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Effect of ZDDP on Lubrication Mechanisms of Linear Fatty Amines under Boundary Lubrication Conditions

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Abstract: The tribological behavior of different linear amines blended to PAO4 alone or in combination with ZDDP was investigated under boundary lubrication regime via the coupling of tribometry and XPS measurements. Using a reciprocating ball-on-flat tribometer, it was evidenced that all tested amines were able to reduce both friction and wear. The combination of primary monoamine (1 wt %) and ZDDP (1 wt %) produced synergistic effect on reduction of both friction and wear in most cases. Experimental investigations suggest that this synergistic effect is due to the fast formation of a **zinc-oxide-enriched tribofilm depleted in phosphates**. Moreover, our results show that the lubrication mechanism and the composition of the tribofilm are strongly dependent on the amine / ZDDP molar ratio. **Keywords:** OFMs, Amine, ZDDP, lubrication mechanism, XPS.

1. Introduction

The growing level of environmental awareness is pushing the lubricant manufacturers to develop new lubricant formulations for passenger cars engine that give low friction, high antiwear performance and that **fulfil** at the same time the actual environmental requirements [1–3]. These eco-friendly lubricants are called low SAPS oils (low sulfated ash, phosphorus, and sulfur) and contain less phosphorus and sulfur than conventional additives like MoDTC and ZDDP. Nevertheless, ZDDP which is a low-cost multifunctional additive acting as antioxidant, antiwear and extreme-pressure remains irreplaceable to this day, despite the important efforts that have been made by additive companies to find alternative molecules having comparable performance [4,5]. On the other hand, one of the best candidates to replace

MoDTC (Molybdenum Dithiocarbamate friction modifier) in such lubricants are the Organic Friction Modifier additives (OFMs). These molecules composed of C, H, O and N atoms are made of hydrocarbon chain attached to a polar head group. They include molecules such as, fatty acids, amines, amides and esters [6].

Over the years, there were many studies on the organic friction modifiers (OFMs) that can act in mixed and boundary lubrication regimes. Both *ex-situ* and *in-situ* techniques, such as scanning force microscopy (SFM) [7–13] surface forces apparatus (SFA) [14], quartz crystal microbalance (QCM) [15], neutron reflectometry (NR) [16], polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) and X-ray photoelectron spectroscopy (XPS) [2,3] have been used in order to investigate the ultra-thin film formed by OFMs on the surface. From these measurements, it is generally accepted in literature that the effectiveness of these OFMs in reducing friction in boundary/mixed lubrication regime depends highly on their ability to form adsorbed molecular layers that separate the rubbing surfaces from each other [6,17].

The present paper is mainly related to the study of the tribological behaviour of OFMs containing amino group. Understanding the nature of their interactions with the steel surface and with ZDDP remain challenging and extremely important for lubricant manufacturers [18]. Numerous studies have already focused on the efficiency of linear amines in reducing friction coefficient [19,20]. It was found that octadecylamine can produce a friction reduction above a critical concentration which varies between 10^{-6} and 10^{-3} M, depending on the temperature. In addition to the concentration, the presence of unsaturation in alkyl chain seems to be a relevant factor affecting the tribological behavior of amines [19]. Campen *et al.* [19] have shown that primary saturated stearylamine gives lower friction than the primary mono-unsaturated oleylamine.

Another important aspect concerns the interaction of amines with other additives, especially ZDDP. Three mechanisms have been proposed to explain the change in composition and/or thickness of the tribofilm as well as the change in the anti-wear performance of ZDDP when used in combination with amine: (i) formation of a complex in bulk oil and competitive adsorption between amine and ZDDP for surface sites [21,22], (ii) formation of a complex in bulk oil leading to the release of thiophosphoryrate anions $(RO)_2PS_2^-$ in the solution [23], (iii) equilibrium between the formation of ZDDP antiwear tribofilm and its removal by the amine [24,25]. It appears from the published literature that the amine effect on anti-wear performance of ZDDP has also been a controversial topic. While some

authors reported that dispersants (additives containing amino groups) reduce the antiwear activity of ZDDP [26,27], others did not find any significant change in the wear rate between ZDDP alone and ZDDP mixed with dispersant [28], Moreover, a recent study showed synergistic reduction in wear between amine and ZDDP [29]. It was also found that the combination of selected amine-based OFMs with ZDDP reduces frictional forces and can mitigate surface fatigue under certain conditions [29,30].

In the following paper, an experimental study combining tribometry and XPS analyses is undertaken to investigate the friction behavior of linear amines OFM additives in presence or not of ZDDP. The objective is to understand the lubrication mechanism of amines in presence of ZDDP on iron/steel surfaces.

2. Materials and methods

2.1. Samples

Balls (RMS ~ 20 nm) and flats (RMS ~ 15 nm), made of AISI 52100 steel, were used for tribological tests. Hardness of both ball and flat are found around 800 Hv. They were purchased from CIMAP and PCS Instruments, respectively.

2.2. Base oil and additives tested

Unless specifically indicated, a poly- α -olefin base oil (PAO 4) was blended with 1 wt % amine alone or with 1 wt % ZDDP. The blending procedure consists in mixing at 100°C the additives in base oil for 30 minutes and let it cool down to room temperature afterward. The molecules of interest have mostly a C18 alkyl chain, with different types and numbers of nitrogen atom substituent (primary, secondary, tertiary) and with the presence or not of ethoxylated groups. Some of these amines are almost pure compounds although others are commercial compounds with less purity. The additives and the base oil are listed and described in table 1.

Product (supplier)	Code	Description
PAO 4 (Total)	Base Oil	Physical properties at 100 °C <ul style="list-style-type: none">– Density = 759.6 Kg/m³– Kinematic viscosity = 4.0 mm²/s– Dynamic viscosity = 3.04 x10⁻³ Pa.s– Pressure-viscosity coefficient = 10.6 (GPa⁻¹)
Octadecylamine (Sigma Aldrich)	Octa	Primary amine; R = C 18 ; assay ≥ 99 %
Armeen® 18D (AkzoNobel)	Ar 18D	Primary amine; R = C 18
Armeen® HTD (AkzoNobel)	Ar HTD	Primary amine; R = C 16 - C 18
N-Methyloctadecylamine (Sigma Aldrich)	MeOc	Secondary amine; R = C 18 ; assay ≥ 98 %
Armeen® DM18D or N,N-Dimethyloctadecylamine (AkzoNobel)	Ar DM18D	Tertiary amine; R = C 18
Duomeen® CD or N-Coco-1,3-diaminopropane (AkzoNobel)	Duo CD	Molecule containing two amino groups (primary and secondary); R = C 12 - C 14
Duomeen® O or N-oleyl-1,3-	Duo O	Molecule containing two amino

diaminopropane (AkzoNobel)		groups (primary and secondary); R = mostly C 18 with one unsaturated bonds
Triameen® (AkzoNobel)	Tria T	Molecule containing three amino groups (one primary and two secondary); R = mostly C 18 with one unsaturated bonds
Ethomeen® O/12 or Bis (2-hydroxyethyl) oleylamine (AkzoNobel)	Eth O /12	Ethoxylated amine containing one amino group (tertiary) and two hydroxyl groups; R = mostly C 18 with one unsaturated bonds
Stearyldiethanolamine (TCI Europe)	Stearyl eth	Ethoxylated amine containing one amino group (tertiary) and two hydroxyl groups; R = C 18; assay > 98 %
Zinc dialkyldithiophosphate (Total)	ZDDP	Neutral primary ZDDP; R = C 8

Table 1: Base oil and additives used in the current study

2.3. Tribological tests

Tribological tests have been performed in reciprocating sliding mode by using a linear tribometer with a ball-on-flat configuration (cf. Figure 1). In each tribo-test, few drops of lubricant (100 μ l) were used. Tribo-tests were run for 9600 cycles at 100 °C with a stroke length of 3 mm. The sliding speed was 8 mm/s and the normal load was 2 N leading to a maximum Hertzian pressure of 504 MPa. Each test was repeated at least three times. **Steady-state friction coefficient values were calculated for each test. Average of steady-state friction coefficient value were then estimated. Standard deviation was calculated considering all steady state friction coefficient values for one set of conditions.** Taking into account these parameters and the physical properties of the base oil (cf. table 1), the minimum film thickness (h_{min}) in the contact was estimated to be around 0.43 nm by using the Hamrock-Dowson equation [31]. Therefore, the specific film thickness or Lambda ratio (λ), defined as the ratio of the minimum film thickness to the composite root-mean-square (RMS) surface roughness, was considerably lower than 1 (\sim 0.02) ensuring that the tribo-tests were carried out in boundary lubrication conditions.

During the friction test, the electrical contact resistance (ECR) was also measured continuously. A small voltage of about 7 mV was applied between the flat and the ball and the resulting current was measured using a logarithmic current amplifier in order to cover a wide resistance range from 1 to 10^7 Ω .

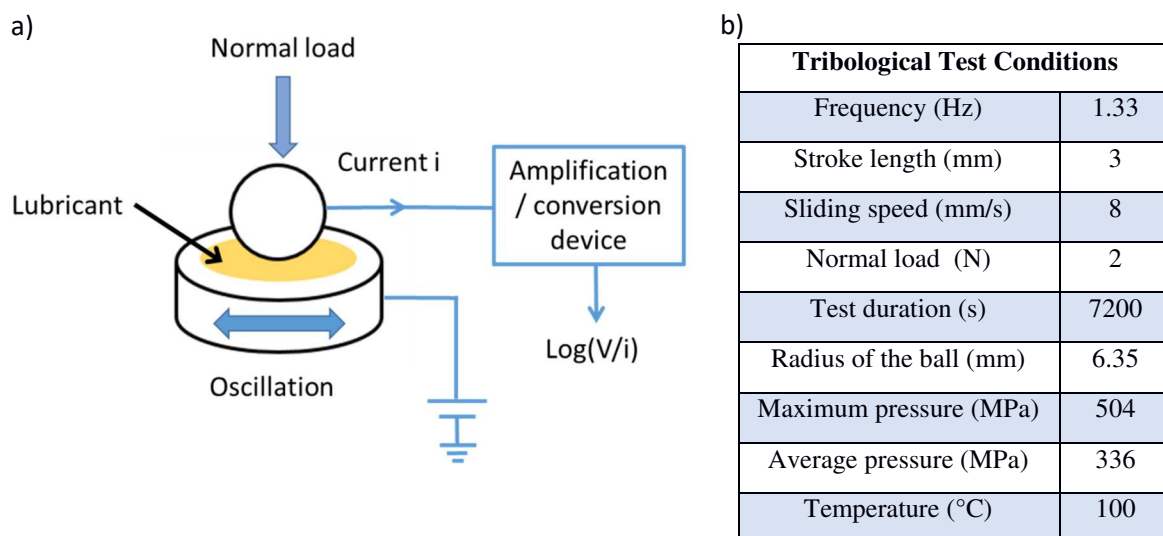


Figure 1: Tribological test in reciprocating sliding mode. (a) Drawing showing the working principle of our home-made tribometer allowing to measure simultaneously the evolution of the friction coefficient and the electrical contact resistance as a function of the number of cycles. (b) Experimental conditions used during friction tests.

2.4. Wear scar analysis

The wear scar width (WSW) was measured on the balls using optical microscopy after each tribo-test. The measured wear scar diameter was then compared with the theoretical Hertzian diameter. For each set of conditions, minimum three measurements were carried out on both balls and flats. As the WSW results from balls were closed to the flat ones, only ball measurements were reported in the paper.

2.5. X-ray photoelectron spectroscopy (XPS) analyses

XPS analyses have been carried out using PHI 5000 VersaProbe II spectrometer equipped with a monochromatic Al K α source (1486.6 eV). The calibration of the binding energy scale was done by using as a reference the Au 4f_{5/2} and Au 4f_{7/2} with known binding energies at 84 and 87.7 eV respectively.

Prior to XPS analyses, the samples were cleaned by ultrapure heptane to remove the residual lubricant from the surface.

The emitted electrons were collected at a 45° take-off angle with respect to the substrate surface. A dual beam charge neutralization system was used to compensate the charging

effect (low energy electrons and Ar⁺ ions). Additional charge compensation was done by fixing the aliphatic carbon binding energy at 284.8 eV.

Firstly, scanning X-ray image (SXI) was used to identify the wear track. Then survey spectrum and high resolution spectra were recorded inside and outside the wear track by using an X-ray beam diameter of 50 μm. Survey spectra were recorded with a pass energy of 187.85 eV and a step size of 0.8 eV when high resolution spectra were recorded with a pass energy of 23.5 eV and a step size of 0.2 eV.

The data processing was performed with the PHI Multipack software. The spectra were fitted by using the product of Gaussian and Lorentzian functions after subtracting a Shirley background. Only small variations in FWHM (full widths at half-maximum) of the peaks were permitted.

The thickness of the tribofilms and the distribution of the elements within depths were characterized using alternate cycles of sputtering and XPS analyses. A beam of argon ions with an energy of 500 V was used to sputter an area of 2 x 2 mm². Then, XPS analysis was performed inside and outside the wear track after each sputtering cycle of 2 minutes with an X-ray beam diameter of 50 μm and a pass energy of 93.9 eV (step size of 0.2 eV). In order to estimate roughly the thickness of the tribofilm from the XPS sputter depth profile, the interface between the tribofilm and the metal substrate was determined by the sputtering time at which the oxygen concentration reached 50% of its maximum value [32,33]. For each profile recorded inside the wear track another profile (not shown here) was also recorded on the oxide film present outside the corresponding wear scar (native oxide). This allowed to estimate the thickness ratio of the tribofilm to the native oxide film by using the following relationship:

$$\frac{d_1}{d_2} = \frac{v_1}{v_2} \times \frac{t_1}{t_2} \quad (1)$$

Where d_1 (d_2), v_1 (v_2), t_1 (t_2) are respectively the thickness, sputtering rate and sputter time required to reach the interface for the tribofilm (native iron oxide film). Taking into account that the same settings are used for recording the depth profiles inside the wear track and outside, we assume that the sputtering rate for the tribofilm and the native oxide film are roughly the same. Equation (1) can then be written as:

$$\frac{d_1}{d_2} \approx \frac{t_1}{t_2} \quad (2)$$

3. Results and discussion

3.1. Tribological behaviour of amines

3.1.1. Friction coefficient

Figure 2-a summarizes the steady-state friction coefficient values obtained at 100°C with the 1 wt % amine blended to PAO 4. It is calculated over the last 4600 cycles. The results indicated that all the tested amines were able to reduce the friction coefficient from 0.137 (PAO4 alone) to values between 0.075 and 0.095. These values are in complete agreement with previous data for amines, used as OFMs, in boundary lubricated steel/steel contacts [5,20,27].

Primary monoamine additives (Octa, Ar 18D and Ar HTD) showed the best friction behaviour ($\mu \sim 0.075 - 0.080$). The friction tests were reproducible (cf. friction curves for PAO4+1%octa Figure 2-b). High standard deviation was observed with the tertiary amine (Ar DM18D). A significant improvement in its friction behaviour with the increase of surface exposition time to the lubricant “t” (immersion time in lubricant at 100 °C prior to commencing rubbing) was found. Indeed in the test procedure represented in Figure 3, the first friction curve is recorded after a surface exposition time of about 30 minutes (time necessary to stabilize the temperature) while the third or fourth curve is recorded after an exposition time of more than 8 hours. In the case of amines such as Octadecylamine, no change in friction coefficient value was found (cf. Figure 3-a) whereas the friction coefficient of the Ar DM18D decreased from 0.102 to 0.076 when the exposition time has increased from ~ 30 to 630 minutes (cf. Figure 3-b).

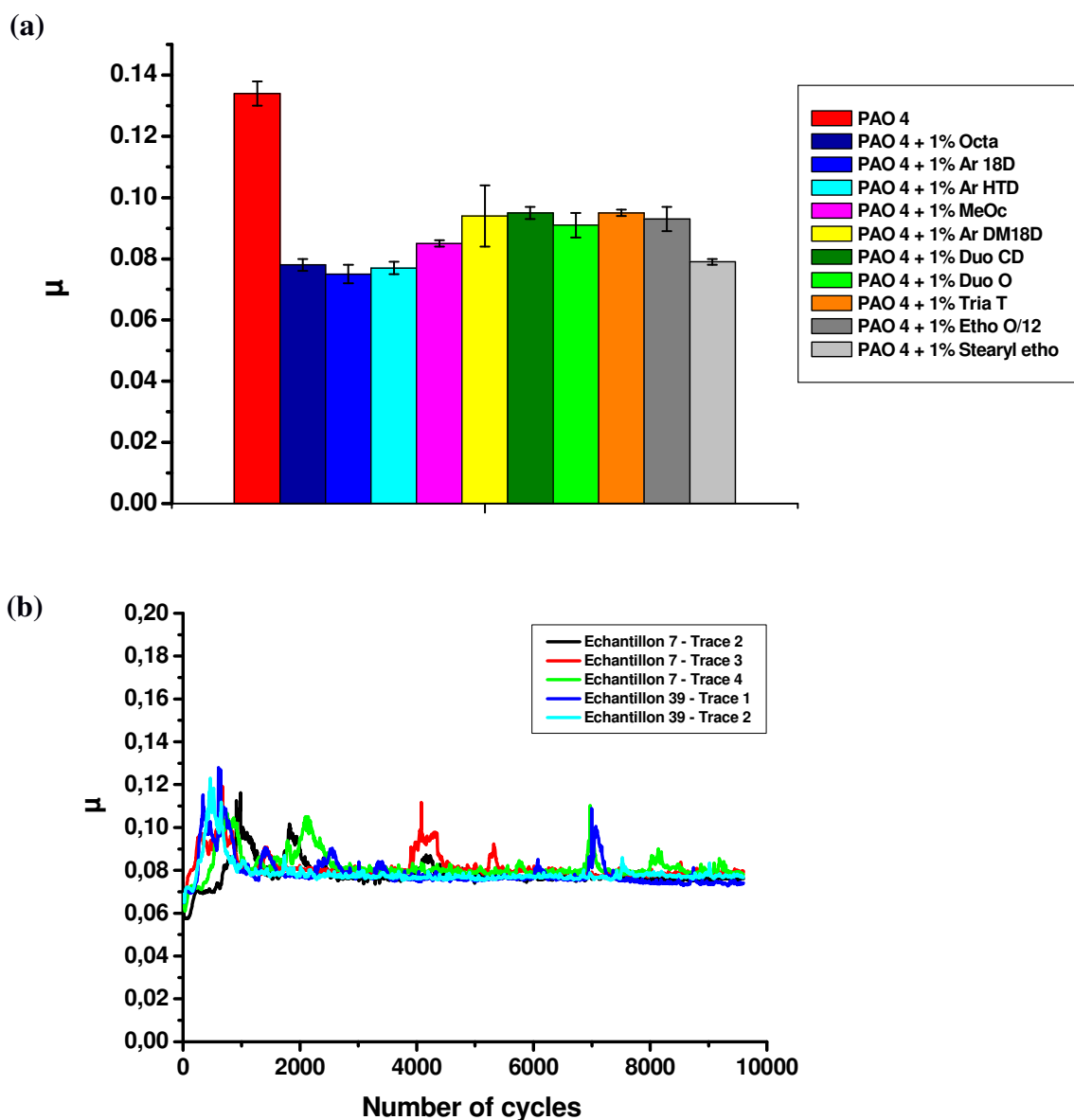


Figure 2: (a) Average steady-state friction coefficients \pm standard deviation obtained at 100°C with and without different types of amines. (b) friction curves obtained for PAO4 +1%octa.

These results suggest that the adsorption kinetics of Ar DM18D is slower than that of Octa. Higher surface coverage can be expected by adsorbed Ar DM18D with increasing exposition time for more than 8 hours.

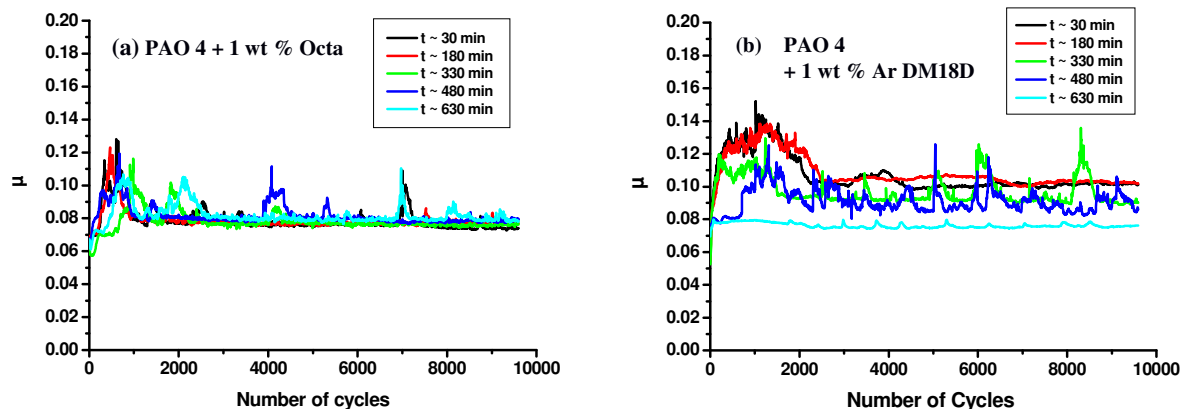


Figure 3: Evolution of friction coefficient at 100°C as a function of exposition time "t" e.g. immersion time in lubricant at 100 °C prior to commencing rubbing: (a) PAO 4 + 1 wt % Octa (b) PAO 4 + 1 wt % Ar DM18D.

The friction measurements also revealed that the presence of an unsaturation in the hydrocarbon chain (Duo O, Tria T and Eth O/12) or the presence of many amino groups (DuO CD, Duo O, Tria T) in the molecule increased the friction coefficient [1,34]. The unsaturated molecules probably form more disordered self-assembled films than saturated chain compounds [1]. In the same way, the packing capability decreases if the polar group is not exclusively present at the end of the molecule as previously shown with alcohols [35]. The presence of several adsorption possibilities (both amino and ethoxilated groups) has apparently increased the disorder in the self-assembled film (Eth O/12 and Stearyl etho). But as stearyl etho contains more saturated C18 chains than Eth O/12, a lower friction coefficient is obtained (less disordered SAM with Stearyl etho compared to Eth O/12).

3.1.2. Wear measurements

Wear scar width (WSW) measurements obtained with the different tested amines (1 wt %) at 100 °C, are recapitulated in Figure 4. It shows that the amines have high effectiveness in reducing wear when blended into the base oil compared to the base oil alone. However, all the WSW values remain larger than the calculated Hertz diameter of 87 μm (see dotted line in Figure 4). The values were reproducible as showed in Figure 4 (low standard deviation). In addition, the large variation in WSW observed with the tertiary amine (Ar DM18D) can be explained in the same way as it was for the friction test. In other words, this molecule showed an increase in its antiwear performance with the increase of surface exposition time to the

lubricant. The **WSW** decreased from 181 to 126 μm when the exposition time has increased from ~ 30 to 630 minutes.

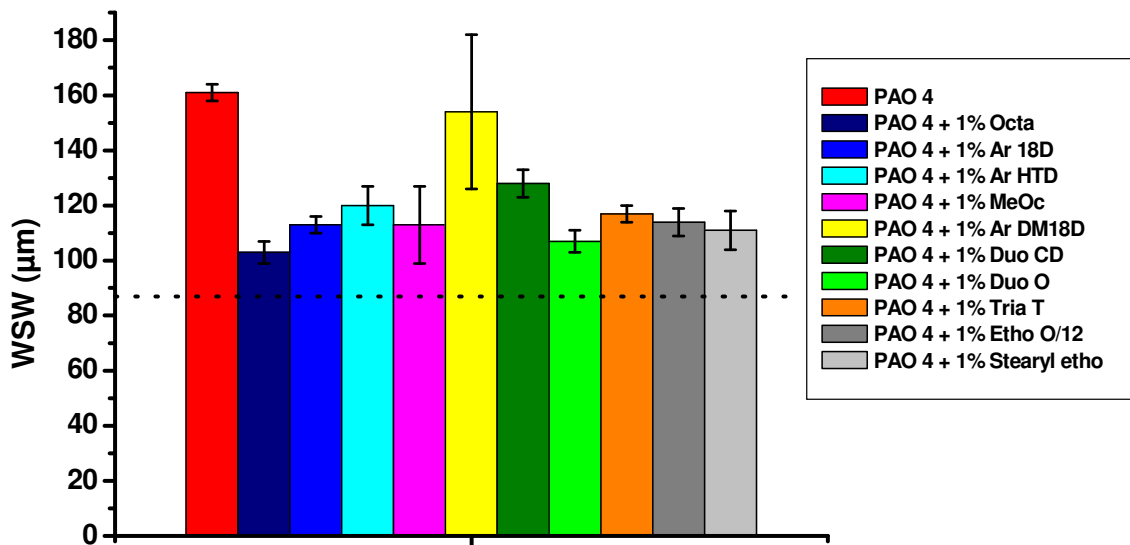


Figure 4: Average wear scar width (WSW) measurements \pm standard deviation obtained at 100°C with different types of amines. The dotted line represents the calculated Hertz diameter (87 μm).

3.2. Tribological behaviour of amines (1 wt %) mixed with ZDDP (1 wt %)

3.2.1. Friction coefficient

Concerning experiments with ZDDP, the friction tests were carried out with the same conditions as in §2.3. The lubricants were prepared by mixing 1 wt % amine + 1 wt % ZDDP to the base oil. All these lubricants, containing both ZDDP and amine, give lower steady-state friction coefficient (cf. Figure 5) than the lubricants of Figure 2, prepared with the amine alone. The steady-state friction coefficient values, obtained with the blends, are between 0.060 and 0.084 (PAO4 + ZDDP). These values confirm earlier data obtained by MTM rolling-sliding tribometer [26,27].

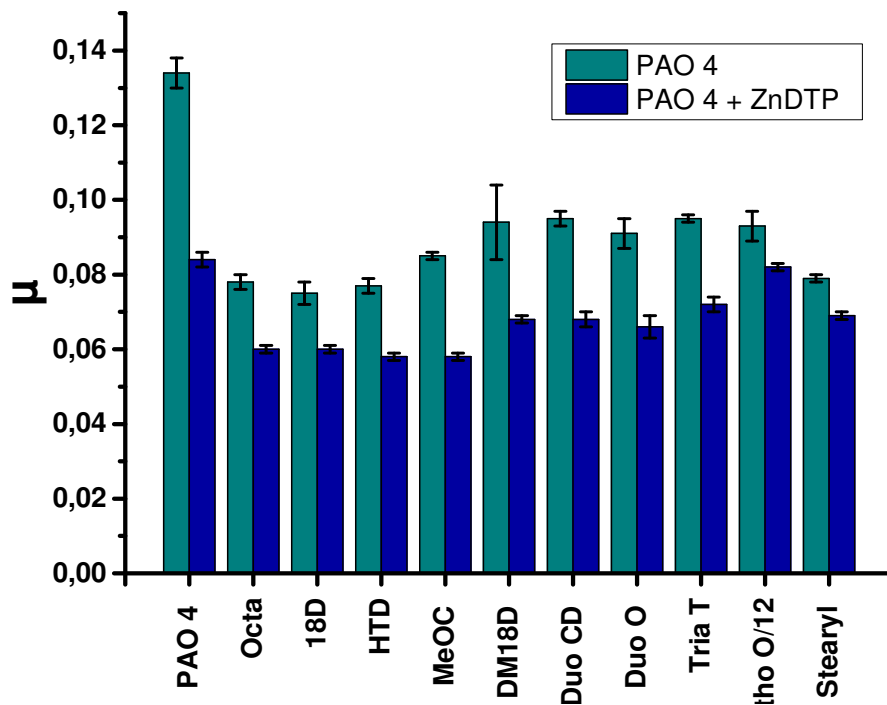


Figure 5: Average steady-state friction coefficient \pm standard deviation obtained at 100°C with different blends: in green, PAO4 alone and PAO4 with 1% of different types of amines (binary mixture), in blue, PAO4+1%ZDDP and PAO4+1%ZDDP with 1% of different types of amines (ternary mixture).

The primary monoamine additives (Octa, Ar 18D and Ar HTD) and the secondary amine (MeOc) showed the best behavior in friction ($\mu \sim 0.06$) in this case. A reduction in friction coefficient between 20-25% when blending such amines (Octa, Ar 18D and Ar HTD) with ZDDP is found compared to the case of amines alone (cf. table 2).

Lubricant	μ (without ZDDP)	μ (With 1% ZDDP)	Reduction (%)
PAO4	0.134 \pm 0.004	0.084 \pm 0.002	37%
PAO4 + 1 wt % Octa	0.078 \pm 0.002	0.060 \pm 0.001	23%
PAO4 + 1 wt % Ar 18D	0.075 \pm 0.003	0.060 \pm 0.001	20%
PAO4 + 1 wt % Ar HTD	0.077 \pm 0.002	0.058 \pm 0.001	25%
PAO4 + 1 wt % MeOc	0.085 \pm 0.001	0.058 \pm 0.001	32%
PAO4 + 1 wt % Ar DM18D	0.094 \pm 0.010	0.068 \pm 0.001	28%
PAO4 + 1 wt % Duo CD	0.095 \pm 0.002	0.068 \pm 0.002	28%
PAO4 + 1 wt % Duo O	0.091 \pm 0.004	0.066 \pm 0.003	27%
PAO4 + 1 wt % Tria T	0.095 \pm 0.001	0.072 \pm 0.002	24%
PAO4 + 1 wt % Etho O/12	0.093 \pm 0.004	0.082 \pm 0.001	12%
PAO4 + 1 wt % Stearyl etho	0.079 \pm 0.001	0.069 \pm 0.001	13%

3.2.2. Wear measurements
In

terms of wear, Figure 6 shows that the WSW values obtained with blends containing both

Table 2: Average steady-state friction coefficient values and standard deviations for the different used lubricants. The reduction of friction coefficient in presence of ZDDP is mentioned for each amines.

amine and ZDDP, with the exception of Stearyl etho, are extremely close to the Hertz diameter of 87 μm (see dotted line in Figure 6). Thus, most of the tested amines improved the antiwear performance of ZDDP. In addition, the higher WSW value obtained with the blend (1 wt % ZDDP + 1 wt % stearyl etho) compared to the value obtained with ZDDP alone indicates that this molecule is detrimental to the antiwear performance of ZDDP.

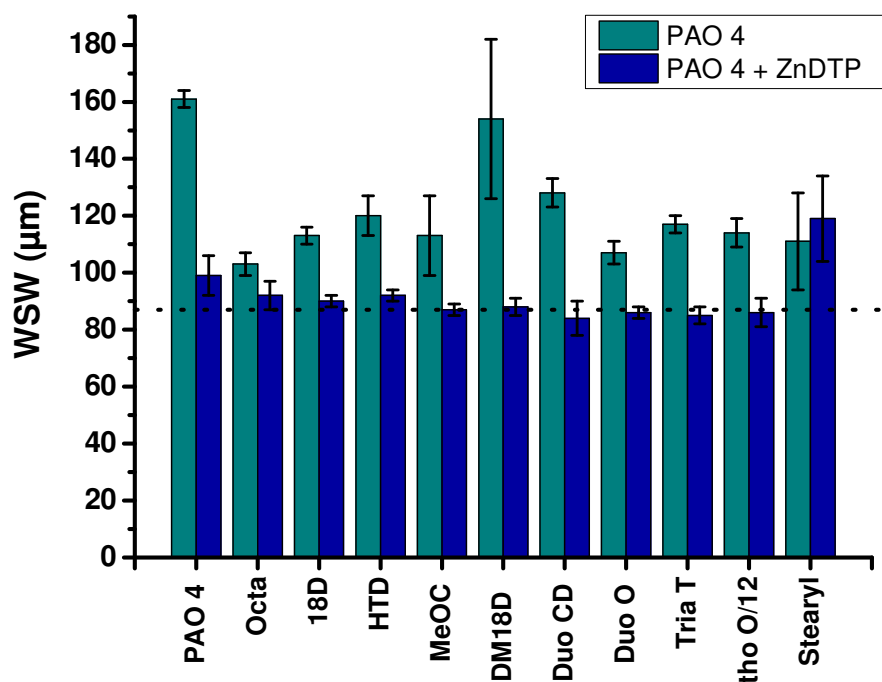


Figure 6: Average wear scar width values \pm standard deviation obtained at 100°C with different blends: in green, PAO4 alone and PAO4 with 1% of different types of amines (binary mixture), in blue, PAO4 + 1% ZDDP and PAO4+1%ZDDP with 1% of different types of amines (ternary mixture). The dotted line represents the calculated Hertz diameter (87 μm).

From the friction and wear measurements (cf. Figure 5 and Figure 6) one can deduce that the combination of amine (except stearyl etho) and ZDDP has produced synergistic effect on reduction of both friction and wear.

3.2.3. Electrical contact resistance measurements

The electrical contact resistance (ECR) was used in order to monitor the formation of insulating tribofilm. Figure 7 shows a typical measurement of the ECR as a function of the number of cycles. The ECR measurements obtained when the contact has been lubricated with the base oil alone (black curve) or with the base oil blended with the octadecylamine (red curve) show that the ECR remains very low ($\text{ECR} < 10^2 \Omega$) in the steady-state regime ($N \geq 5000$ cycles). However the addition of ZDDP to the base oil leads to obtain very high ECR

value, around $10^{6.4} \Omega$ (close to the saturation value at $10^7 \Omega$). This high ECR value is reached after ~ 450 cycles and can be attributed to the formation of an electrically insulating antiwear tribofilm [36]. Moreover, the ECR reached $10^{6.4} \Omega$ after only 50 cycles when the contact has been lubricated with base oil containing both octadecylamine and ZDDP. One can deduce that the addition of the amine to ZDDP has accelerated the formation of the tribofilm.

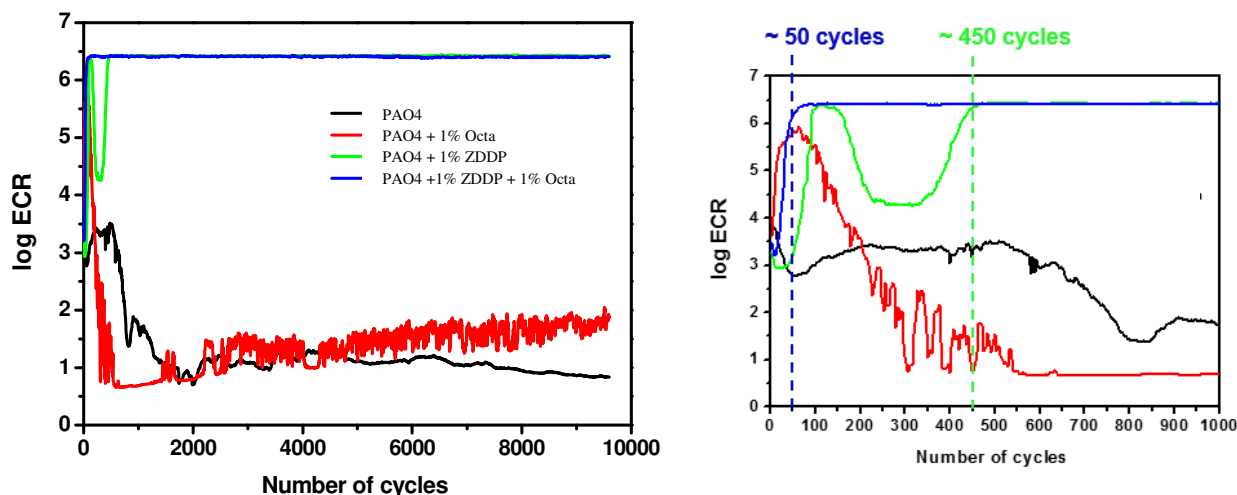


Figure 7: (a) Evolution of the electrical contact resistance during friction tests with PAO4, PAO4 + 1 wt % Octa, PAO4 + 1 wt % ZDDP and PAO4 + 1 wt % octa + 1 wt% ZDDP. (b) Zoomed in view of the first 1000 cycles.

The same trends for the values of the electrical contact resistance have been observed with the other amines (except the Stearyl etho). In other words, the value of the ECR (in the steady-state regime or at the end of the test) was always less than $10^2 \Omega$ when the amine was added alone to the base oil and greater than $10^6 \Omega$ when the amine was added in combination with ZDDP. Moreover, ECR values $\geq 10^6 \Omega$ with the blend of ZDDP and one of the amines (except Stearyl etho) were reached faster ($N \leq 120$ cycles) than with ZDDP alone ($N = 450$ - 800 cycles).

The Stearyl etho is the only amine, among all the molecules tested, that did not lead, once mixed with the ZDDP, to obtain a high value for ECR. It remains very low (in the steady-state regime) and close to the value measured with the base oil alone suggesting that this molecule has prevented the formation of an antiwear tribofilm (cf. Figure 8). This result is consistent with the pronounced wear obtained with the mixture of 1 wt % ZDDP + 1 wt % Stearyl etho (cf. Figure 6).

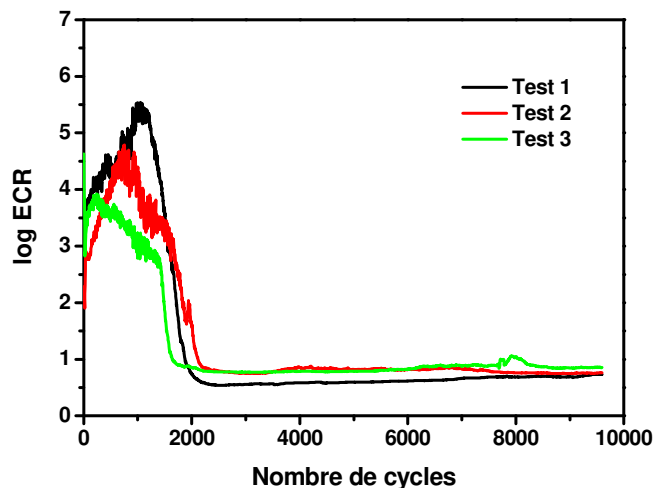


Figure 8: Evolution of the electrical contact resistance during friction tests with PAO4 + 1% Stearyl etho + 1% ZDDP. The test was repeated three times (tests 1,2 and 3).

3.2.4. XPS analyses of the tribofilms obtained using blends with amines (1 wt %) mixed with ZDDP (1 wt %)

Considering the fact that the primary monoamines retained the best tribological behaviour in the presence of ZDDP, XPS analyses were carried out on the tribofilms formed on the surface lubricated with PAO4 + 1wt % ZDDP or PAO4 + 1 wt % ZDDP + 1 wt % Octa. XPS survey spectra (not shown here) recorded inside and outside the wear scar showed the peaks that correspond to carbon, iron, oxygen, phosphorus, sulfur, zinc and nitrogen (in case of base oil containing octadecylamine). The high resolution spectra are obtained for all the elements present in the tribofilm. Only the peaks that showed a significant variation in the chemical composition of the tribofilm after the addition of the amine are presented here. Figure 9 (a) and (b) shows the zinc, phosphorus and oxygen peaks recorded on the tribofilm formed in PAO4 + 1 wt % ZDDP whereas the Figure 9 (c) and (d) shows the peaks recorded on the tribofilm formed in PAO4 + 1wt % ZDDP +1 wt% Octa. The Zinc 3s signal was fitted with one peak and the phosphorus 2p signal was fitted with two peaks, $2p_{3/2}$ and $2p_{1/2}$, due to the spin-orbit splitting in this case. The fitting procedure for the phosphorus consists of applying an area ratio of 2:1 and an energy difference of 0.84 eV for its two components ($2p_{3/2}$ and $2p_{1/2}$) [37]. The oxygen 1s signal was fitted with two contributions: the first at

531.6 ± 0.3 eV is assigned to non-bridging oxygen (NBO) in polyphosphates (-P=O, P-O-Zn or P-O-Fe), carbon-oxygen bond [37]. The second at 533.3 ± 0.3 eV is assigned to bridging oxygen (BO) in polyphosphates (P-O-P). In some cases, a third contribution in addition to these two appeared at 530 ± 0.3 eV indicating the presence of **metallic** oxide contribution in the tribofilm. The binding energy values for Zn 3s, P 2p_{3/2}, O 1s (oxide, NBO, BO) and N 1s are given in **table 4**. They are in agreement with previous XPS analyses of ZDDP antiwear tribofilm or synthesized (poly)phosphate glasses [38–41].

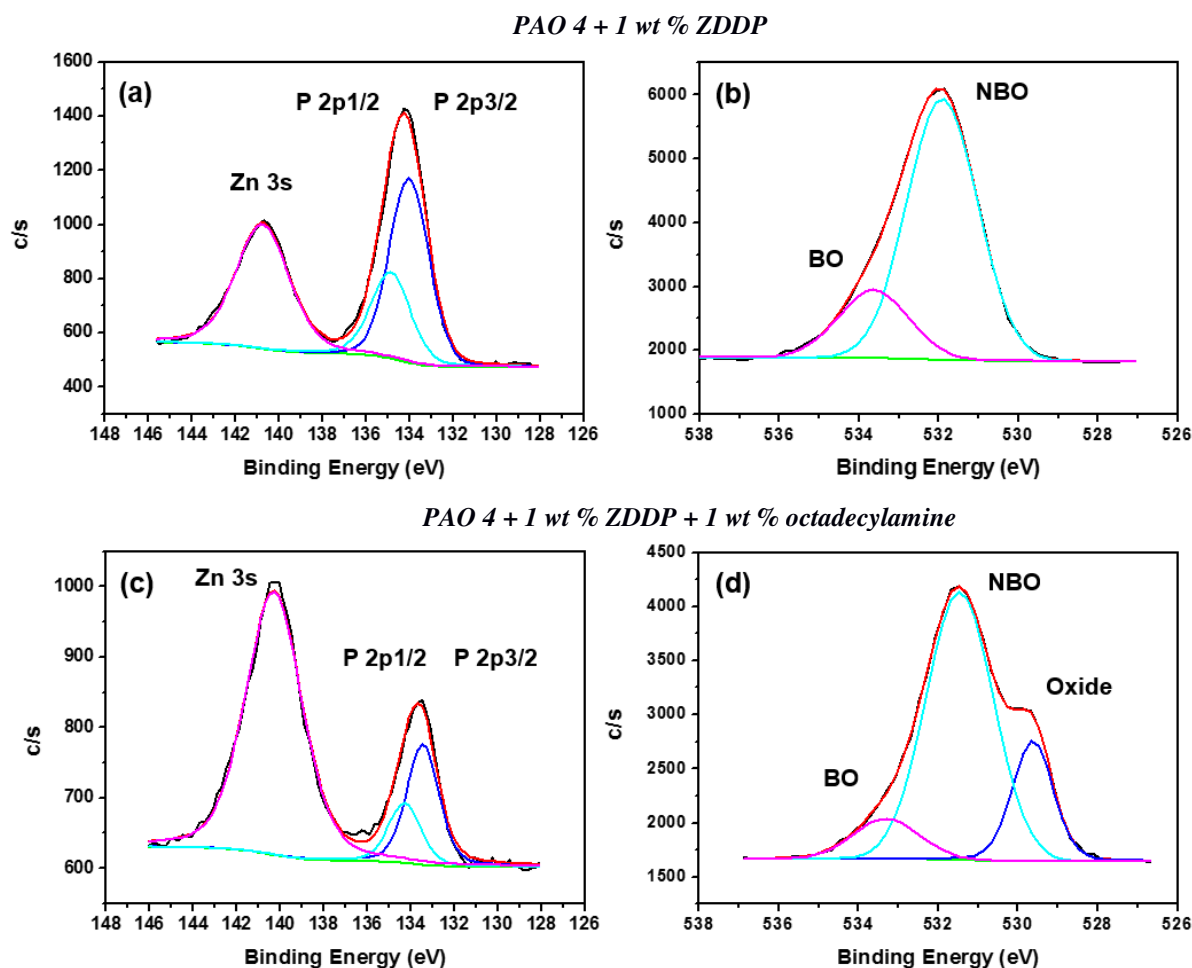


Figure 9: XPS spectra of (a) P 2p, Zn 3s and (b) O 1s recorded on the tribofilm formed in PAO 4 + 1 wt % ZDDP. XPS spectra of (c) P 2p, Zn 3s and (d) O 1s recorded on the tribofilm formed in PAO 4 + 1 wt % ZDDP +1% octadecylamine.

Considering relative intensities of P2p and Zn3s peak in Figure 9 (a) and (c), it can be concluded that the addition of the amine to the ZDDP has led to a decrease in the amount of

phosphate accompanied by an increase in that of zinc. At the same time, the oxygen spectrum has shown the appearance of a new contribution attributed to the oxide in case of tribofilm formed in the PAO4 + 1 wt % ZDDP + 1 wt % octa. From these two observations, it is possible to deduce that the presence of the amine has induced a strong enrichment of zinc oxide and a phosphate depletion within the tribofilm. This depletion is in agreement with previous AES analysis of tribofilms formed in PAO 4 blended with ZDDP and compounds containing amino groups [43]. The presence of ZnCO_3 is excluded as no carbonate contribution is found in C1s peak [42].

The high resolution N 1s spectrum recorded on the tribofilm formed in PAO4 + 1 wt % ZDDP + 1 wt % Octa showed one contribution assigned to C-N bonds (peak at 399.8 ± 0.1 eV) of amine molecules adsorbed on the tribofilm enriched in zinc oxide (cf. Figure 10 (b)).

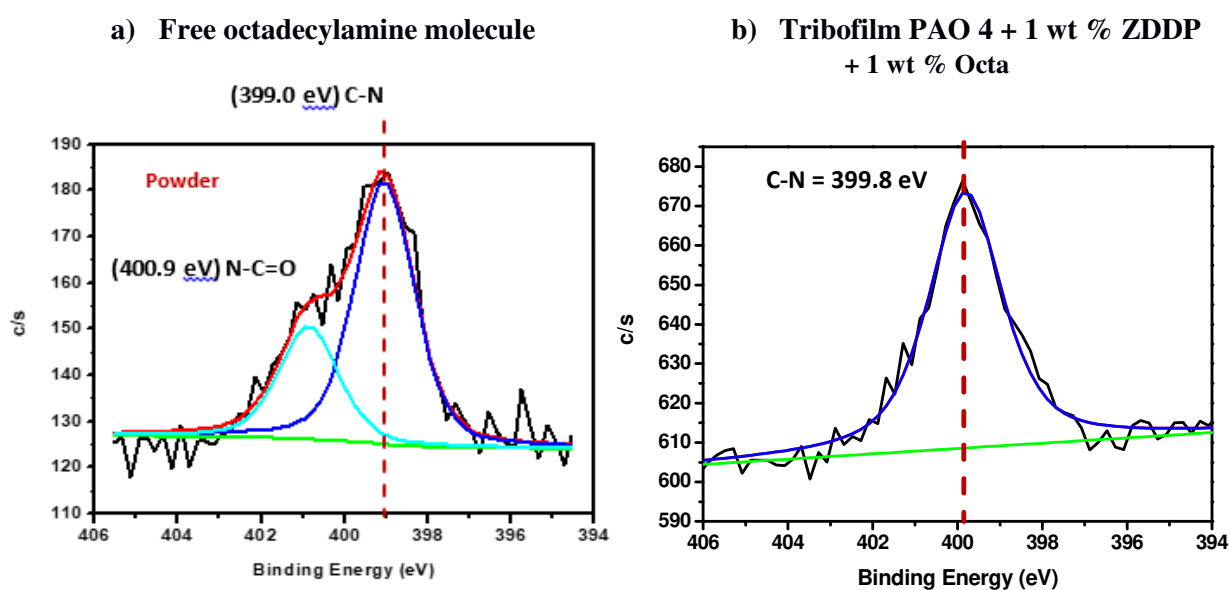
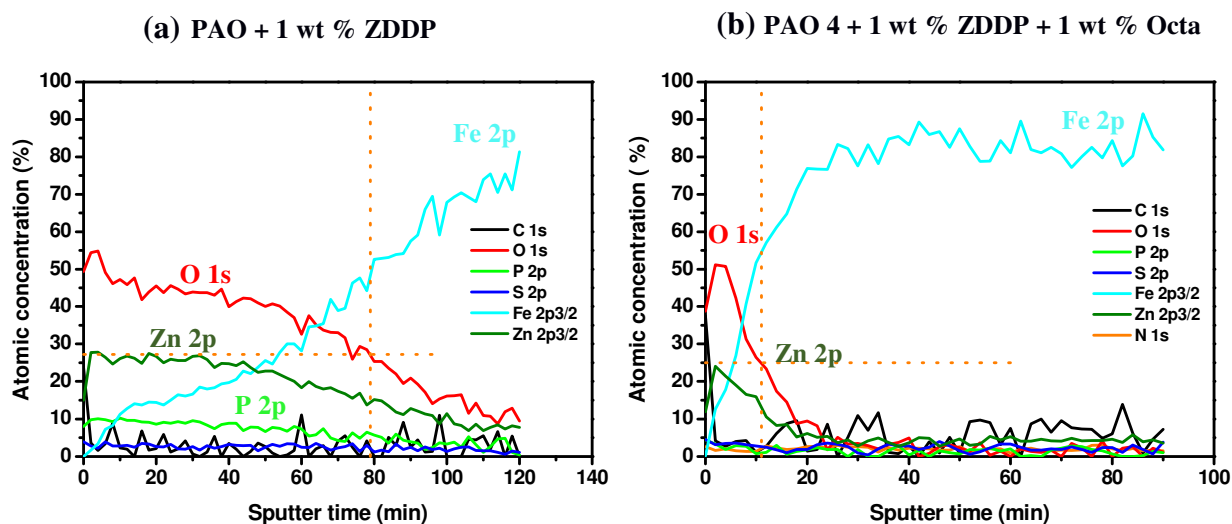


Figure 10: High-resolution XPS N 1s spectra of : a) free amine molecule (standard octadecylami). The amide contribution at 400.9 eV is contamination b) the adsorbed octadecylamine on the tribofilm formed in PAO 4 + 1 wt % ZDDP + 1 wt % Octa

The C-N peak of adsorbed amine molecules on tribofilm (Figure 10 (b)) is shifted toward higher binding energy by 0.8 eV compared to the C-N peak of free amine molecules (399 eV – Figure 10 (a)). It could be explained by the formation of C-N-Zn bonds through donation of electron density from the nitrogen atom (via its lone pair electrons) to the zinc oxide in this case.

In order to investigate the amine effect on the tribofilm thickness, XPS sputter depth profiles were recorded on the wear scar (inside and outside) lubricated with PAO4 + 1 wt % ZDDP as well as on that lubricated with PAO4 + 1 wt % ZDDP + 1 wt % octa (cf. Figure 11). According to the equation 2 the thickness of tribofilms formed in PAO 4 + 1 wt % ZDDP and PAO 4 + 1 wt % ZDDP + 1 wt % octa are evaluated to be respectively 12 and 2 times the native oxide film thickness.



Thus, the presence of the octadecylamine induced the formation of a thinner antiwear tribofilm. This is in agreement with previous work which showed that the tribofilm resulted from the N-tallow-1,3-diaminopropane in combination with ZDDP is thinner than the tribofilm formed with ZDDP alone [29]. In addition, the XPS depth profiles shown in Figure 11 confirm that the tribofilm formed in PAO 4 + 1 wt % ZDDP + 1 wt % Octa is depleted in phosphate compared to that formed in PAO 4 + 1% ZDDP. Therefore, the tribofilm formed in presence of the amine is composed mainly of zinc oxide covered by octadecylamine molecules as described previously (the nitrogen is only present at the top surface of the tribofilm) and possibly iron oxides.

3.3. Tribological behaviour of octadecylamine mixed with ZDDP in various ratios

In order to understand the lubrication mechanism of amine + ZDDP blends, tribological behaviour of various concentration ratios of octadecylamine to ZDDP have been carried out (Molar ratio from 0.53 and 0.82). The results are then compared with those obtained with the blend PAO4 + 1 wt % octadecylamine + 1 wt % ZDDP previously studied (§ 3.3) which correspond to a molar ratio of 0.27. Weight percentages and number of moles of additives used as well as the molar ratios are indicated in table 3. These ratios were chosen based on previous work [23] which showed that the amine reacts with the entire quantity of ZDDP to form complexes in the solution when molar ratios equal to or lower than 0.3 are used. However, the solution contains both complexes and free ZDDP when molar ratios larger than 0.5 are used.

Molar Ratio	n octa (mole)	n ZDDP (mole)	Octa (wt %)	ZDDP (wt %)	Octa (mol/L)	ZDDP (mol/L)
1		2.3×10^{-4}		1		1.01×10^{-2}
0.82	4×10^{-4}	1.81×10^{-3}	0.6	7.9	2.00×10^{-2}	9.06×10^{-2}
0.53	1×10^{-3}	1.14×10^{-3}	1.6	5.1	5.01×10^{-2}	5.70×10^{-2}
0.27	3.95×10^{-4}	1.47×10^{-4}	1	1	2.88×10^{-2}	1.09×10^{-2}

Note: The molar ratios, x , are defined by the equation $x = \frac{n_{ZDDP}}{n_{ZDDP} + n_{amine}}$ where n_{ZDDP} and n_{amine} are the number of moles of ZDDP and octadecylamine, respectively.

3.3.1. Friction coefficient and wear measurements

Figure 12 (a) shows that the use of octadecylamine in combination with ZDDP whatever the molar ratio used, reduced the friction coefficient from 0.084 (ZDDP alone, ratio

= 1) to values between 0.057 and 0.060. Thus, the octadecylamine + ZDDP blends are always more effective in reducing friction than ZDDP alone regardless of the molar ratio used.

Comparison of the wear trends is shown in the histogram in Figure 12 (b). If we assume that there is no concentration effect on antiwear capabilities of ZDDP alone, it can be deduced that octadecylamine improved the antiwear performance of ZDDP when the molar ratios are ≤ 0.5 . However, a slight alteration in the ZDDP anti-wear performance was observed when the molar ratio is equal to 0.8.

It is interesting to note that at molar ratio equal to 0.5, the ERC showed same trend as the molar ratio 0.27. In other terms, high ECR values ($10^6 \Omega$) were reached faster with the ratios 0.27 and 0.5 ($N \sim 170$ cycles cf. Figure 13 (a) and (c)) than with the ZDDP added alone ($N \sim 500$ cycles) (cf. Figure 13 (a) and (c)). On the other hand with the molar ratio ~ 0.8 , the ERC first increases and then decreases after 200 cycles (figure 13 (d)) to then increased again and reach only $10^4 \Omega$ after ~ 3500 cycles (cf. Figure 13 (b)). This longer induction period than that observed with ZDDP used alone is consistent with the increase of the wear scar at molar ratio ~ 0.8 .

3.3.2. XPS analyses of the tribofilms formed on the surface at molar ratios 0.5 and 0.8

Figure 14 (a) and (b) shows the zinc, phosphorus and oxygen peaks recorded on the tribofilm formed in PAO4 + Octa + ZDDP at molar ratio ~ 0.8 whereas Figure 14 (c) and (d) shows the peaks recorded on the tribofilm formed in PAO4 + Octa + ZDDP at a molar ratio of ~ 0.5. The peaks were fitted as reported above (Table 4).

The XPS spectra recorded on the tribofilm formed in PAO 4 + Octa + ZDDP at molar ratio ~ 0.5 (cf. Figure 14 (c) and (d)) confirm that the tribofilm is markedly enriched in zinc oxide and depleted in phosphate when ZDDP is mixed with the amine. However, the tribofilm formed in PAO 4 + Octa + ZDDP at molar ratio ~ 0.8 doesn't show significant modification in its composition when compared with the tribofilm formed in PAO + 1 wt % ZDDP (cf. Figure 9 (a) and (b)). The small increase in oxide contribution at molar ratio ~ 0.8 could be attributed to the presence of small amount of iron and/or zinc oxide within the tribofilm. The thickness of the tribofilms formed at molar ratios 0.5 and 0.8 were estimated as before from XPS sputter depth profiles (not shown here). The thickness ratios of the tribofilm to the corresponding native oxide film (t_1/t_2) are given in table 5.

Lubricant	Atomic concentration ratio			Chain length n	Thickness ratio $\frac{t_1}{t_2}$
	$\frac{P2p_{3/2}}{Zn3s}$	$\frac{Oxide}{NBO}$	$\frac{BO}{NBO}$		
PAO 4 + 1 wt % ZDDP	0.74	0	0.35	5-6	12
PAO 4 + ZDDP + Octa (Ratio = 0.8)	0.80	0.17	0.3	4	1.3
PAO 4 + ZDDP + Octa (Ratio = 0.5)	0.24	0.36	0.23	2-3	1.6
PAO 4 + ZDDP + Octa (Ratio = 0.27)	0.18	0.47	0.24	2-3	2

The zinc phosphate chain length (n) was calculated from the ratio of bridging oxygen (BO) (i.e. P-O-P) to non-bridging oxygen (NBO) (i.e. -P=O, P-O-Zn or P-O-Fe) [40,41] after subtracting the contribution of carbon-oxygen bonds to the NBO signal. The corrected ratio BO/NBO is equal to $(n-1)/2(n+1)$ where n is the glass polymerization number [41]. From the values of n summarized in table 5, one can conclude that the mixture of amine and ZDDP at molar ratios ≤ 0.5 has led to the formation of tribofilms with shorter phosphate chains compared to those of the tribofilm derived from ZDDP alone. This is in agreement with previous studies which showed that the presence of amine as dispersant [18,44] in the lubricant decreases the chain length of the phosphate in the ZDDP tribofilm. Moreover, similar effect of dispersant on phosphate chain length in the ZDDP thermal film has also been observed [45].

3.4. Proposed Lubrication Mechanism of amines in presence of ZDDP

Two lubrication mechanisms could be suggested to explain the differences in results obtained above when the molar ratio has been changed. The mechanism for molar ratios ≤ 0.5 probably proceeds in two steps. Firstly, the octadecylamine (amine) promotes the hydrolysis of neutral ZDDP added initially to corresponding basic ZDDP in presence of adventitious water contamination. This chemical reaction, given by Equation (3), has been proposed by Harrison *et al.* [46,47].

Secondly, the formed basic ZDDP molecules spontaneously decompose in the bulk oil into neutral ZDDP and ZnO as the temperature is increased to 100 °C (cf. Equation 4) [48,49].

The ZnO released into the base oil may precipitate and be deposited on the steel surface. Moreover, the presence of amine and ZnO in the base oil could lead to the formation of hard-core reverse micelles (amine molecules strongly bonded to the zinc oxide core) that dissolve in hydrocarbon base oil [50]. This step of the mechanism is supported by the fact that no precipitation was observed in the lubricant prepared by mixing amine and ZDDP at a temperature of 100 °C. It is also possible that ZnO form complex with amines [49].

Finally, these reverse micelles are supposed to react with rubbed surfaces to form tribofilm enriched in zinc oxide during friction test under boundary conditions. Further investigations are needed to confirm this hypothesis but others studies have already shown the antiwear capabilities of ZnO nanoparticles in presence of surfactant [51–55].

From the above reaction mechanism given by equation (3), one can notice that 4 moles of neutral ZDDP need only 2 moles of amine to be converted into basic ZDDP (exact stoichiometric proportions). This means that for molar ratios ≤ 0.5 , the amine was added in large stoichiometric excess. Such an excess should drive the equilibrium of the equation 3 strongly towards the formation of basic ZDDP. The increase in the concentration of the latter should be followed by an increase in the concentration of ZnO in the bulk oil (Equation 4). This mechanism can explain our XPS results that indicated strong enrichment of ZnO in the tribofilm as well as our ECR measurements that revealed a shorter induction period (time necessary to reach stable antiwear tribofilm) when ZDDP was mixed with the amine at molar ratios ≤ 0.5 .

In addition, the synergistic effect on reduction of both friction and wear obtained at molar ratios ≤ 0.5 is not consistent with the hypothesis of complexes formation in the bulk oil and

competitive adsorption between amine and ZDDP for surface sites [20]. On the one hand complexes formation should decrease ZDDP reactivity with the metallic surface due to the steric hindrance and/or its better solubility in the base oil [23]. An increase in wear rate should follow, which is not our case. On the second hand, if there was a competitive adsorption between ZDDP and amine, almost complete inhibition of antiwear tribofilm formation (or an increase in the delay for ZDDP tribofilm formation) would be expected at high amine concentration. However, the increase in amine concentration (molar ratio = 0.27) has accelerated the tribofilm formation ($N \sim 50$ cycles).

Like previously discussed, the formation of complexes needs anhydrous conditions [48]. Thus, we suggest that the presence of small amounts of water in the products used to prepare our lubricants has inhibited the complexes formation and promoted the release of ZnO into the blend.

The mechanism for molar ratio equal to 0.8 seems to be different. In this case, ZDDP was added in large stoichiometric excess with respect to the amine. Thus, the majority of ZDDP used was not converted into ZnO and one can expect that the mechanism of tribofilm formation at molar ratio = 0.8 to be similar to that of the tribofilm formed with the ZDDP alone. XPS analyzes, which showed that the composition of these two tribofilms is very close, confirm this hypothesis. In addition, the lower thickness and the longer induction period obtained with the molar ratio = 0.8 compared to those obtained with ZDDP alone suggest a partial removal of the initially formed tribofilm by amine as a contributing mechanism. In other words, the data obtained at molar ratio = 0.8, suggest a mechanism based on equilibrium between the formation of ZDDP antiwear tribofilm and its removal by the amine, as also seen in previous work [25,27]. According to our ECR data, the tribofilm thickness stabilized after ~ 3500 cycles as shown in Figure 13 (b).

4. Conclusions

A multi-technique approach combining tribological experiments, ECR measurements and surface analyses (XPS), has been used to understand lubrication mechanisms of amines in presence (or not) of ZDDP in boundary lubricated steel/steel contacts. The following conclusions can be drawn:

- All the tested amines (without ZDDP) reduced the friction coefficient and improved the antiwear performance compared to the base oil without additives.
- The primary monoamine additives (Octa, Ar 18D and Ar HTD) have shown the best tribological behaviour even after being mixed with ZDDP.
- The mixture of amine and ZDDP shows a tribological behavior that depends strongly on the molar ratio.
- For molar ratios ≤ 0.5 , a synergistic effect on reduction of both friction and wear was observed. The addition of the amine to the ZDDP accelerates the formation of an ultrathin antiwear tribofilm enriched in ZnO. The increase in the amine concentration is accompanied by a faster tribofilm formation as well as further enrichment in zinc oxide
- The enrichment in zinc oxide is caused by the addition of amine molecules to ZDDP (molar ratio < 0.5) that probably promote hydrolysis of neutral ZDDP to basic in presence of water contamination.
- For molar ratios = 0.8, while the synergistic effect on friction reduction was preserved, wear rate was slightly increased and the tribofilm formation was delayed. An equilibrium between the formation of ZDDP antiwear tribofilm and its removal by the amine is suggested as the main mechanism in this case.

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