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## **An ESCA Study of the Effectiveness of Antiwear and Extreme-Pressure Additives Based on Substituted Phosphorodithioate Derivatives, and a Comparison with ZDDP**

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### **Abstract**

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Ashless substituted dithiophosphoric acid derivatives (ADPs) are a new generation of multifunctional additives with promising antiwear (AW) and extreme-pressure (EP) characteristics. Three such additives synthesised in the authors' laboratory have been evaluated for their AW and EP properties by standard four-ball friction and wear tests. The friction-reducing properties of these additives were compared with those of a commercial zinc dialkyldithiophosphate (ZDDP). It was found that the phosphorodithioate compounds studied here possessed excellent AW/EP properties. Their AW characteristics were found to be comparable to those of ZDDP at low loads. However, at higher loads they show inferior AW characteristics in comparison to ZDDP. Nevertheless, ADP derived from cashew nut shell oil had a higher load-carrying capacity than ZDDP.

The mechanism of the AW and EP behaviour exhibited by the different additives was investigated using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM) of the worn surfaces formed during friction. XPS and AES analyses of the worn surfaces reveal that the tribochemical film formed on the ADP-tested surfaces consisted mainly of metal phosphates and only a small amount of metal sulphides, even though the ADPs contained twice the number of sulphur atoms than phosphorus atoms. The ZDDP-tested surface showed a mixture of metal sulphides and metal phosphates. Alkylamino substitution appeared to have no significant effect on the AW/EP properties of the additive.

XPS and AES analyses also revealed that the tribochemical film formed on an ADP-tested surface was thicker than that present on the ZDDP-tested surface at low loads, whereas at higher loads the reverse was true. The higher weld load obtained for the blend containing cashew nut shell oil-derived ADP is attributed to the thicker adsorbed reaction film formed on the surface due to the long alkyl groups present in the original additive structure. Short-chain alkyl groups, however, form only a thin adsorbed layer, which may get rubbed off during the friction at high load. The low sulphide formation on ADP-tested surfaces was attributed to the absence of any metal atom in the additive, which would help in the formation of metal sulphides during tribofragmentation and further tribochemical reactions.

**Table 1 Elemental composition of different additives**

Additive	Origin	Chemical formula	Elemental composition (%)	
			S	P
ADP-A	C <sub>5</sub> acid + P <sub>2</sub> S <sub>5</sub> + 1-octene	$\begin{array}{c} \text{S} \\    \\ \text{C}_5\text{H}_{11}\text{O}-\text{P}-\text{S}-\text{C}_8\text{H}_{17} \\   \\ \text{OC}_5\text{H}_{11} \end{array}$ (No amine substitution)	16.7	7.87
ADP-B	C <sub>5</sub> alcohol + P <sub>2</sub> S <sub>5</sub> + amine	$\begin{array}{c} \text{S} \\    \\ \text{C}_5\text{H}_{11}\text{O}-\text{P}-\text{S}^-\text{NH}_3\text{R}^+ \\   \\ \text{C}_5\text{H}_{11}\text{O} \end{array}$	11.55	7.37
ADP-C	Cashew nut shell oil + P <sub>2</sub> S <sub>5</sub> + amine	$\begin{array}{c} \text{S} \\    \\ m\text{-C}_{15}\text{H}_{31}(\text{C}_6\text{H}_{11})\text{O}-\text{P}-\text{S}^-\text{NH}_3\text{R}^+ \\   \\ m\text{-C}_{15}\text{H}_{31}(\text{C}_6\text{H}_{11})\text{O} \end{array}$	6.81	3.8
ZDDP	Commercial	$\begin{array}{c} \text{S} \qquad \qquad \text{S} \\    \qquad \qquad    \\ \text{RO}-\text{P}-\text{S}-\text{Zn}-\text{S}-\text{P}-\text{OR} \\   \qquad \qquad   \\ \text{OR} \qquad \qquad \text{OR} \end{array}$	12.55	6.74

### Keywords

*dithiophosphoric acid derivative, ZDDP, XPS, AES, SEM, lubrication reaction film, cashew nut shell oil*

### INTRODUCTION

The incorporation of antiwear (AW) and extreme-pressure (EP) additives in lubricating oils can effectively protect mating or moving surfaces under boundary lubrication conditions. These AW and EP agents are generally phosphorus,

sulphur, nitrogen, and chlorine organic compounds without and with metals such as zinc and molybdenum. However, the design and performance specifications of engines and machines produce increasingly severe operating conditions of high load and temperature. Under these conditions, profound advances in oil-additive technology have been achieved in recent years. Severe environmental restrictions demand even the replacement of widely accepted multifunctional additives, such as phosphorodithioate complexes of transition metals, e.g., zinc and molybdenum.<sup>1-4</sup> A number of ashless compounds based on derivatives of dialkyldithiophosphoric acids have been developed as AW/EP additives.<sup>5-20</sup> These compounds are formed by the reaction of dialkyldithiophosphoric acids or their alkali metal salts with various amines, alkyl halides, substituted *p*-hydroxybenzaldehydes, etc.<sup>7,12,16-20</sup>

The chemical composition and structure of lubricant-derived surface films strongly influence friction and wear of rubbing surfaces under boundary lubrication conditions. Understanding the relationship between lubricant formulation, film composition and structure, and the resulting tribological behaviour is essential in the development of new lubricant formulations. Development of experimental techniques aimed at improved and detailed characterisation of lubricant-derived surface films is important for understanding the chemistry behind the action of AW additives. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique and has been widely utilised in the characterisation of lubricant-derived surface films. In this study, the tribochemistry of lubrication films formed under four-ball friction test conditions using several ashless substituted dithiophosphoric acid derivatives (ADPs) was investigated by XPS, Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). Their tribological properties are compared with those of conventional AW/EP additives such as zinc dialkyldithiophosphate (ZDDP).

### **EXPERIMENTAL: Lubricants**

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Three different dithiophosphoric acid derivative-based additives and a ZDDP additive, as described in **Table 1**, were synthesised in the laboratory.<sup>19,20</sup> The elemental compositions of the additives are also given in **Table 1**. Lubricant blends were prepared by mixing 1.0% (w/w) each of ADP-A, ADP-B, ZDDP, and 2% (w/w) of ADP-C with a sulphur-free base oil so that all the blends contained approximately the same amount of sulphur and phosphorus. The characteristics of the base oil are given in **Table 2** (overleaf). The blends were prepared by a standard procedure by mixing the appropriate quantity of additive in the base oil at 65°C for 45 min.<sup>21</sup> The lubricant was a sulphur-free group II commercial base oil.

**Table 2 Properties of the sulphur-free base oil**

Name	Mobil J 500
Viscosity at 40°C (cSt)	93.73
Viscosity at 100°C (cSt)	10.8
Viscosity index	97
Density (g/cm <sup>3</sup> )	0.89
Sulphur content	Nil

### *Tribological tests*

All the blends were subjected to four-ball wear and EP tests according to standard ASTM procedures (ASTM D 4172 and ASTM D 2783). AISI E-52100 steel balls of 12.7 mm diameter and with a Rockwell hardness of C 64–66 were used in the tribological tests.<sup>21</sup> The specimen ball was tested at 40 kg load. After the test, the balls were washed using petroleum spirit followed by acetone to remove any physically adsorbed material or species and were stored in a desiccator before being put into the spectrometer for surface analysis. The wear-scar diameter and weld load obtained from the four-ball tests were taken as criteria for the wear and load-carrying capacity of the lubricants.

### *SEM and AES analyses*

SEM and AES analyses of the worn surfaces were conducted using a field emission electron gun (FEG 1000), with a 5 kV/10 nA beam with a spatial resolution of 190 nm and a sensitivity of 602 kCPS. AES analysis of the balls after the wear test at 40 kg load was carried out using the FEG 1000 gun following the same procedure as described below for the XPS analyses.

### *XPS analysis*

After the wear tests, the surfaces of the balls were analysed with a VG Scientific ESCALAB-220i-XL spectrometer using a monochromatised Al K $\alpha$  radiation (1486.6 eV) X-ray source with a spot size of about 1 mm. The energy scales were calibrated with Ag 3d<sub>5/2</sub> and Cu 2p<sub>3/2</sub> lines. The sample was first loaded into the preparation chamber of the spectrometer, which was evacuated to a pressure of  $\sim 10^{-7}$  mmHg. The sample was then transferred into the analysis chamber, which was kept at a pressure of around  $5 \times 10^{-10}$  mmHg. During the analysis, the pressure slowly increased to a value of  $10^{-9}$  mmHg. The spectra

**Table 3 Tribological test results from wear and EP tests\***

Additive	Wear scar at 40 kg load (mm)	Wear-scar diameter at 2SBWL (mm)	Weld load (kg)
ADP-A	0.70	2.8	160
ADP-B	0.90	3.7	180
ADP-C	0.60	4.0	225
ZDDP	0.70	2.6	180
Mobil J 500	2.20	NM	95

\*NM = not measured; 2SBWL = two stages below weld load.

were acquired under constant analyser energy mode with a fixed pass energy of 20 eV and mono XPS lens mode. The binding energies of the peaks were referenced to C 1s binding energy as 284.6 eV. Sputter depth profiles of the samples were obtained using a rastered 3 keV Ar<sup>+</sup> ion beam with a current density of 1.0 nA/mm<sup>2</sup>. A VG Eclipse data system was used to acquire and process the data. Shirley background subtraction and Scofield sensitivity factors were used for the quantification.

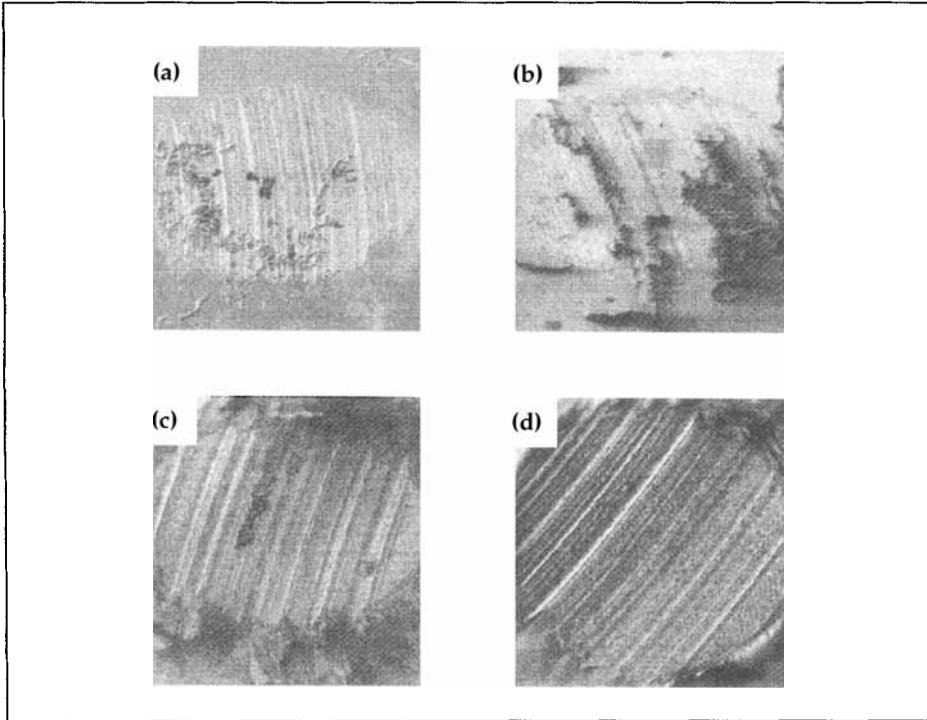
### **RESULTS AND DISCUSSION: Tribological tests**

The tribological test results for the four additive blends are given in **Table 3**. All the ADP-based additives possessed excellent wear prevention and EP properties, as the wear-scar diameter was significantly reduced and the weld load significantly increased by addition of these additives to the base oil. Their AW/EP characteristics are comparable to those of ZDDP. Among the three phosphorodithioate additives, ADP-C, which was derived from cashew nut shell oil, shows the lowest wear-scar diameter at 40 kg load and the highest weld load. Further, ADP-C had a higher weld load than ZDDP and hence was superior to ZDDP in load-carrying capacity. However, the ADP-based additives showed higher wear-scar diameters at higher load when compared to ZDDP, suggesting that their AW properties are not as good as those of ZDDP at higher loads.

### **SEM analysis**

**Figure 1** (overleaf) gives SEM images from the worn surface of the balls after wear testing at 40 kg load. The ADP-derived surfaces show some deposits in the form of wear debris, the maximum being observed on the ADP-B-derived surface. No such deposits or debris formation can be observed on the ZDDP-

**Figure 1** SEM images from the worn surfaces of balls tested with different ADP-based additives and a commercial ZDDP additive at 40 kg load: (a) ADP-A, (b) ADP-B, (c) ADP-C, and (d) ZDDP



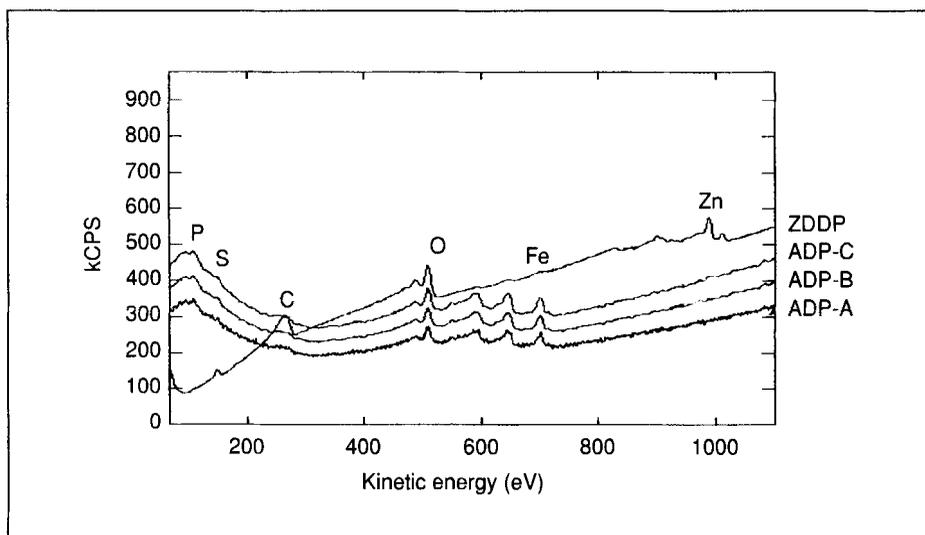
derived surface. There is also no indication of any adhesive wear on any surface. The wear tracks of the ADP-derived surfaces appear similar to those of the ZDDP-derived surface, indicating that the AW action of the ADP-based additives is comparable to that of ZDDP at this load.

### *AES analysis*

**Figure 2** shows the AES spectra of the worn surfaces tested with different ADP-based additives and ZDDP. It can be seen that elements such as P, S, O, C, and Fe were present on the three ADP-tested surfaces and P, S, O, C, Fe, and Zn were detected on the ZDDP-tested surface. The ADP-tested surfaces had a higher intensity P and a lower intensity S peak whereas the ZDDP-tested surface showed a higher intensity S peak and a lower intensity P peak.

The P and S peak intensities obtained for ADP-C as a function of etching time are plotted in **Figure 3** (see p. 114). The AES spectra of P and S for ZDDP

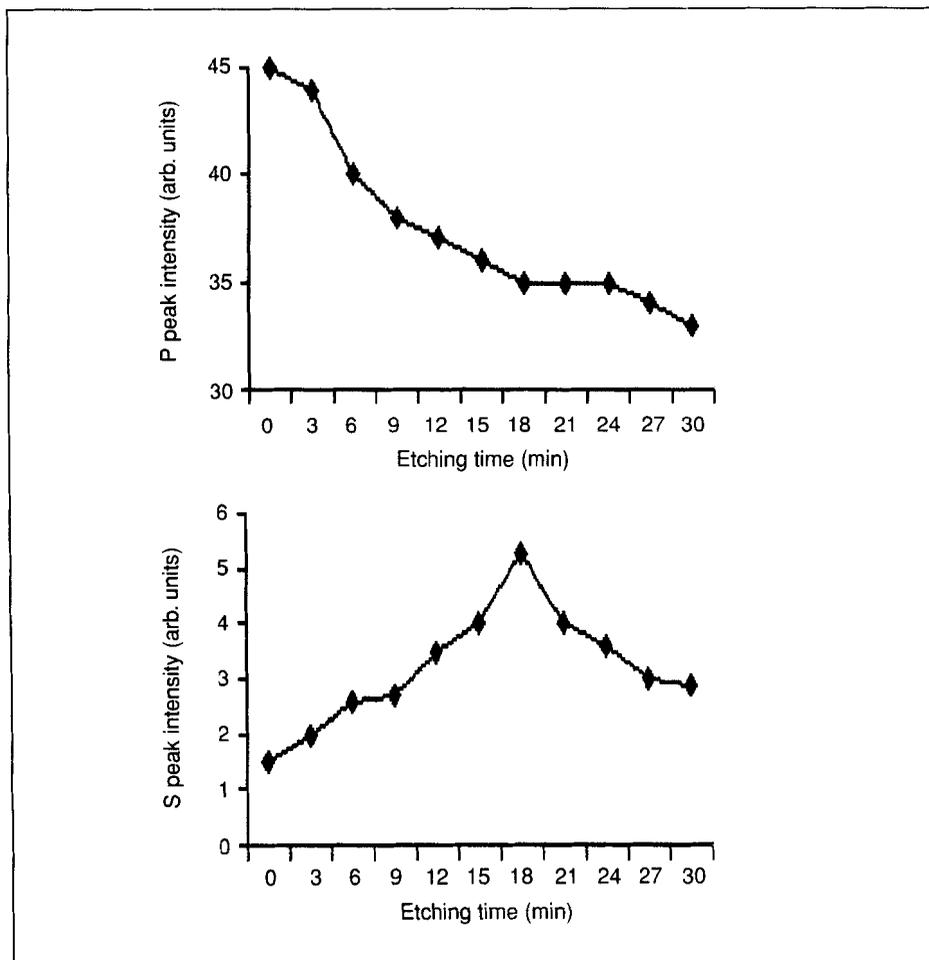
Figure 2 AES spectra from the worn surfaces of balls tested with different ADP-based additives and a ZDDP additive at 40 kg load



are presented in **Figure 4** (see p. 115). It can be seen in **Figure 3** that the P peak intensity is greater at the top surface whereas the S peak intensity slowly increases towards the inside of the film on the ADP-C-tested surface. The same pattern can be observed for all the ADP-tested surfaces. However, both the P and S peak intensities (**Figure 4**) are higher at the top surface in the case of the ZDDP-tested surface and both decrease towards the inside. This indicates that a predominantly phosphate layer was formed on the top and a sulphide layer formed underneath on the ADP-tested surfaces, whereas the ZDDP-tested surface contained a mixture of phosphate and sulphide films. Another important observation from the surface spectra profiles is the disappearance of the S and P peak intensity after 18 min of etching on the ZDDP-tested surface whereas these peaks are still present on the ADP-tested surface even after 30 min of etching. This suggests that a thicker lubrication layer is formed on the ADP-tested surfaces than on the ZDDP-tested surface at 40 kg load. This is further confirmed by the higher intensity Fe obtained for the ZDDP surface than for the ADP surface at 40 kg load.

**Figure 5** (see between pp. 116 & 117) shows the scanning Auger maps of P and S obtained from the ADP-C- and ZDDP-tested surfaces. The ADP-tested surface shows a high-intensity P image and a low-intensity S image, suggesting the greater amount of phosphate layer on the surface. However, both P and S images were of similar intensity for the ZDDP-tested surface, indicating that the tribofilm formed was a mixture of sulphide and phosphate.

Figure 3 P and S peak intensities obtained from AES spectra profiles as a function of etching time from the worn surfaces of the ball tested with ADP-C at 40 kg load

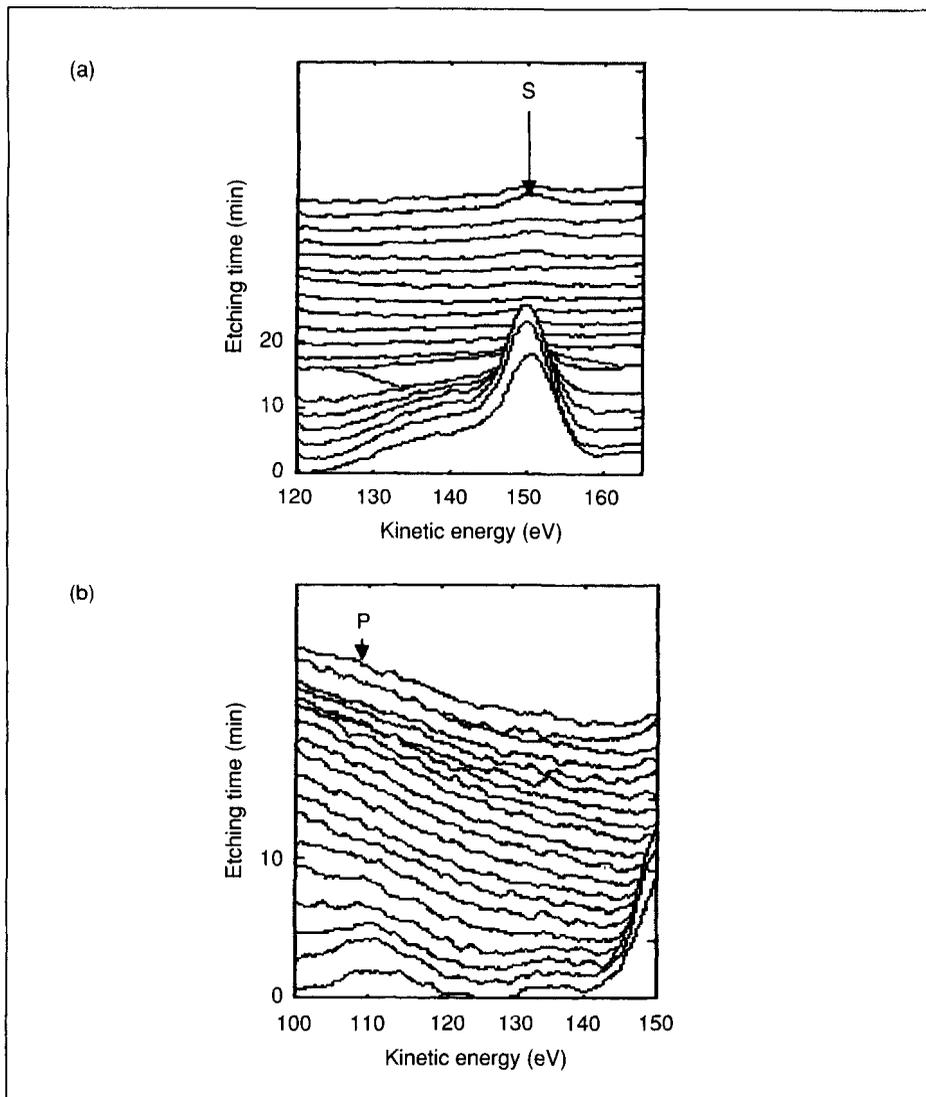


AES selected-area analysis of the wear debris formation (lower right in **Figure 1(b)**) showed that it was basically Sn. This must have come from the steel ball, which contained Fe and Sn along with other metals.

### *XPS analysis*

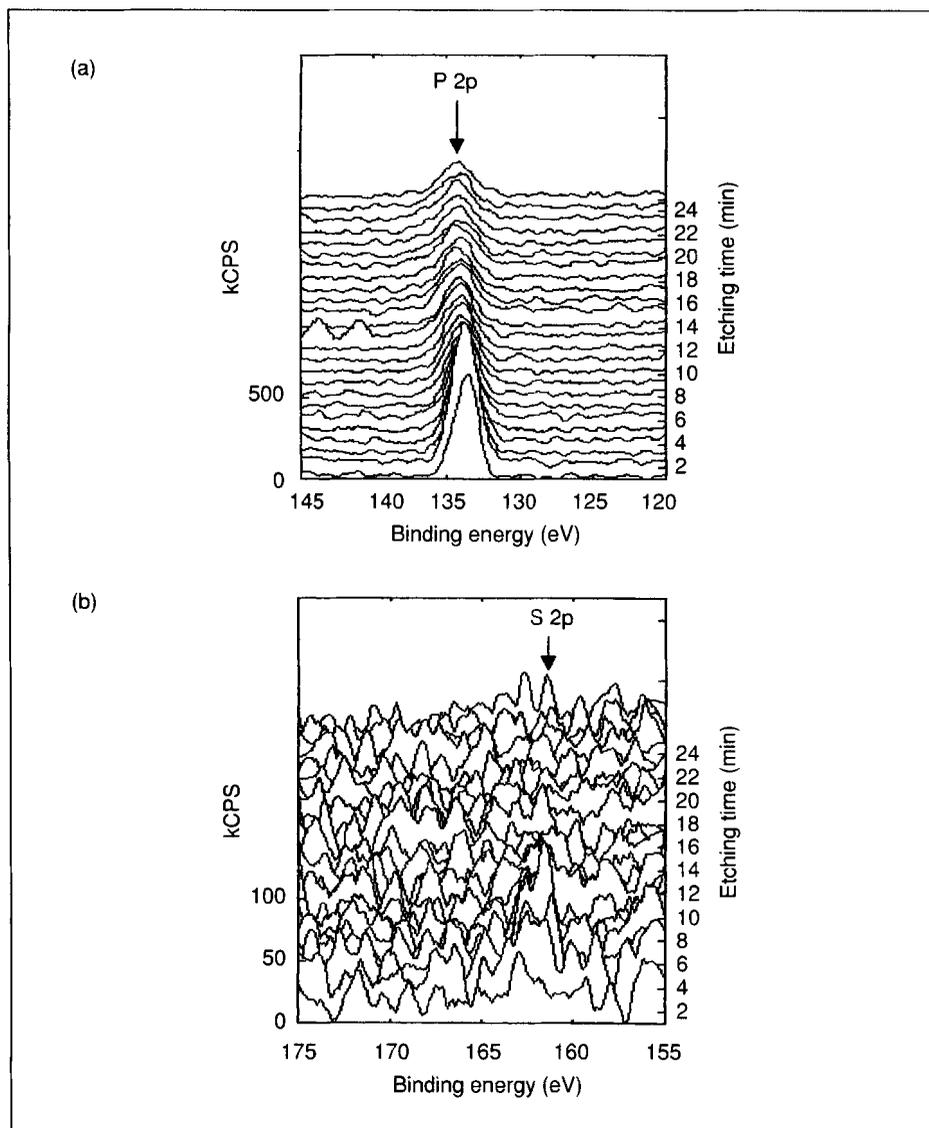
XPS scans from the worn surfaces show the presence of C 1s, O 1s, P 2p, S 2p, N 1s, and Fe 2p on the ADP-tested surfaces. In addition to these, Zn 2p was also observed on the ZDDP-tested surface. Fe 2p narrow-scan XPS spectra

Figure 4 AES spectra profiles of (a) S and (b) P from the worn surfaces of the ball tested with ZDDP at 40 kg load



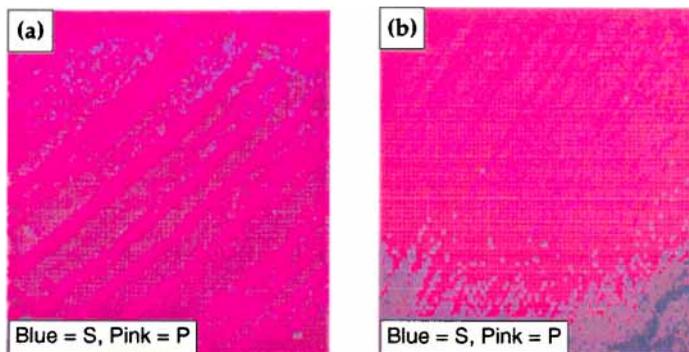
from the worn surfaces tested with all the additives show two main peaks, one in the range 710–712 eV, the other centred on 707.4 eV. The peak in the range 710–712 eV indicates the presence of iron in different forms, such as iron phosphate (711.3 eV) and iron oxide (710.6 eV). The peak at 707.3 eV is indicative of iron metal.<sup>22</sup> P 2p XPS spectra from the worn surfaces show peaks centred on

Figure 6 XPS spectra profiles of (a) P 2p and (b) S 2p from the worn surfaces of the ball tested with ADP-C at 40 kg load



133.7 eV, indicating the formation of metal phosphates such as iron phosphate.<sup>22</sup> S 2p spectra from the worn surfaces show peaks at 161.7 and 162.8 eV, indicating the presence of metal sulphide and metal disulphide.<sup>22</sup> The Zn 2p spectrum from the ZDDP-tested surface shows peaks at 1022.8 and 1023.9 eV, indicating

**Figure 5 Scanning Auger maps (SAMs) of P and S from the worn surfaces of the balls tested with (a) ADP-C and (b) ZDDP additive at 40 kg load**



**Figure 8 P 2p and S 2p X-ray photoelectron images (XPIs) from the worn surfaces of the balls tested with (a) ADP-C and (b) ZDDP additives at 40 kg load**

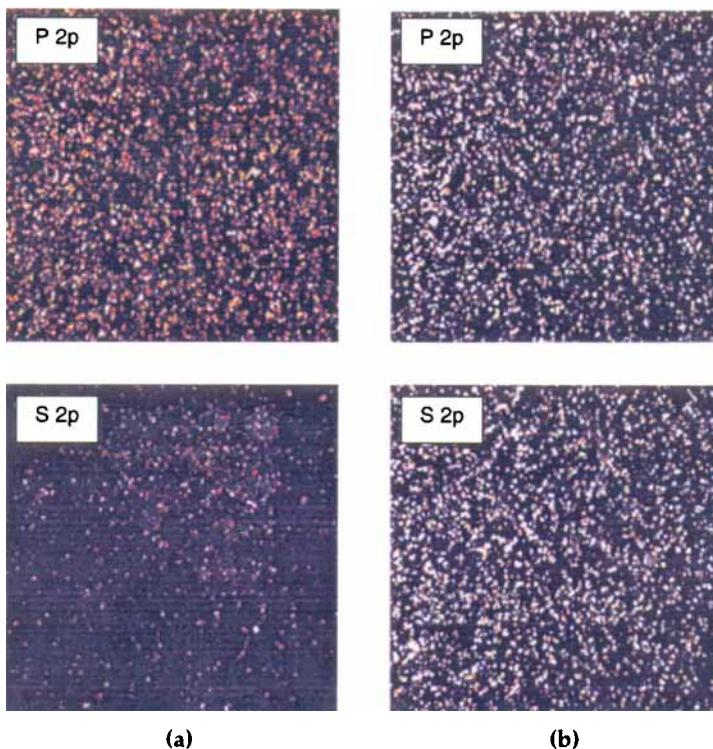
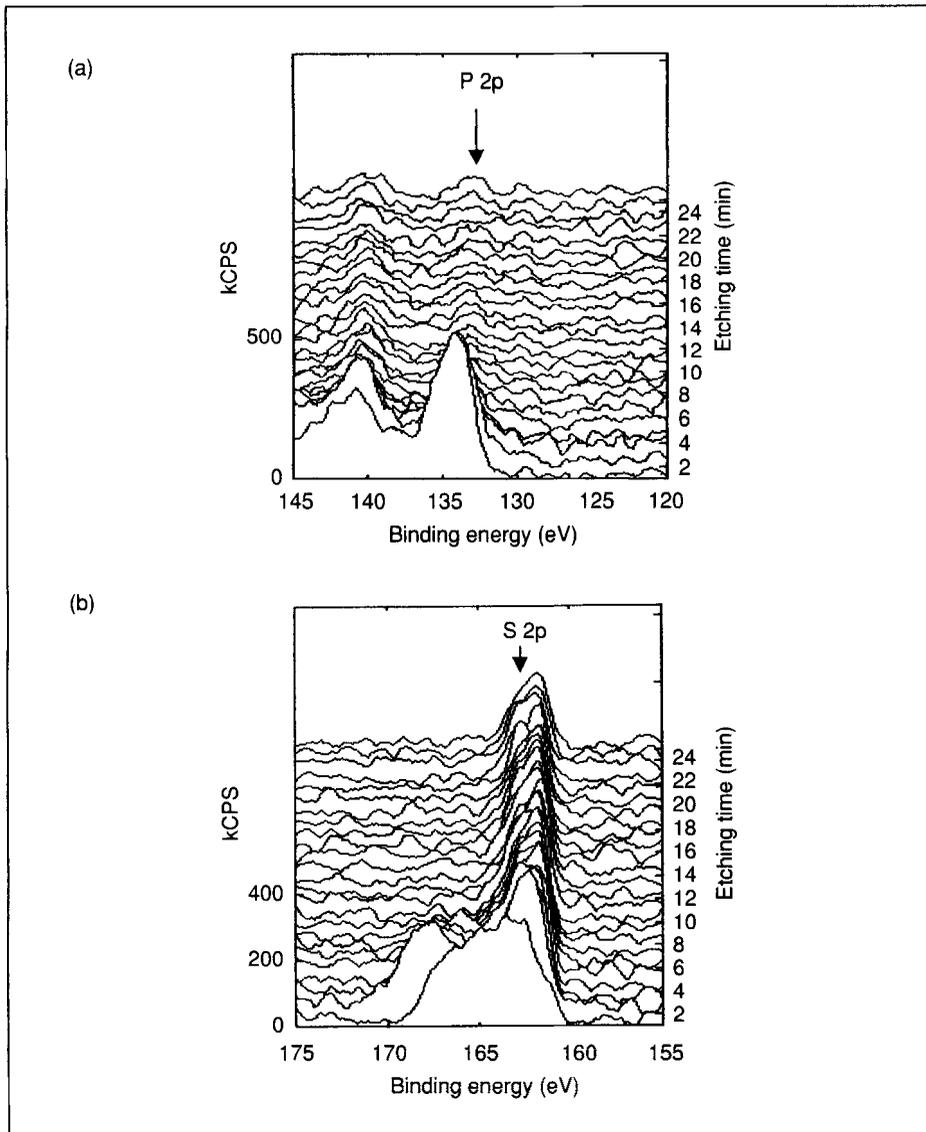
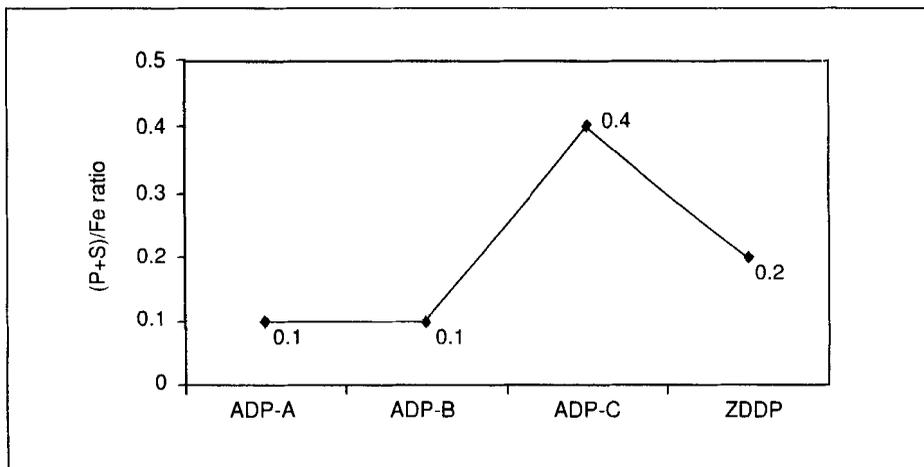


Figure 7 XPS spectra profiles of (a) P 2p and (b) S 2p from the worn surfaces of the ball tested with ZDDP at 40 kg load



the formation of zinc sulphide, zinc oxide, and zinc phosphate.<sup>22</sup> N 1s spectra from the worn surfaces show peaks in the range 398–402.5 eV, indicating the presence of –C–N–C– (402 eV) and iron nitride (398.2 eV).<sup>16,22</sup> The nitrogen peak intensity was very low for all the surfaces. Since the amount of nitrogen

**Figure 9** The (P+S)/Fe ratio after 60 min of etching on the worn surface of a ball tested with different ADP-based additives and a commercial ZDDP additive



observed was almost the same for all the surfaces including ZDDP (where it was not expected), no importance has been assigned to the role of nitrogen.

The S 2p and P 2p XPS spectra profiles from ADP-C and ZDDP depicted in **Figures 6** and **7** show that the ADP-tested surface contained a higher level of P 2p but a very low level of S 2p. The ZDDP-tested surface, however, showed a very high level of S 2p and also a significant amount of P 2p. This confirms the AES results that the ADP-tested surface was primarily composed of a metal phosphate tribochemical film, whereas the ZDDP-tested surface consists of a mixture of metal sulphide and metal phosphate layers.

XPS images from ADP-C- and ZDDP-tested surfaces are shown in **Figure 8** (see between pp. 116 & 117). Bright P 2p and less intense scattered S 2p images were obtained for the ADP-C-tested surface, whereas bright images of both P 2p and S 2p were obtained for the ZDDP-tested surface. This again confirms that a phosphate layer was mainly formed on the ADP-tested surface, whereas a mixed phosphate and sulphide layer was formed on the ZDDP-tested surface.

An approximate indication of the thickness of the tribochemical film formed on the worn surface can be obtained by determining the (P+S)/Fe ratio (**Figure 9**). The highest value for the (P+S)/Fe ratio can be obtained for the ADP-C-tested surface at 40 kg load, suggesting that a better lubrication film is formed on this surface. This further indicates that the ADP-C possessed better wear prevention characteristics than ZDDP at lower loads.

However, at higher loads (two-stage below weld load, 2SBWL), the wear surface contained mostly carbon and no significant amount of phosphorus or sulphur on the three ADP-derived surfaces (**Table 4**). On the contrary, there

**Table 4** Approximate surface composition (%) of the worn surface of the balls tested with oil containing different ADP-based and ZDDP AW/EP additives at 2SBWL

Peak	ADP-A		ADP-B		ADP-C		ZDDP	
	0 min etch	60 min etch						
Fe 2p	0.10	6.40	0.09	7.0	0.21	15.90	7.30	41.80
O 1s	14.10	15.3	15.70	11.90	12.90	25.40	37.0	28.90
C 1s	85.60	77.6	84.0	78.10	86.50	57.50	37.10	12.50
N 1s	0.07	0.40	0.01	2.30	0.00	0.42	0.20	0.80
S 2p	0.14	0.18	0.15	0.21	0.09	0.59	6.30	4.80
P 2p	0.11	0.22	0.03	0.42	0.25	0.26	8.70	4.70
Zn 2p	-	-	-	-	-	-	3.40	6.50

appears to be an appreciable amount of tribochemical film still present on the ZDDP-derived surface as evident from the higher amount of P and S present on its surface (see **Table 4**). This further confirms the superior wear prevention characteristics of ZDDP over those of ADP-based additives at higher loads as suggested by the friction test results. Another important observation is that a lot of carbon was deposited on the ADP-derived surfaces at higher loads (2SBWL) and the ball was blackened as a result. This, however, did not happen on the ball tested with ZDDP-containing oil, further emphasising the better antifriction characteristics of ZDDP.

Nevertheless, ADP-C had a higher weld load than ZDDP. Even though this appears unusual, it can be explained by the structure of the boundary lubrication film formed during frictional motion. The boundary lubrication film is composed of mainly three layers: a top adsorbed reaction layer, a diffused reaction layer on the bottom, and a chemical reaction layer in the middle.<sup>23</sup> The AW/EP properties of the additive or lubricant are provided by the collective action of all three layers formed on the surface. Therefore, it can be deduced that the higher weld load of ADP-C could be due to the presence of a more adsorbed reaction layer on the surface even though the chemical reaction layer is found to be less than that of ZDDP. ADP-C is derived from cashew nut shell oil and contains two very long alkyl groups in its structure ( $-C_6H_{11}-C_{15}H_{31}$ ). ZDDP and the other ADP-based additives, however, contain only short alkyl groups. The long-chain alkyl groups form a relatively thicker adsorbed reaction film on the surface during tribofragmentation, thereby providing a better cushion between moving surfaces. Short-chain alkyl groups form only a thin adsorbed layer, which may get rubbed off during frictional motion at high load.

As mentioned above, all the ADP-derived surfaces showed only a very low S concentration even though the original additive structure contained twice the number of S atoms than P atoms. This observation was unexpected, and a precise explanation is difficult from the data available. However, it can be tentatively ascribed to the absence of any metal atom in the ADPs unlike in ZDDP where zinc is present. When a metal atom such as zinc or molybdenum is present in the additive structure, the corresponding metal sulphide is first formed during the initial tribofragmentation and forms as a part of the tribofilm. This metal sulphide can further react with the nascent iron surface derived during frictional motion to produce iron sulphide.\* However, in the absence of a metal atom in the additive structure, most of the sulphur derived during the tribofragmentation of the additive may be lost due to the low adsorption capacity of sulphur on the surface. It may require more time for this sulphur to react with the nascent iron surface produced to form an iron sulphide film. Also, it may be noted that phosphorus has a higher reactivity towards metal surfaces than sulphur.<sup>24</sup> Under this condition, the phosphorus from the additive would react with the metal surface to form a thick layer of phosphate. The low concentration of the sulphide layer may be the reason for the inferior wear prevention characteristics of the ADP at higher loads, as it is known that sulphides have better AW properties than phosphates at higher loads.

## CONCLUSIONS

Ashless substituted dithiophosphoric acid derivatives (ADPs) possess excellent AW and EP properties, which are comparable to those of ZDDP. They exhibit better AW characteristics at low loads, but poorer ones at higher loads. However, a higher weld load was obtained for the ADP derived from cashew nut shell oil. This can be attributed to the formation of a thicker tribochemical film on the surface during friction due to the presence of long alkyl groups in the additive structure. Long alkyl groups form thicker adsorbed reaction films during friction. ADP-derived surfaces formed mainly metal phosphate lubrication films with the metal sulphide constituting only a small fraction, even though ADPs contained twice the number of S atoms than P atoms in their structure. A mixture of metal sulphides and metal phosphates was formed as the lubrication layer on the ZDDP-tested surfaces. The formation of small amounts of metal sulphide on ADP-derived surfaces is explained by the absence in the additive

\* The following are tentatively proposed here: (i) The melting point and heat of fusion of Zn (mp = 692 K and heat of fusion = 7.38 kJ/mol) are much lower than those of iron (mp = 1808 K and heat of fusion = 13.8 kJ/mol). Therefore, it is assumed that sulphur will react preferentially with zinc in comparison to iron during tribofragmentation under friction. However, once more and more heat/energy are available at the contact point, ZnS may undergo defragmentation and finally lead to a more stable form of FeS film on the surface. (ii) ADP does not form an appreciable FeS film on the surface even though it has double the amount of sulphur atoms in the molecule by comparison with ZDDP. Therefore, it is proposed that the zinc atoms present in ZDDP may play a catalytic role during tribofragmentation that finally may lead to the formation of FeS.

structure of any metal atom which would help in the formation of metal sulphides. The inferior wear prevention characteristics of ADPs at high loads may be due to the absence of a strong or effective sulphide reaction layer.

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