EFFECT OF BASE OIL POLARITY ON MICRO AND NANO FRICTION BEHAVIOUR OF BASE OIL +ZDDP SOLUTIONS

A. Bogus-Tomala, I.C. Gebeshuber
Institut für Allgemeine Physik, Vienna University of Technology,
Wiedner Hauptstrasse 8-10/134, 1040 Wien, Austria

A. Naveira-Suarez, R. Pasaribu
SKF Engineering and Research Centre,
Kelvinbaan 16, 3439 MT Nieuwegein, The Netherlands

A. Naveira-Suarez
Lulea University of Technology,
Universitetsområdet, Porsön, 971 87 Lulea, Sweden

I.C. Gebeshuber
AC2T research GmbH, Austrian Center of Competence for Tribology,
Viktor Kaplan-Strasse 2, 2700 Wiener Neustadt, Austria

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1 Abstract

Ball-on-disc tribo tests and atomic force microscopy (AFM) were used to analyze 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 optimization of lubrication in various solutions, in particular with regard to the type of additive and amount needed.

To characterize the influence of oil polarity, two reference base oils (hexadecane – non polar and diethylenglycol - polar) were blended with different concentrations of ZDDP-C_4, and the solutions were tested. A monolayer of base oil/additive solution is deposited on an ASI 52100 steel plate and is scanned on AFM contact mode under several rubbing time and applied load conditions.

An AFM technique is developed to estimate 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) we observed a significant different of friction behaviour (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 that will be discussed in more detail below. This results display the importance of base oil polarity on the friction behaviour of formulated lubricants containing additives.

2 Introduction

Commercially available lubricants contain base oil and functional additive packages to achieve a desired performance for a specific application. ZDDPs have been widely used in the past decades as additives in engine lubrication oil. ZDDPs were initially used as antioxidants, but their excellent antiwear properties were quickly recognized. They can also act as mild extreme pressure agents and corrosion inhibitors. ZDDP additives have also been the object of a great deal of research due to that multifunction performance and the complexity of the mechanism that leads to it. Several studies have proved ZDDP to have detrimental effects on wear under certain operation conditions [1], and to enhance a friction increase when the system is operating under mixed and boundary lubrication conditions [2,3].

The atomic force microscope (AFM) is a fundamental instrument for the study of surfaces at the nanoscale, providing a method of measuring ultra small forces between a single asperity probe tip and the sample surface. AFM does not provide information about the chemical nature of surfaces. AFM now is a widely-used tool in tribology to study dry lubricant films (i.e. coatings) and also films formed by liquid lubricants. Concerning the last, AFM can provide information of the morphology and topography [2-4] 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 sample can be investigated.

The aim of the present study is to explore the use of atomic force microscopy to provide information on the relation between the friction behaviour of ZDDP derived anti-wear films formed on tribological specimens under conditions matching the real conditions in bearing applications (macrotribological tests) and the friction resulted from using the AFM tip as a simulation for an asperity contact [5]. The objective is to characterize the origin of the differences observed in friction behaviour for tribological tests when ZDDP is blended in oils with different polarity.

3 Experimental details

3.1 Macro-tribological tests

3.1.1 WAM5 ball-on-disc test rig

A WAM5 test rig was utilised to evaluate the tribological performance of additive-base oil blends at controlled temperature, load, speed and slip ratio. The test configuration is ball-on-disc. The ball and the disc are driven independently by motors allowing controlled slip ratio.

3.1.2 Test samples

The steel balls (20 mm diameter) were of AISI 52100 steel with a hardness of 59-66 HRC and an average roughness (Ra) of 10 nm. The rings were washers (WS 81212) from SKF Cylindrical Thrust Roller Bearings (CRTB) of AISI 52100 steel with hardness 59-66 HRC and Ra=100nm. The rings are assembled in a holder to attach them to the rotating shaft of the test rig. The specimens were cleaned prior to testing by successive immersion first in an ultrasonic bath of petroleum ether for 10 minutes and then acetone for 10 minutes.

In order to study the influence of base oil polarity on tribological performance, one polar oil, diethylenglycol diethyleter (DEG), and one non polar oil, hexadecane (HeD), were selected. Both are low-viscosity model base oils. C_4 primary zinc dialkyldithiophosphate (ZDDP), with 99% purity, is employed in simple solution in both base oils without other additives present.

3.1.3 Test conditions

Base oil polarity effect on ZDDP behaviour is studied in mixed rolling/sliding contact with a 5% slip. The tribotests were carried out at applied loads of 100 and 600N. , 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 slip ratio was set constant at 5%. The %slip is defined as sliding 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 speed was set as 0.5 m/s. Temperature for all the tests was set constant at 90°C. The tests were conducted for 1 hour rubbing time. Pure base oil and two different concentrations, 2 and 5 wt% ZDDP, were tested. Under these conditions the EHD 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.

3.2 Nanotribological tests

3.2.1 Atomic Force Microscopy

Measurements were performed with an AFM MFP-3D atomic force microscope (by Asylum Research, Santa Barbara, CA) in contact, constant force mode using non conductive silicon nitride cantilevers with a spring constant k = 0.2 N/m and a resonant frequency f_0 = 38 kHz (Veeco).

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

3.2.2 Test samples

The steel plates used were of AISI 52100 steel with a hardness of 59-66 HRC and an average roughness (Ra) of 10 nm.

3.2.3 Test conditions

The main measurement parameters were: a scan size from 5x5 to 80x80 μm² (512 scan points and 512 scan lines), a scan rate from 0.5 to 2 Hz, scan angle of 90°, and a set point from 10 nN to 50nN in contact mode. The recorded data was 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 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 whilst 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 the ball on disc experiments we estimate AFM single asperity contact pressure. For the tip we used for measurements the radius is 20 nm and the applied load has a maximum of 50nN; the range of contact pressure is on the order of 100 MPa. The ball on disc experiments were performed at comparable contact pressures in the range of 1-2GPa.

3.2.4 Friction calculations

Bhushan introduces two methods to measure the friction [6]. For the presented 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, since there is relative motion between the sample and 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 set point parameter in the feedback loop, the normal force applied between probing tip and sample surface can be changed.

The scan sizes were 5 µm by 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 (LTVavg) and Lateral Retrace (LRTVavg) 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 [1].

$$FFV = \frac{|LTV_{avg} - LRTV_{avg}|}{2} \qquad (1)$$

The measurements of the friction force values were repeated ten times in every environment (water, water + additive) to obtain representative and repeatable results.

Assuming that the friction in the nanoscale follows Amonton's law, the friction force is given by:

$$FFV = \mu \cdot (SP + F_0) \qquad (2)$$

Where µ is the friction coefficient, the set point (SP) is the applied load and F_0 is a force constant. Following the procedure suggested by Beake et al. [6], the force constant is nearly equal to the pull off force determined from the force distance curves.

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

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 Newtons, the lateral force needs to be calibrated by the determination of the slope of deflection vs. 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:

FFV [V] × InvOLS [nm/V] × spring constant [nN/nm] = FFV [nN]

SP [V] × InvOLS [nm/V] × spring constant [nN/nm] = SP [nN]

4 RESULTS AND DISCUSSION

4.1 Friction

A series of ball-on-disc tests with different base oil/additives blends were conducted under the conditions described above. In the beginning of each tests, the coefficient of friction decreases as a function of time for some time and stays constant afterwards. The coefficients of friction of the different solutions at different normal load are shown in Table 2.

Table 2: Steady state coefficient of friction after one hour rubbing time for polar base oil.

	Hexadecane		Diethylenglycol	
	1.3 GPa	2.4 Gpa	1.3 GPa	2.4 Gpa
0 % ZDDP	0.08	0.06	0.125	0.1
2 % wt ZDDP	0.12	0.08	0.14	0.105
5 % wt ZDDP	0.11	0.085	0.135	0.11

4.2 Surface analysis

Scanning Electron Microscopy (SEM) and X-Ray Diffraction Spectroscopy (EDS) analysis performed on the balls after tribological tests show 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 reveals that the traces of additive are only found at the asperity tip where the real contact is occurred.

An example of SEM-EDS analysis is presented in the following figure.

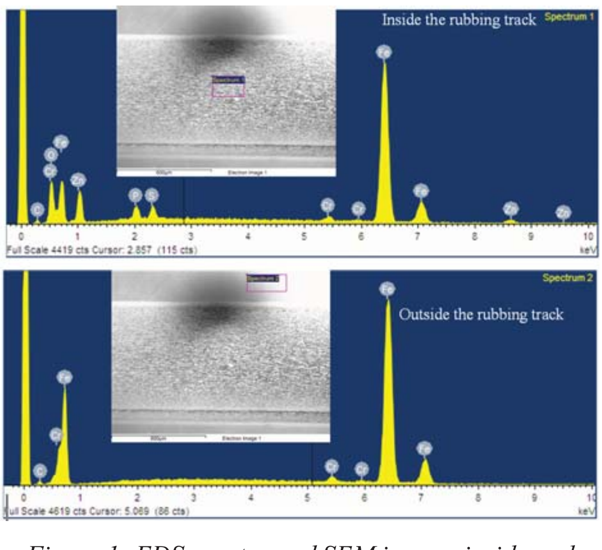

Figure 1: EDS spectra and SEM images inside and outside the running track of specimen tested with DEG + 2% wt ZDDP.

Surface roughness of the rubbing track after each experiment were analysed using a WYKO optical profilometer and the results are shown in the following figure.

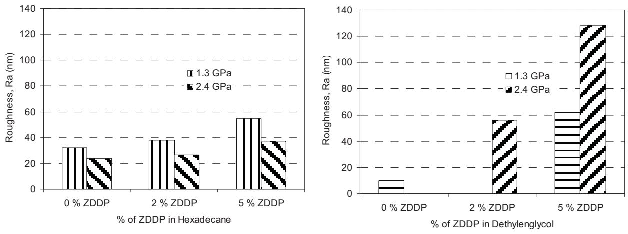

Figure 2: Comparison of roughness after the tribo tests.

It is apparent from Figure 2 that the addition of ZDDP to base oil increases the surface roughness but the degree of surface roughness increase is more pronounced when ZDDP is blended with diethylenglycol.

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 larger for the case of hexadecane base oil.

4.3 AFM 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 novel route to study wear and film formation processes.

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 cases, the full line indicates the tip approach to the surface and the dashed line represents the tip being pulled away from the surface. The vertical separation between the point where the tip is touching the film (A) and the point where the tip is pulled off the film (B) together with the spring constant of the cantilever (0.22 nN/nm) are used to calculate the pull off (adhesive) force [7]. The pull off forces for samples with DEG+0%ZDDP, DEG+5%ZDDP, DEG+90%ZDDP are 16.8nN, 70.4nN, 66.7nN respectively (+-sd). It can clearly be seen that the pull off force decreases significantly with the addition of ZDDP, compared to the value obtained for pure base oil. When ZDDP is added to the base oil, the pull off force values are very similar for all the additive concentrations investigated. This fact is related to plastic deformation due to the presence of a relatively soft surface film.

Additionally pull of force comparison between pure DEG and pure HeD base oils have been carried out.

Figure 4 show 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 this rubbing conditions there is no film formation in the absence of ZDDP additive.

In the table 3 detail information about AFM measurements and calculation were summarized.

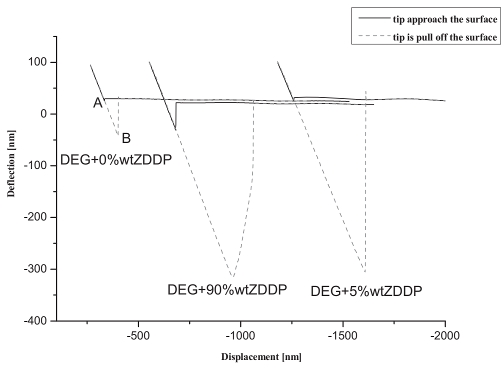

Figure 3: Pull of force curves of investigated samples.

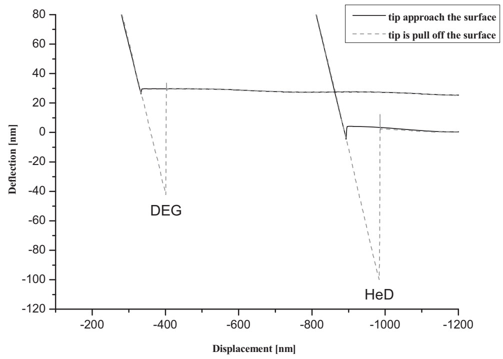

Figure 4: Pull of force curves of surface with DEG and HeD oil.

Figure 5 show the dependency of Friction Force Value (representative of friction coefficient) versus Set Point (representative of load) for DEG mineral oil without and with additives in different concentrations.

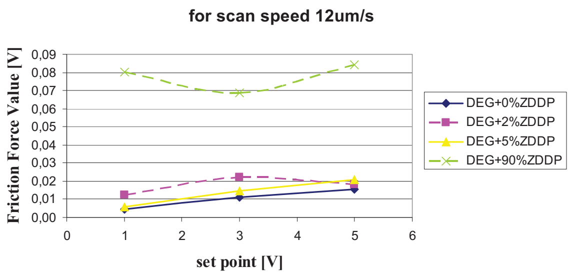

Figure 5: Friction force value vs. set point for a scanning speed of 12 μm/s.

The friction-additive concentration relation observed in the nanoscale measurements, shows the same tendency as observed in the macroscale tests.

Table 3: AFM data

Set point [V]	Set point [nN]	Scan speed [µm/s]	FFV [V]	FFV [nN]	Spring constant [nN/nm]	Defl INVOLVS [nm/V]	Distance [nN]	µfrictionCoefficient
				DEG + 0% ZDDP				
1	10,405	12,52	0,0042	0,044	0,235	44,18	16,863	0,00161
1	10,405	37,56	0,0041	0,042	0,235	44,18	16,863	0,00157
3	31,215	12,52	0,0110	0,114	0,235	44,18	16,863	0,00238
3	31,215	37,56	0,0181	0,188	0,235	44,18	16,863	0,00392
5	52,025	12,52	0,0156	0,163	0,235	44,18	16,863	0,00268
5	52,025	37,56	0,0245	0,255	0,235	44,18	16,863	0,00370
				DEG + 5% ZDDP				
1	9,105	12,52	0,0058	0,05	0,224	40,60	74,779	0,00063
1	9,105	37,56	0,0075	0,07	0,224	40,60	74,779	0,00082
3	27,314	12,52	0,0145	0,13	0,224	40,60	74,779	0,00129
3	27,314	37,56	0,0145	0,13	0,224	40,60	74,779	0,00130
5	45,523	12,52	0,0208	0,19	0,224	40,60	74,779	0,00157
5	45,523	37,56	0,0185	0,17	0,224	40,60	74,779	0,00140
				DEG + 90% ZDDP				
1	9,556	12,52	0,0801	0,76	0,229	41,63	66,71	0,01004
1	9,556	37,56	0,0876	0,83	0,229	41,63	66,71	0,01097
3	28,670	12,52	0,0688	0,66	0,229	41,63	66,71	0,00690
3	28,670	37,56	0,1169	1,11	0,229	41,63	66,71	0,01172
5	47,783	12,52	0,0840	0,80	0,229	41,63	66,71	0,00701
5	47,783	37,56	0,0919	0,87	0,229	41,63	66,71	0,00767

Figure 6 show the dependency of friction force value versus scan speed.

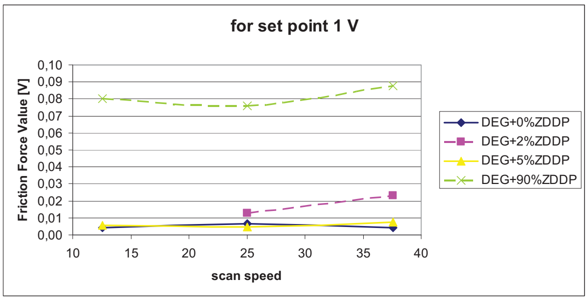

Figure 6: Friction force value vs. scan speed for set point 1V.

As it can be seen from Figure 6 the scanning speed does not influence friction force values.

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

Figure 7 presents the behavior of friction force values with the number of scans.

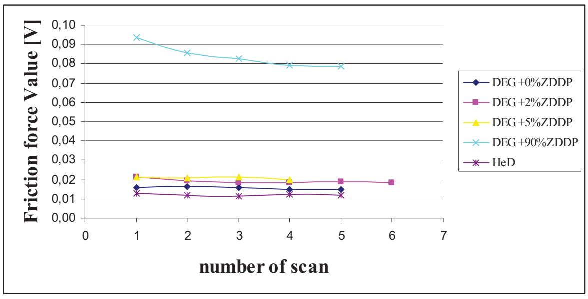

Figure 7: Friction force value vs. number of scans for a set point of 5V and a scan speed of 12 µm/s.

It can be assumed from Figure 7 that in the nN load range there is no influence of rubbing time on friction force values. There is no evidence for the build-up of anti-wear film.

In order to compare conditions in the AFM wear test with those in the ball on disc test, we may crudely estimate the peak AFM local contact pressure, assuming an elastic Hertzian contact with a tip radius of 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). Despite the comparable contact pressures, 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, whereas in a cam and tappet system in an internal combustion engine the parts may move with peak relative velocities of the order of several meters per second over several hours with oil temperatures in the range 80-120 C.

5 Conclusions

The results presented here showed clearly that base oil polarity change the tribological behaviour and the effect it makes when ZDDP is added. Non-polar base oil (Hexadecane)-ZDDP solution generates a tribofilm more rapidly and thicker than that of polar base oil (Diethylenglycol) solutions. The nature of ZDDP as polar molecules will of course make ZDDP to have higher 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. The same tendency is observed for the tests carried out using atomic force microscopy (AFM), for different additive concentrations and applied loads, showing the connection between the phenomena occurring at the atomic level and the overall macroscopic behaviour. Polarity of the oil influences the growth rate and film thickness of ZDDP antiwear films. The polarity of the molecules determines the way they cover and attach to the surface, influencing the final structure and characteristics of the reaction film.

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