Effect of base oil polarity on micro and nanofriction behaviour of base oil + ZDDP solutions

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Ball on disc tribometer and atomic force microscopy (AFM) were used to analyse the effect of base oil polarity on the friction behaviour of steel–steel contacts lubricated with base oil + zinc dialkyldithiophosphate (ZDDP) solutions. Understanding the lubrication properties of the first chemisorbed layer of additives on work pieces yields important information for the optimisation of lubricant formulation, in particular with regard to the type of additive and amount needed. To characterise the influence of base oil polarity, two reference base oils [hexadecane (non–polar) and diethylenglycol (polar)] were blended with different concentrations of C_4-ZDDP, and the solutions were tested. A monolayer of base oil/additive solution was deposited on an ASI 52100 steel plate and scanned in AFM contact mode under various rubbing times and applied load conditions. An AFM technique was developed to estimate the microscopic values of friction coefficients showing how the oil polarity contributes to the differences in friction behaviour of the solution due to the addition of ZDDP. With different base oils [(hexadecane (non-polar base oil) and diethylenglycol (polar oil)] the authors observed significant different friction behaviours (in micro scale and nano scale) due to the addition of ZDDP compared to the base oil alone. This observation may be attributed to the contribution of base oil to transport the ZDDP additive onto the surface which will be discussed in more details in the paper. These results display the importance of base oil polarity on the friction behaviour of formulated lubricants containing additives.

Keywords: ZDDP, Base oil polarity, Friction

Introduction

Commercially available lubricants are formulated products composed of a base oil (or base stock), which is either mineral or synthetic, and a functional additive package designed to achieve a required performance for a specific application.[1] Zinc dialkyldithiophosphates (ZDDP), which have been widely used in the past decades as additives in engine lubrication oil, were initially used as an antioxidant, but their excellent antiwear properties were quickly recognised. They can also act as mild extreme pressure agents and corrosion inhibitors. Additives of ZDDP have also been the object of a great deal of research due to their multifunctional performance and the complexity of the mechanisms that lead to it. The antiwear properties of ZDDP additives arise from their ability to interact chemically with rubbing metal surfaces to form a protective layer. The additive decomposes under certain conditions and that decomposition products react to generate a 50–150 nm thick layer.[2–4] The structure and chemical composition of the layer have been analysed using advanced spectroscopy techniques, such as X-ray photoelectron spectroscopy,[5–8] Auger electron spectroscopy[9,10] and X-ray absorption near edge spectroscopy,[11,12] and found to be dependent on temperature and tribological conditions. The layers are composed of a mixture of short and long polyphosphates[13,14] with the presence of sulphides and oxides in the in the layer bulk.[15] A two-layer structure for the ZDDP derived reaction layers has also been proposed, where a thin long chain zinc poly(thio)-phosphate layer is superimposed on a thicker short chain mixed Fe/Zn polyphosphate layer, containing embedded nanocrystallites of ZnO and ZnS.[16] However, several studies have proved ZDDP to have detrimental effects on wear under certain operation

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conditions,[17] and to enhance friction when the system is operating in mixed and boundary lubrication regimes.[18,19]

Friction and wear of tribological systems depend strongly on the chemical and physical properties of atoms and molecules of the interface between the contacting surfaces in lubricated contacts,[20] therefore it is necessary to study the surfaces at the atomic level to understand the effect of ZDDP additives on tribological performance. Atomic force microscopy (AFM) allows the study of surfaces at the nanoscale, providing a method of measuring ultra small forces between a single asperity probe tip and the surface of the sample. AFM has become a widely used tool in tribology to study dry lubricant films (i.e. coatings) and also films formed by liquid lubricants. Concerning the latest, AFM can provide information of the morphology and topography[21–23] of reactions films formed by lubricant. Recording simultaneously lateral and height signals from the scanning tip, topography and friction can be obtained in the same time. By recording pull off forces, adhesion, elastic and viscoelastic properties of the additive derived layer can be investigated.[24] However, the technique has not been previously used to provide an insight on the initial stage of additive molecules attaching to the surface and their friction behaviour.

The base oil polarity has proven to play an important role in the formation[25] and characteristics[26] of ZDDP derived reaction layers. The present study explores the use of AFM to provide information on the relation between the friction behaviour of ZDDP derived reaction layers formed on tribological specimens under conditions matching the real conditions in bearing applications (macrotribological tests) and the friction resulting from using the AFM tip as a simulation for an asperity contact.[27] The objective is to characterise the origin of the differences observed in friction behaviour for tribological tests when ZDDP is blended in oils with different polarity.

Experimental

Macrotribological test

WAM5 ball on disc test rig

WAM5 ball on disc test rig (Wedeven Associates Inc., Edgmont, PA, USA) was utilised to evaluate the tribological performance of additive based oil blends at controlled temperature, load, entrainment speed and slide/roll ratio (SRR). The ball and the ring are driven independently by motors allowing controlled SRR.

Test samples

The steel balls (20 mm diameter) were of AISI 52100 steel with hardness 59–66 HRC and an average roughness R_a of 10 nm. The rings were washers (WS 81212) from SKF cylindrical thrust roller bearings of AISI 52100 steel with hardness 59–66 HRC and R_a=100 nm. The rings are assembled in a holder to attach them to the rotating shaft of the test rig. The specimens were cleaned before testing by successive immersion first in an ultrasonic bath of petroleum ether for 10 min and then acetone for 10 min.

In order to study the influence of base oil polarity on tribological performance two low viscosity model base oils were selected: one polar oil, diethylenglycol diethyleter (DEG) and one non-polar oil, *n*-hexadecane (HeD), both by Acros Organics, NJ, USA. Iso-butyl-zinc dithiophosphate (ZDDP), 99% purity by A&S Chemie, Tubingen, Germany, was employed in simple solution in both base oils without other additives present.

Test conditions

Base oil polarity effect on ZDDP behaviour was studied in mixed rolling/sliding contact. The tribological tests were carried out at applied normal loads of 100 and 600 N, resulted in a maximum Hertz contact pressure of 1·34 GPa (contact diameter 0·38 μm) and 2·43 GPa (contact diameter 0·69 μm). The SRR was set constant at 0·05. [The SRR is defined as sliding speed, or entrainment speed, $U_S = U_B - U_R$ divided by the rolling speed, $U = (U_B + U_R)/2$ where U_B and U_R are the ball and ring surface speed in contact respectively]. The entrainment speed was set at 0·5 m s^{-1}. Temperature for all the tests was set constant at 90°C. The tests were conducted for 1 h rubbing time. Pure base oil and two different concentrations, 2 and 5 wt-% ZDDP, were tested. Under these conditions the elastohydrodynamic film thickness is calculated at the centre of the contact to be ~10 nm for the different systems which indicates that the system is operating in the boundary lubrication regime.

Nanotribological test

Atomic force microscopy

Measurements were performed with an AFM MFP-3D atomic force microscope (by Asylum Research, Santa Barbara, CA, USA) in contact, constant force mode using non-conductive silicon nitride cantilevers with a spring constant k=0·2 N m^{-1} and a resonant frequency f_0=38 kHz (Veeco Instruments, Santa Barbara, CA, USA).

Test samples

The steel plates used were of AISI 52100 steel with hardness 59–66 HRC and an average roughness R_a of 10 nm. The same base oils and additives used for the macrotribological were tested.

Test conditions

The main measurement parameters were: a scan size from 5×5 to 80×80 μm (512 scan points and 512 scan lines), a scan rate from 0·5 to 2 Hz, scan angle of 90°, and a set point (SP) from 10 to 50 nN in contact mode. The recorded data were both trace/retrace of height, deflection and lateral force.

Force curves (cantilever spring force as a function of z-piezo extension) were also determined at fixed positions on the specimens. Away from the specimen the lever maintains its free deflection, and first makes a surface contact at S (‘snap-in’). In air, this initial contact

Table 1 Cantilever specification*

Material	Silicon nitride
Thickness *t* (Nom)	0·6 μm
Thickness *t* (RNG)	0·59–0·61 μm
Bottom layer back	15 nm of Cr
Top layer back	60 nm of Au
Tip specification	
Geometry	Cast
Tip height *h*	2·5–3·5 μm
Tip radius (Nom)	20 nm
Length *L*, μm	140

is frequently with a surface layer of adsorbed water vapour or other contaminants, and is accompanied by formation of a meniscus around the tip–surface contact. Retraction of the lever results in an increasing cantilever spring force acting against the meniscus related and other adhesive forces, until the 'pull-off' force P is reached, when the cantilever jumps back to its free deflection position. Hysteresis during contact indicates that some plastic deformation has occurred while load was applied to the surface, due to the presence of a relatively soft surface film.

In order to compare the conditions in the AFM tests with ball on disc experiments, the authors estimate AFM single asperity contact pressure. For the tip we used for these measurements the radius is 20 nm and the maximum applied load of 50 nN, therefore the range of contact pressure is in the order 100 MPa.

Friction calculations

Bhushan introduced two methods to measure friction.[28] For the present measurements the lateral force technique was used since it is described as more reliable and objective. The sample is scanned perpendicularly to the long axis of the cantilever beam and the lateral force signals in trace and retrace (LT, LRT) are recorded.

In this arrangement, as the sample moves under the tip, the friction force will cause the cantilever to twist. Therefore the signal intensity between the left and the right detectors will be different, denoted as FFM signal $[(L-R)/(L+R)]$.

This signal can be related to the degree of twisting, hence to the magnitude of friction force. By changing the SP parameter in the feedback loop, the normal force applied between probing tip and sample surface can be changed.

The scan sizes were 5×5 μm, consisting of 512 scan lines with 512 scan points each.

First, the average value of all of the 512 lines with 512 points for lateral trace LTV_{avg} and lateral retrace $LRTV_{\mathrm{avg}}$ from every scan were calculated. To obtain the friction force value (FFV), these two mean values have to be subtracted from each other, and divided by two,[28] see equation (1)

$$FFV=\frac{|LTV_{\mathrm{avg}}-LRTV_{\mathrm{avg}}|}{2} \tag{1}$$

The measurements of the FFVs were repeated ten times in every environment to obtain representative and repeatable results.

Assuming that the friction in nanoscale follows Amonton's law, the friction force is given by equation (2)

$$FFV=\mu(SP+F_0) \tag{2}$$

where μ is the friction coefficient, the SP is the applied load and F_0 is a force constant. Following the procedure suggested by Beake *et al.*,[29] the force constant is nearly equal to the pull off force determined from the force distance curves ,therefore the friction coefficient can be calculated using equation (3)

$$\mu=\frac{FFV}{(SP+F_0)} \tag{3}$$

Usually, the FFV and SP values are given in volts as acquired from lateral force measurements. However, the results can be easily compared with each other because findings in Volts are connected with the forces between tip and surface. In order to obtain commonly used units (newton), the lateral force needs to be calibrated by the determination of the slope of deflection versus LVDT. The calibration delivers an accurate value of the inverse optical lever sensitivity (InvOLS) describing the sensitivity of the detector–cantilever combination. With the knowledge of the accurate value of InvOLS, it is possible to calculate FFV and SP in Newton as follows

$$\mathrm{FFV\ (V)\times InvOLS\ (nm\ V^{-1})\times spring\ constant\ (nN\ nm^{-1})=FFV\ (nN)} \tag{4}$$

$$\mathrm{SP\ (V)\times InvOLS\ (nm\ V^{-1})\times spring\ constant\ (nN\ nm^{-1})=SP\ (nN)} \tag{5}$$

Results and discussion

Friction

A series of ball on disc tests with different base oil/additives blends were conducted under the conditions described before. In the beginning of teach tests, the coefficient of friction is decreasing as a function of time for a period of time and stayed constant afterwards. The coefficients of friction of the different solutions at different normal loads are shown in Table 2.

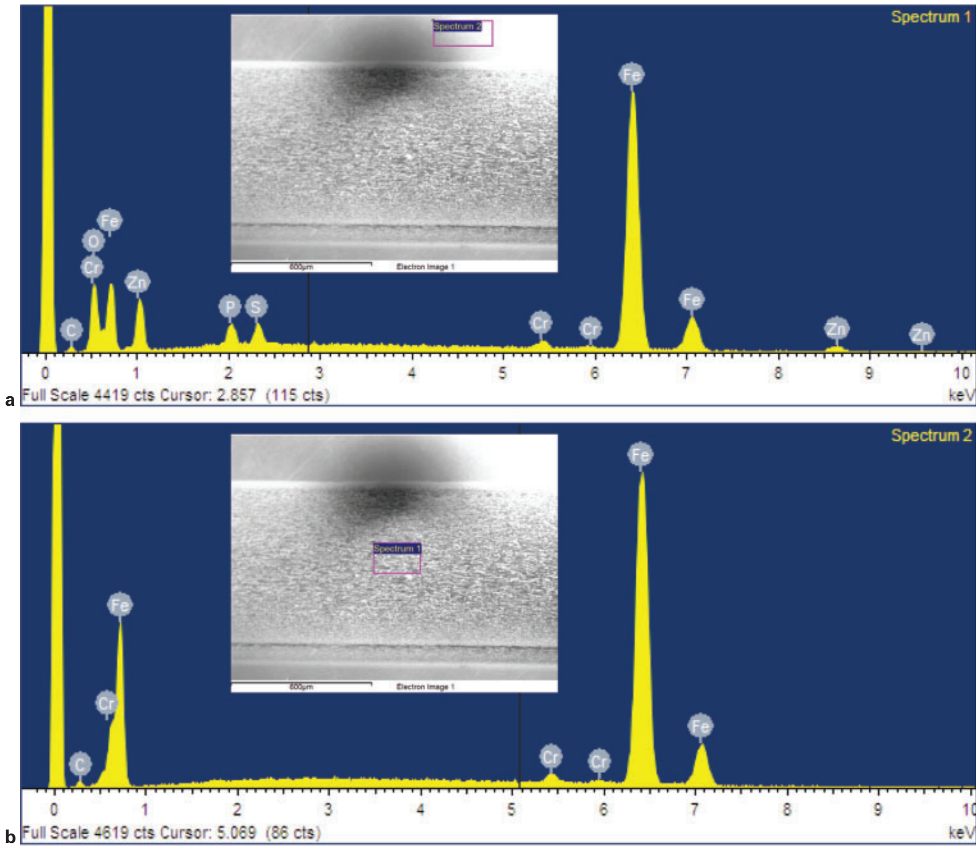
As can be seen from Table 2 the coefficient of friction increases when ZDDP is present in the lubricant. However, one can notice that the degree of friction increase is higher for the case of hexadecane base oil.

Surface analysis

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis performed on the balls after tribological tests showed that the traces of elements present in the additives are only found inside the rubbing track. No traces of additive reaction could be found outside the rubbing track. Further analysis revealed that the traces of additive are only found at the asperity tip where the real contact is occurred. An example of SEM and energy dispersive X-ray spectroscopy analysis is presented in Fig. 1.

Table 2 Steady state coefficient of friction after 1 h rubbing time for polar base oil diethylenglycoldiethyleter and non-polar oil hexadecane with different contents of ZDDP

	n-hexadecane		Diethylenglycol dibutyl ether	
	P=1·3 GPa	P=2·4 GPa	P=1·3 GPa	P=2·4 GPa
0% ZDDP	0·080	0·060	0·125	0·100
2% ZDDP	0·120	0·080	0·140	0·105
5% ZDDP	0·110	0·085	0·135	0·110



1 Energy dispersive X-ray spectroscopy spectra and SEM images *a* inside and *b* outside rubbing track of specimen tested with DEG+2 wt-% ZDDP

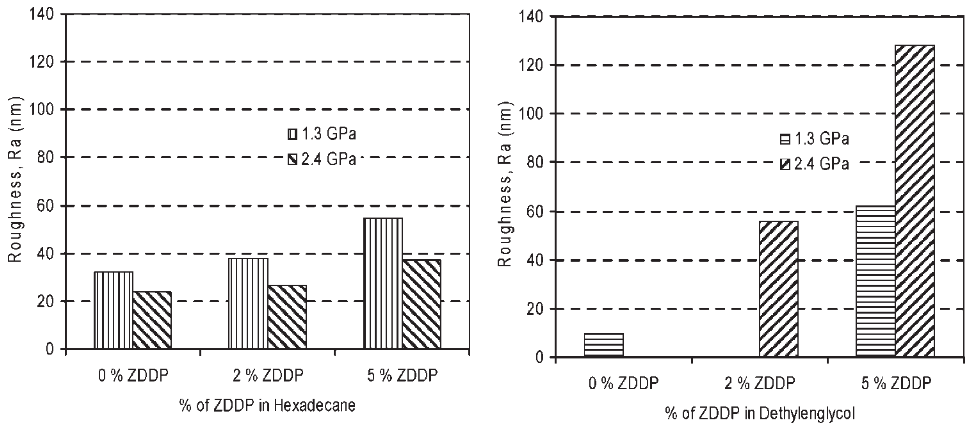
Surface roughness of the rubbing track after each experiment was analysed using WYKO optical profilometer and the results are shown in Fig. 2.

It is apparent from Fig. 2 that the addition of ZDDP increases surface roughness in both base oils, however, the roughening of the layer is more prominent when ZDDP is blended in the polar base oil. The authors' investigations using an adapted interferometry technique[25,26] suggest that the reaction layer formed when ZDDP is blended in a non-polar base oil is thicker than the reaction layer derived from polar base oil ZDDP solution. The interaction of the base oil molecules with the additive molecules determine the reaction layer formed and it is in the origin of the different tribological behaviour observed. The different characteristics of the ZDDP derived layer formed on rubbing surfaces are thought to be responsible for the difference in the measured coefficient of friction.

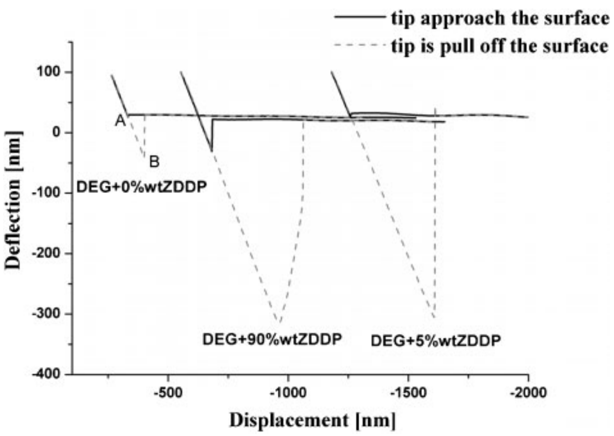
Atomic force microscopic results

The objectives of the experiments under oil were to establish the feasibility of imaging and friction force measurement, and to investigate the possibility of using the AFM tip to simulate a single asperity contact in a tribological situation, thereby providing a route to study additive derived layer formation processes[28] and explain the differences observed in the macrotribological tests.

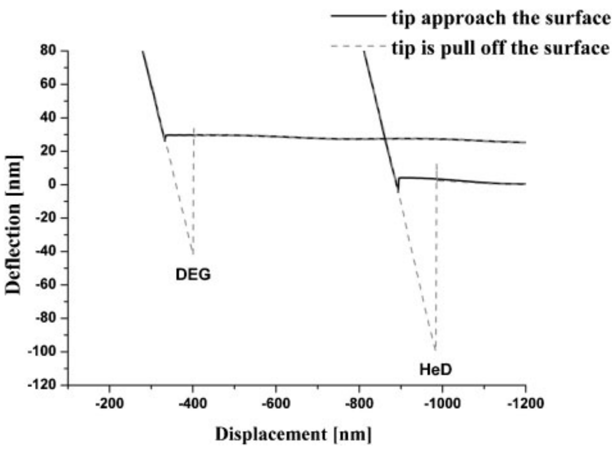
To understand the nature of interaction between the cantilever tip and the surface, the deflection displacement curves were recorded, before every measurement. Figure 3 shows the deflection of the cantilever tip as a function of the distance from the film surface. In all



2 Comparison of roughness after tribo tests



3 Pull of force curves of investigated samples



4 Pull of force curves of surface with DEG and HeD oil

cases, a full line indicates the tip approach to the surface and a dashed line represents the tip being pulled away from the surface. The vertical separation between the point where the tip was touching the film A and the point where the tip was pulled off the film B together with the spring constant of the cantilever (0·22 nN nm^{-1}) were used to calculate the pull off (adhesive) force.[30] The pull off forces for samples with DEG+0%ZDDP, DEG+5%ZDDP, DEG+90%ZDDP were 16·8, 70·4 and 66·7 nN respectively. It can clearly be seen that the pull off force decreases significantly with the addition of ZDDP, with respect to the value obtained for pure base oil. The pull off forces values when ZDDP was added to the base oil were very similar for any additive concentration. This fact is related to some plastic deformation that occurred due to the presence of a relatively soft surface film.

Additionally, pull of force comparisons between pure DEG and pure HeD base oils were carried out. Figure 4 shows the deflection of the cantilever tip as a function of the distance from the surface.

The pull off force values of these samples are similar indicating that under these rubbing conditions there is no layer formation in the absence of ZDDP additive.

In Table 3 detailed information about AFM measurements and calculation is summarised.

Figure 5 shows the dependency of FFV (representative of friction coefficient) versus set point (representative of load) for DEG mineral oil without and with additives is different concentrations.

Since results for HeD were very similar to those for DEG and they are presented in the following figures.

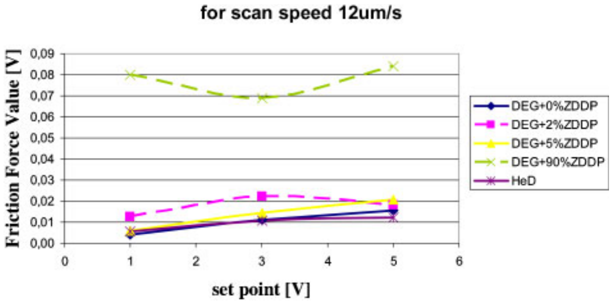
The friction additive concentration relation observed in the nanoscale measurements shows the same tendency as observed in the macrotribological tests, i.e. increase in friction by addition of ZDDP.

Figure 6 shows the dependency of FFV versus scan speed.

As can be seen from Fig. 6 the scanning speed does not significantly influence FFVs.

Table 3 Atomic force microscopic data

Set point, V	Set point, nN	Scan speed, μm s^{-1}	FFV, V	FFV, nN	Spring constant, nN nm^{-1}	Defl INVOLVS, nm V^{-1}	Distance, nN	μ friction coefficient
DEG+0% ZDDP								
1	10·405	12·52	0·0042	0·044	0·235	44·18	16·863	0·002
1	10·405	37·56	0·0041	0·042	0·235	44·18	16·863	0·002
3	3..215	12·52	0·0110	0·114	0·235	44·18	16·863	0·002
3	31·215	37·56	0·0181	0·188	0·235	44·18	16·863	0·002
5	52·025	12·52	0·0156	0·163	0·235	44·18	16·863	0·003
5	52·025	37·56	0·0245	0·255	0·235	44·18	16·863	0·004
DEG+5% ZDDP								
1	9·105	12·52	0·0058	0·05	0·224	40·60	74·779	0·001
1	9·105	37·56	0·0075	0·07	0·224	40·60	74·779	0·001
3	27·314	12·52	0·0145	0·13	0·224	40·60	74·779	0·001
3	27·314	37·56	0·0145	0·13	0·224	40·60	74·779	0·001
5	45·523	12·52	0·0208	0·19	0·224	40·60	74·779	0·002
5	45·523	37·56	0·0185	0·17	0·224	40·60	74·779	0·001
DEG+90% ZDDP								
1	9·556	12·52	0·0801	0·76	0·229	41·63	66·71	0·010
1	9·556	37·56	0·0876	0·83	0·229	41·63	66·71	0·012
3	28·670	12·52	0·0688	0·66	0·229	41·63	66·71	0·007
3	28·670	37·56	0·1169	1·11	0·229	41·63	66·71	0·012
5	47·783	12·52	0·0840	0·80	0·229	41·63	66·71	0·007
5	47·783	37·56	0·0919	0·87	0·229	41·63	66·71	0·008



5 Friction force value versus SP for scanning speed 12 μm s^{-1}

Additional experiments were performed to study the effect of rubbing time on friction for DEG base oil with or without the additive and for HeD.

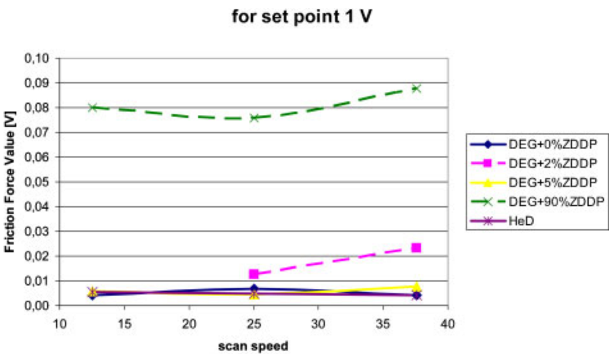
Figure 7 presents behaviour of FFVs with number of scans.

It can be assumed from Fig. 7 that in nanoNewton load range there is no influence of rubbing time on FFVs. There is no evidence for the build-up of an antiwear film.

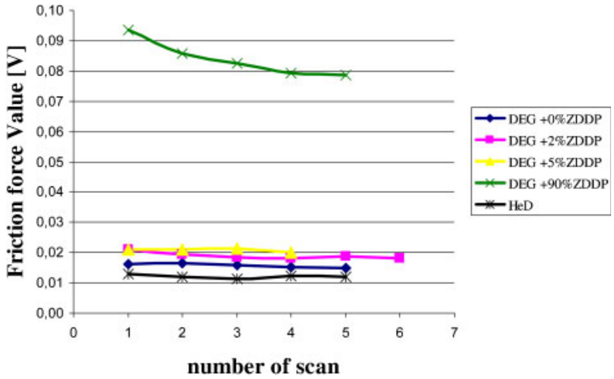
In order to compare conditions in the AFM wear test with those in the ball on disc test, the authors may a crude estimation of the peak AFM local contact pressure, assuming an elastic Hertzian contact with a tip radius of 10–50 nm and an applied load of 500 nN, to be of the order of 1 GPa. In the WAM ball running at 100 and 600 N load, the calculated Hertzian contact of 1·34 GPa (contact diameter 0·38 μm) and 2·43 GPa (contact diameter 0·69 μm). In case of single asperity contact with AFM tip and sample, there does not appear to be evidence for the presence of a reacted ZDDP based layer in the AFM images. This is perhaps not surprising given that the AFM test is carried out at room temperature with a maximum scan speed of 30 μm s^{-1}, whereas in a pin on disc experiment the parts may move with peak relative velocities of the order of several metres per second over several hours with oil temperatures in the range 80–120 C.

Conclusions

The results presented here clearly show that base oil polarity changes the tribological behaviour and the effect it makes when ZDDP is added. Non-polar base oil (HeD) ZDDP solution generates a tribofilm more rapidly and thicker than that of polar base oil (DEG) ZDDP solutions. The nature of ZDDP as polar molecules will of course make ZDDP to have higher



6 Friction force value versus scan speed for set point 1V



7 Friction force value versus number of scans for set point 5V and scan speed 12 μm s^{-1}

probability to reach the steel surface when dissolved in non-polar oil compared to the case when dissolved in polar base oil. Furthermore, since it is known that the reaction layer formed by ZDDP increases friction, the amount of the ZDDP reaction layer on the rubbing track will also determine the degree of friction increase. Therefore, since the authors observed that for the case of non-polar base oil the reaction layer is thicker compared with that of polar base oil, the increase of the degree of friction is also expected to be higher. The same tendency was observed for the test carried out using AFM, for different additive concentrations and applied loads, showing the connection between the phenomena occurring at the atomic level and the overall macroscopic behaviour. Atomic force microscopic force distance curves indicate the existence of soft surface layer when ZDDP is added to the base oil for any additive concentration. Micromechanical properties of this layer are important in relation to the formation action of antiwear film during severe tribological stresses. Unfortunately, AFM scanning in base oil containing ZDDP, at a high load and scan rate did not lead to the build-up of an anti wear film. This fact shows that single asperity contact temperatures during AFM scans are much lower compared to those presented in real machine parts.[27] However, this technique is a perfect choice for investigation of already built-up layers after tribological tests, their morphology, topography and micromechanical properties, additionally deflection displacement measurements allow to understand adhesion, elastic and viscoelastic characteristics.

The polarity of the base oil molecules determines the way the additive molecules can reach and attach to the surface, influencing the final structure and characteristics of the ZDDP derived reaction layer.

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