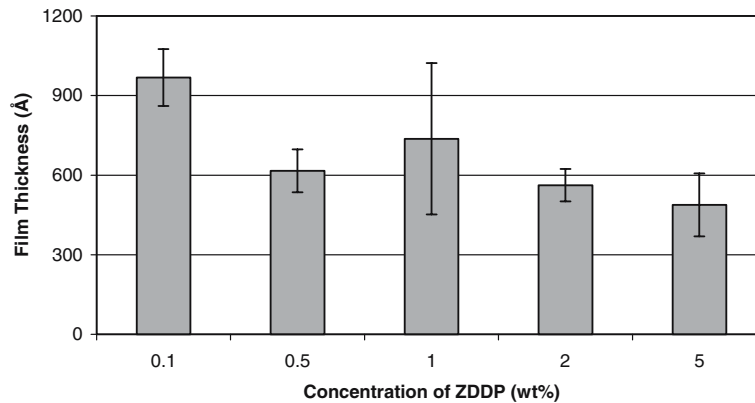


Figure 3. Thickness of tribofilms as a function of the different concentrations of ZDDP for 1 h rubbing time.

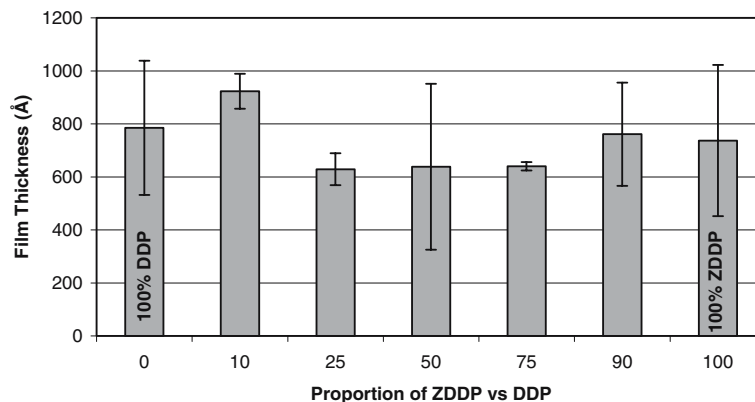


Figure 4. Thickness of tribofilms as a function of the different concentrations ratio of ZDDP/DDP for 1 h rubbing.

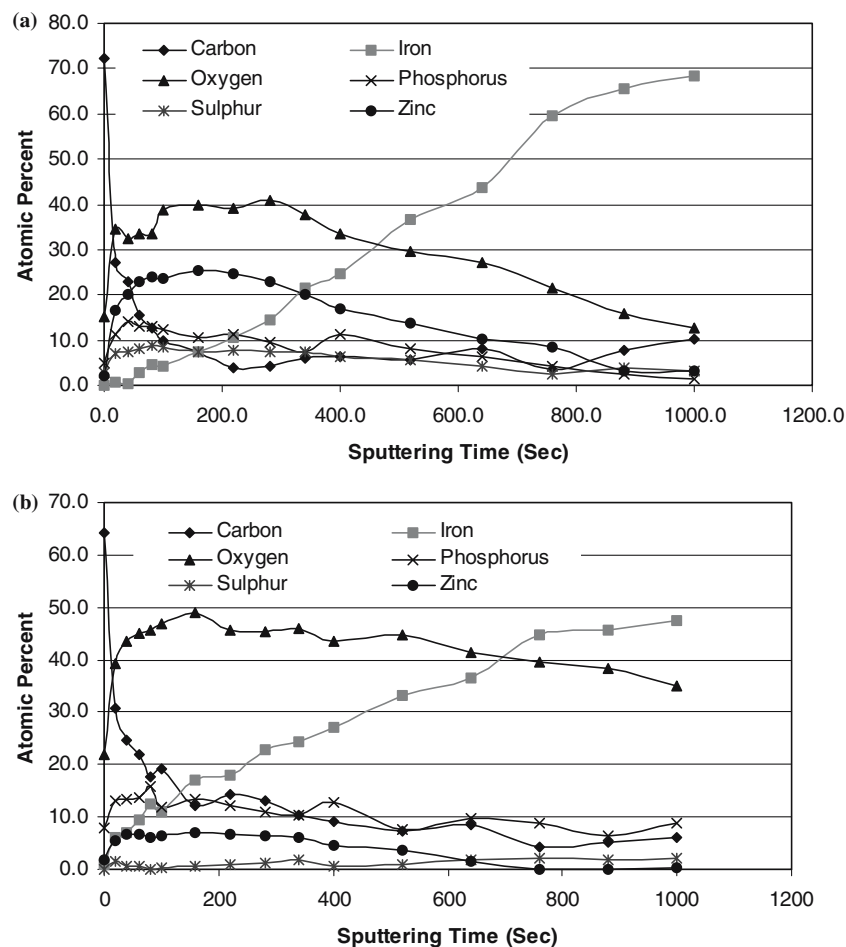


Figure 5. Atomic percent of different elements in tribofilms as a function sputtering time: (a) for ZDDP film and (b) for DDP film.

is contributing to any Fe present in the film. This is probably expected for an inhomogeneous film, as is apparent in figure 6 (See next section). Therefore the presence of Fe in the film from the XPS profiling cannot be very reliable (See section on O K-edge, Part 2). The P/S ratio ( $\sim 1.6$ ) does not change substantially from surface to the bulk, and as has been reported in the literature [31] is much higher than that of the undecomposed ZDDP (P/S = 0.5). This value is close to what was found for 1 h film by XANES in figure 2.

The sputtering data shown in figure 5(b) for the 1 h DDP film is qualitatively different from that of the ZDDP film. The proportion of Fe from the onset of sputtering is much higher than that of ZDDP film and increases very rapidly as the sputtering progresses and levels off at  $\sim 700 \text{ \AA}$ , indicating that mostly the iron in the steel substrate is being detected. However, the P proportion does not drop substantially even after 1000 s sputtering ( $850 \text{ \AA}$ ) > This is very strange and we cannot explain it. It may be due to a very rough surface. The proportion of S is very low ( $< 1\%$ ) compared with the ZDDP film ( $\sim 7\%$ ) as found in figure 2 by XANES. This suggests that in the absence of Zn, sulfur is lost mostly in

the oil and does not seem to react strongly with Fe to remain on the surface (see S characterization section, Part 2). It is also noticed that the carbon proportion is always higher in the DDP film (see Part 2). As in our previous study on DDP films [16], the XPS broad scan results (see figure 5) show some “Zn contaminant” in the long term films, despite repeated cleaning of the Cameron Plint machine. There is no detectable Zn in the 10 s, 30 s and 1 min DDP films, and the Zn in the longer films is still a fairly small percentage ( $< 25\%$ ) of the Zn in the ZDDP films. However, considering that the Zn concentration in the DDP oil solution after rubbing is about 1 ppm [16], the amount of Zn in these films is surprisingly large. We have not been able to find the source of the Zn, but it does not appear to affect qualitatively the results reported here.

### 3.2. Wear properties

The antiwear performance of ZDDP and DDP (1%) at different rubbing times was also investigated. Figure 6 shows the wear scar width (WSW) as a function of rubbing time. The WSW was measured from the pin

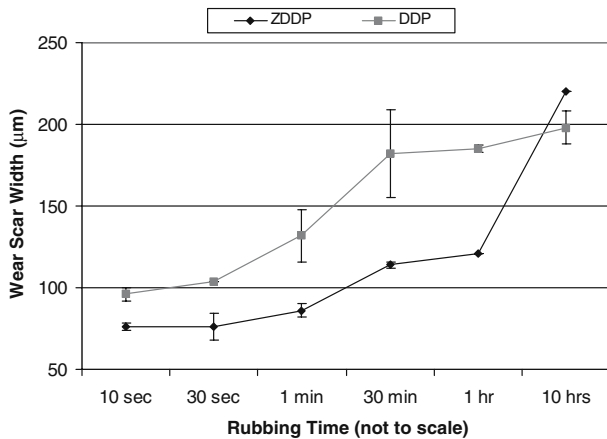


Figure 6. The wear scar width as a function of rubbing time for ZDDP and DDP.

using a calibrated microscope. The wear for ZDDP additive for very short rubbing times (10–60 s) is relatively small and constant at  $\sim 75 \mu\text{m}$  and gradually increases to  $130 \mu\text{m}$  after 1 h rubbing. However, the WSW for DDP is always higher than those of ZDDP. The wear scar width for both additives coincide after 10 h rubbing. This high WSW value for ZDDP may not reflect a real value. For some reason we were not able to obtain reproducible wear data for 10 h rubbing. Some of the WSW values were even much higher than  $200 \mu\text{m}$ . This is probably due to a short starvation of the surfaces with oil during the long rubbing time. We could not increase the volume of oil in the Plint oil compartment to check this possibility. This discrepancy was also observed in figure 1 for the thickness of the film for 10 h rubbing.

The effects of ZDDP concentration on wear is illustrated in figure 7. The WSW for ZDDP concentrations of 0.1–1.0% remains almost constant at  $\sim 120 \mu\text{m}$ ,

consistent with the findings of the thickness for these films (see figure 3). Once a relatively thick tribofilm is formed for 0.1% concentration, the wear performance is expected to be good. However, as the concentration exceeds 2%, the wear increases significantly, although the film thickness remains almost unchanged (figure 3). This may be due to the formation of thicker films which cannot withstand the load for long and break away which will result in higher wear rate due to a 3rd body effect.

The antiwear performance of mixed ZDDP/DDP for 1 h rubbing is presented in figure 8. As was shown in figure 5, the WSW value for pure DDP blend is much higher than that of corresponding ZDDP value (180 versus  $120 \mu\text{m}$ ). As soon as the blend is fortified with 10% ZDDP (see figure 8) the wear drops to a low value of 120. Further addition of ZDDP seems to have little or no effect on the wear, under the test conditions. This is also reflected in the morphology of the film (see below). These results may not be surprising. It was shown in figure 3 that a very small concentration of ZDDP (0.1%) is sufficient to produce a thick film and give a good wear performance (figure 5). However, what is important is the fact that DDP has no adverse effects on the performance of ZDDP. Thus one may envisage to replace partially the ZDDP in oil with DDP to reduce zinc in the system. Obviously more detailed study is essential to establish the minimum amount of ZDDP that is required in oil.

### 3.3. Morphology of tribofilms

Figure 9 presents the AFM images for the ZDDP and DDP films. The area of high topography (light brown in the colour image) is where the tribofilm (polyphosphate) has formed, whereas the low area (dark brown) represents the thin covered area or bare steel. This has

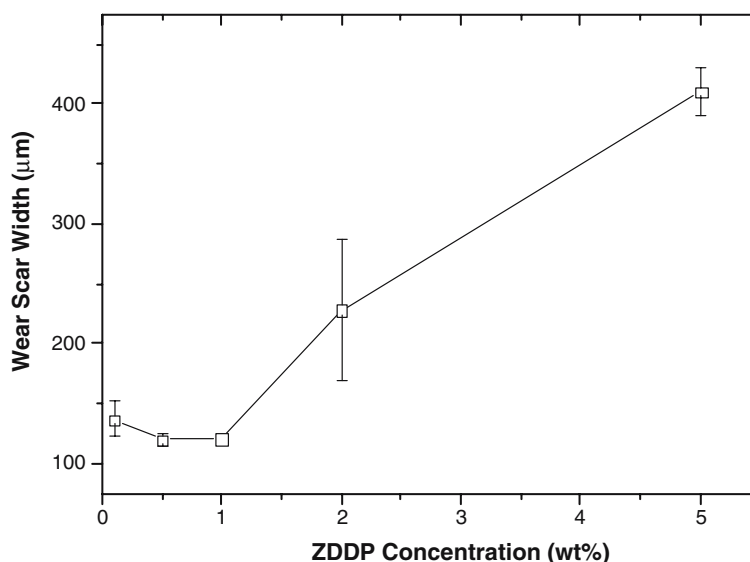


Figure 7. The wear scar width as a function of ZDDP concentration.

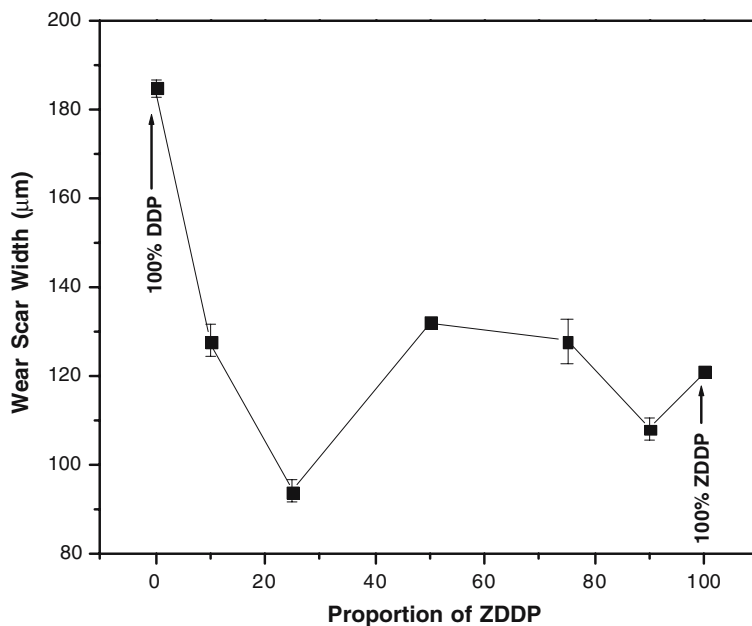


Figure 8. The wear scar width as a function of ZDDP/DDP proportion.

been confirmed by our very recent studies using X-ray microscopy [32–34]. At short rubbing times (10 s, figure 9(a)) the ZDDP films are much rougher than the DDP films, and at 30 s of rubbing noticeable “pads” have formed (not shown). At 1 min rubbing (figure 9(b)) the ZDDP pads are very obvious, whereas there are no obvious pads for DDP. The pads are elongated along the rubbing direction. At the 30-min rubbing times (figure 9(c)), the ZDDP pads are very well developed, whereas the DDP pads are much smaller and more “streaky”. The scratch marks are quite apparent for the DDP film. After 1 h rubbing (figure 9(d)) the ZDDP large pads begin to break down to smaller pads and as a result a more “uniform” film is being formed. This may be the cause of high wear noticed in figure 5. The small pads do not protect the rubbing surfaces as well as large pads. However, for the DDP film, one can still observe the scratch (wear) marks. After 10 h of rubbing (figure 9(e)), the pad size decreases noticeably in both cases and the surfaces become smoother. Pad heights obtained from the line scans of AFM images (not shown) show that the heights are larger for ZDDP films and increase up to 30 min rubbing for both ZDDP and DDP films and then drop thereafter when the film becomes smoother. These trends are consistent for the long rubbing time AFM results published earlier on DDP [16].

Figure 10 shows the AFM images of the tribofilms generated from a mixture of ZDDP and DDP. The wear results for these films were shown in figure 8. The image for a film generated from pure DDP does not show the large pad formation and one can observe the scratch marks. Once ZDDP is added (10%), large pads are formed and further addition has no qualitative apparent

effects on the pad size and the morphology of the AFM image. Indeed the image for 10% ZDDP and pure ZDDP are very similar, showing that the addition of a small amount of ZDDP to DDP changes the surface morphology. This finding is consistent with the above results on antiwear characteristics and thickness of the films.

The AFM technique has been used recently by several researchers to investigate the topography of tribofilms generated from ZDDP. In a recent paper Molina *et al.* [35] have used AFM in conjunction with EDX and XPS to investigate tribofilms formed from ZDDP based lubricants. Their AFM results cannot be compared directly with our data as their lubricants, apart from ZDDP, contains detergents and dispersants. However, after 8 h rubbing a fairly smooth film is formed which covers the rough substrate and is similar to our 10 h rubbing films. They have also investigated the effects rinsing samples in different solvents such as heptane and acetone. Solvents have partially removed a layer which is suggested to be an organic layer, possibly alkyl phosphate [23]. Further vigorous cleaning in ultrasonic bath for 30 min has revealed the underlying surfaces. However, ZDDP elements (Zn, P, S) are still found on ultrasonically clean surface, indicating the presence of an antiwear film. They do not report the change in the thickness after each cleaning step, possibly due to the lateral inhomogeneity of these films. The observance of the multilayer structure of the tribofilm is in agreement with our previous investigation using XANES (see also Part 2) [36]. Ye *et al.* [37], using AFM and nano-indentation techniques have also shown that tribofilms are graded and the surface has somewhat different mechanical properties than the

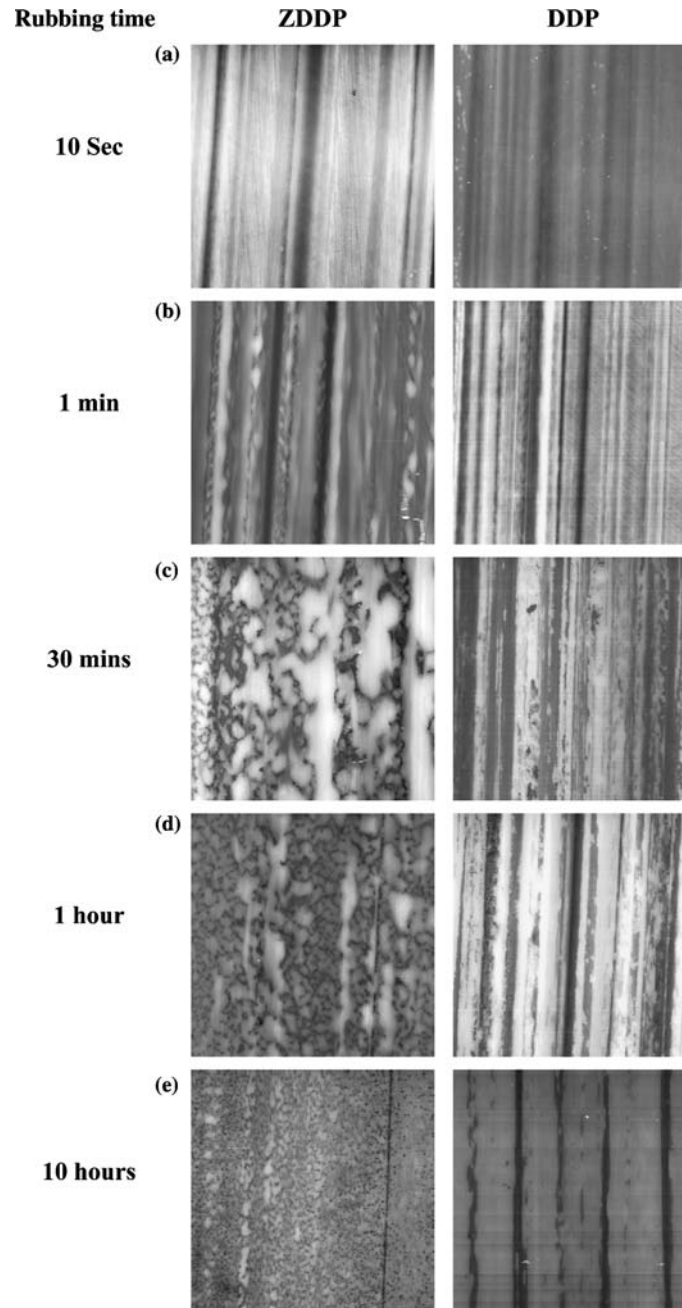


Figure 9. AFM of tribofilms generated from 1 wt% ZDDP under different rubbing.

bulk. Nicholls *et al.* [32] using X-ray Photoelectron Emission Microscopy (X-PEEM) in conjunction with nano-indentation have found that large antiwear pads have different mechanical properties compared to smaller pads. All the researchers are in agreement that tribofilms are laterally and vertically heterogeneous and are composed of multilayers and AFM can be used as a powerful diagnostic tool to investigate the topography of tribofilms.

The lack of good tribofilm (pad) formation in the DDP film in the early stage of film formation is obviously related to the chemistry of the films which will be discussed in Part 2. Briefly, since the Zn cation is not

available for zinc polyphosphate formation, and iron phosphate is forming at much lower rate, antiwear pads are not generated fast enough to protect the surface, and as a result there will be more initial wear to the rubbing surfaces.

#### 4. Conclusion

Using multiple analytical tools (XANES, XPS, and AFM), the average thickness and the morphology of tribofilms formed from ZDDP and DDP was investigated. The results can be summarized as follows:



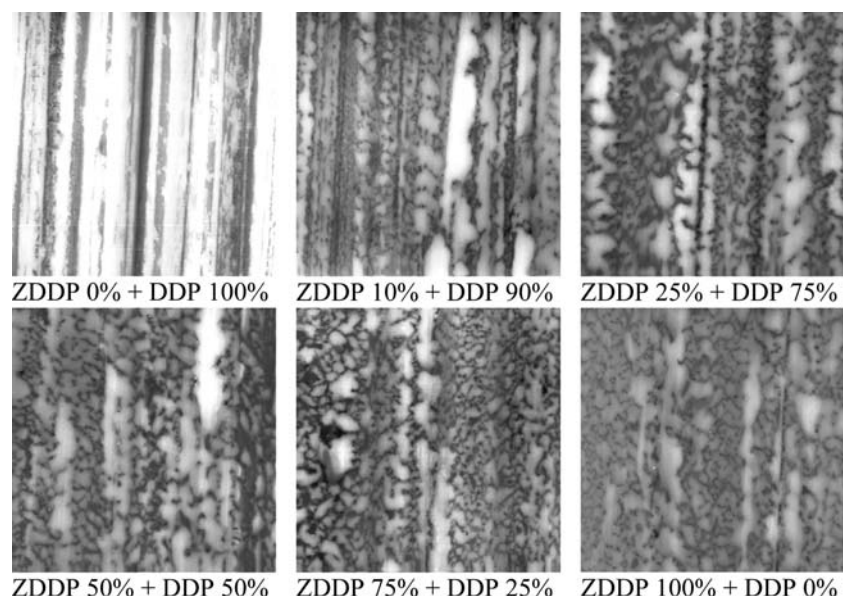


Figure 10. AFM of tribofilms generated from different ZDDP/DDP combinations.

1. For ZDDP, a phosphate film (about 100 Å thick) forms after only 10 s, while the rate of DDP film formation is much slower. It was clearly shown, that rapid, early film formation with ZDDP must be the cause of the better wear protection obtained with ZDDP compared to DDP. These results suggest that much lower concentrations of ZDDP (perhaps combined with some DDP) could be used in normal engine oils for maximum wear protection.
2. The presence of small amount of ZDDP in combination with DDP is sufficient to provide very good wear protection, and under all conditions used, antiwear performance of ZDDP was superior to DDP.
3. The morphology of the tribofilms was measured using AFM. It was shown that at short rubbing times (10 s), the ZDDP films are less uniform than the DDP films. However after 30 s rubbing, antiwear pads have formed for ZDDP and not for the DDP films. At the 30-min rubbing times, the ZDDP pads are very well developed, whereas the DDP pads are much smaller and more “streaky”, and the scratch marks are quite apparent for the DDP film. Combination of small amount of ZDDP with DDP changes drastically the morphology of the tribofilm
4. Despite the difference in chemistry and morphology of the films, the average thickness of both films is very similar after many minutes of rubbing. It does not appear that film thickness has any direct relationship to wear performance for long rubbing times.

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