Effect of ZDDP on Friction and Wear in Fretting Contacts

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Abstract: The effect of ZDDP on fretting wear was investigated in a ball on flat machine. The results confirm previous work that anti-wear agents may reduce friction and wear in fretting contacts. It was further found that temperature, adsorption time and base oil polarity were all important parameters affecting the ability of ZDDP to protect the surfaces against fretting wear.

Key words: Fretting, ZDDP, Friction

1. INTRODUCTION

The term fretting is used for describing contact conditions where two surfaces in mechanical contact are subjected to low amplitude oscillatory movements, thus vibrations in machine components is a classical source for fretting conditions. Fretting causes damage to the contacting surfaces in the form of wear, corrosion and fatigue crack initiation. The damaged surfaces may eventually result in failure of the components. The low amplitudes typical for fretting conditions results in such contact conditions where the central parts of the contact are not directly exposed to the surrounding atmosphere. Further, any wear debris created during the wear process may because of the low amplitudes get trapped inside the contact.

Several different factors are affecting fretting wear, viz. contact pressure, temperature, amplitude of motion, frequency, number of cycles, surface hardness, friction coefficient, lubrication, type of base oil, humidity as well as other environmental parameters[1-3].

From the literature, three means of attacking the problem of fretting may be identified viz. 1) reducing relative slip or vibration, 2) increase the surface strength of the contacting surfaces by changing material or coating the surfaces, 3) reduce friction. The latter mean, i.e. reducing friction, can frequently be obtained by the introduction of a lubricant.

Despite the wide use of liquid lubricants, surprisingly little work is reported on the effect of these on fretting, and in particular, reports on the effect of lubricant additives such as anti-wear or extreme pressure agents are scarce. However, some previous work indicates that these additives may be effective in preventing fretting wear. Godfrey [2] found that certain phosphorous based additives, e.g. tricresyl phosphate and triethyl phosphorothioate were capable of reducing fretting wear by forming reaction films on the contacting surfaces. Law and Rowe [3] investigated the effect of additives commonly used in transmission- and gear oils on fretting and found that the result was highly dependent on the additive system. Qiu and Roylance [4] investigated the effect of various sulfur containing anti-wear additives on friction and wear in fretting contacts. The results show that these additives were effective in reducing friction and wear under the conditions studied.

In this work, the effect of iso-C_4-ZDDP (zinc dialkyl dithiophosphate) on friction in fretting contacts was investigated, and in particular the effect of adsorption time and base oil polarity was addressed. A polar base oil is expected to compete with ZDDP for a place on the surface to a larger extent than a non-polar base oil,[5] thus reducing any effect of ZDDP.

2. EXPERIMENTAL

The fretting tests were conducted on an in-house designed fretting rig with a ball-on-flat configuration with a sample cell facilitating immersion of the contact in the oil as well as control of the oil temperature. Hexadecane (Acros chemicals, purity 99%) and Diethyleneglycol dibuthyl ether (DEGB) (Acros chemicals, 99%) were used as non-polar and polar low-viscosity model base oils, respectively. The iso-C4-ZDDP used in the experiments was supplied from A&S Chemie. The test samples (ball and flat) were of 52100 steel with a surface roughness (Ra) of 10 nm, the test conditions are summarized in table 1.

Table 1. Contact conditions.

Pressure	1 GPa
Frequency	20Hz
Amplitude	25µm
Temperature (bulk)	Room temperature or 80°C

The tested surfaces were subsequently characterized by optical microscopy, Scanning electron microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) and with as Wyko surface profiler.

each statement, note or the surname of the author(s) cited, e.g., “it was shown by Jones [1] that…”. Where more than two authors are involved, the reference in the text should be of the form “it was shown by Jones et al [4]”.

3. RESULTS AND DISCUSSION

Firstly, the fretting behavior of the pure model base oils were evaluated in the fretting rig. Measurements were performed at different adsorption times i.e. the surfaces were exposed to the lubricant at different times before the measurements were executed. Figure 1 shows the evolution of friction coefficient with number of cycles for DEGB at room temperature.

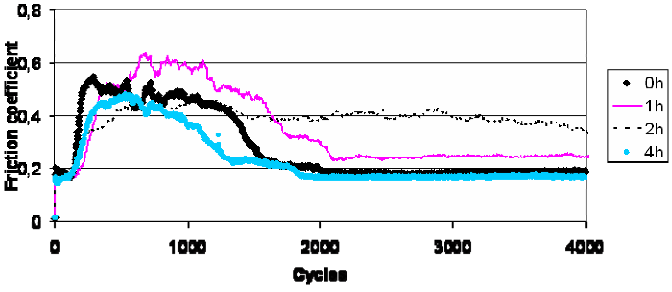

Figure 1. Friction coefficient as a function of fretting cycles for DEGB at room temperature and at four different adsorption times.

As can be seen in the figure, the friction coefficient is low (~0.2) for the first 170 cycles implying that the DEGB is protecting the surfaces, probably by forming an adsorbed layer on the surfaces. It is expected that DEGB will adsorb on the polar steel surfaces as it also is quite polar. It is desirable to have a low friction as this helps minimize the damage of the surface and the first period of low friction likely corresponds to adsorbed DEGB being able to protect the surfaces against wear, as this protective layer finally, after ca 170 cycles, breaks down, friction increases and wear of the metal surfaces are observed (the correlation between friction and wear will be shown later). At higher cycles, wear debris is formed acting effectively as rolling elements decreasing the friction. It can also be seen that the friction coefficient curves are very similar i.e. there is no obvious effect of adsorption time.

As the temperature is raised to 80°C, the induction time more or less vanishes for DEGB, see Figure 2. This behavior is most likely due to a weaker adsorption of DEGB at the higher temperature, consistent with physisorption of the lubricant molecules to the surface. Again, no effect of waiting time is observed as the curves more or less coincide.

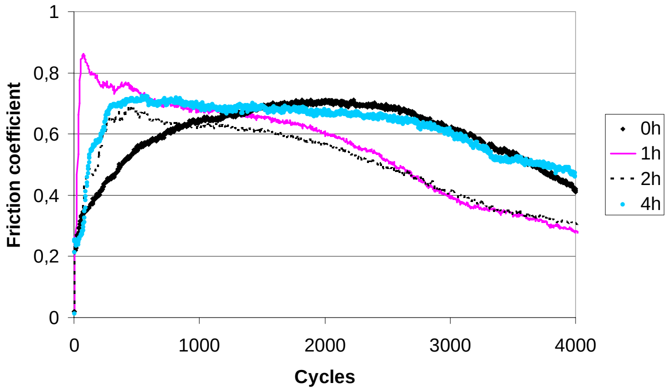

Figure 2. Friction coefficient as a function of fretting cycles for DEGB 80°C and at four different adsorption times.

Figure 3 shows the friction curves determined for the pure non-polar base oil (hexadecane) at room temperature. The curves show no induction period as the curves immediately goes to high friction coefficients i.e. the hexadecane is not able to protect the surfaces even at very few cycles. This is expected as the non-polar hexadecane is expected to interact weakly with the polar steel surfaces i.e. the hexadecane molecules are less strongly adsorbed to the surfaces than the polar DEGB molecules. At 80°C, very similar curves as in Figure 3 were obtained (not shown), again suggesting a weak interaction between hexadecane and the steel surfaces.

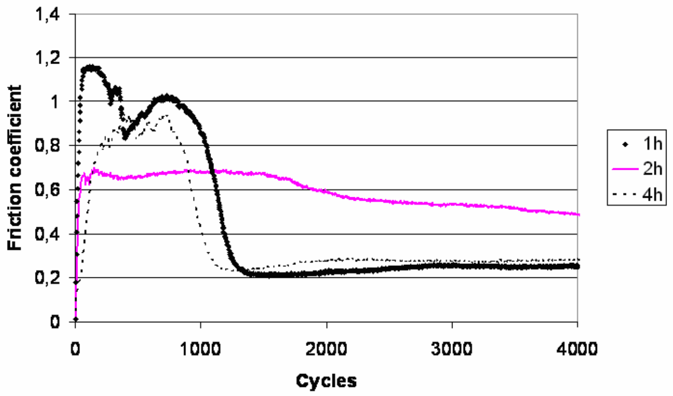

Figure 3. Friction coefficient as a function of the number of fretting cycles determined at different waiting times for pure Hexadecane at room temperature.

Optical micrographs of the wear scar after fretting revealed that the base oil caused differences in the appearances of the scars. Figure 4 shows typical optical micrographs of wear scars obtained with pure hexadecane and DEGB as lubricants.

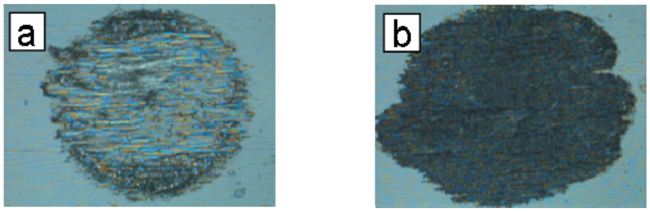

Figure 4. Optical micrographs of typical wear scars after fretting tests obtained with a) hexadecane and b) DEGB. The diameter of the scares were ca 160µm.

The wear scar obtained with hexadecane had a metallic appearance whereas the wear scar obtained with DEGB showed a black and matt appearance. An EDS analysis of the wear scars showed that the black surface obtained with DEGB as a lubricant was iron oxide, possible Fe3O4, as the oxygen levels were elevated whereas the carbon levels were in the same range as outside the scar. It has been reported that one of the functionalities of liquid lubricants in fretting contacts is that they may regulate the availability of oxygen which may react with the surfaces to create iron oxides during fretting. The solubility of oxygen in lubricant is one important parameter determining the availability of oxygen in the contact. However, for DEGB oxygen may also be supplied directly from the molecule since one molecule of DEGB contain 3 oxygen atoms. To elucidate if the oxygen originates from dissolved oxygen or directly from the lubricant molecules, more experiments are needed. The wear scars showed the same appearance irregardless if an additive was present or not under the conditions studied. When the behavior of the pure base oils had been established, the effect of ZDDP could be addressed. Figure 5 shows the friction coefficient as a function of the number of cycles for a 1% solution of ZDDP in DEGB at room temperature.

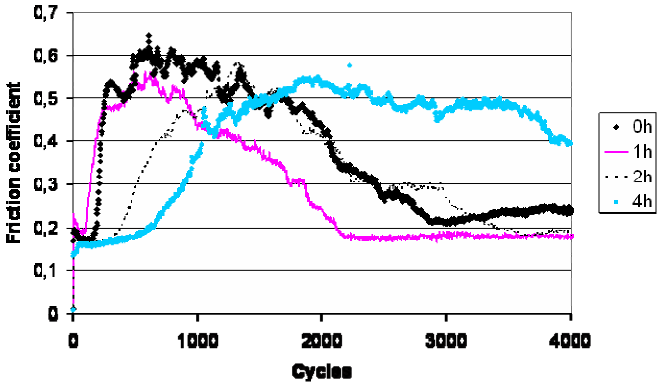

Figure 5. Friction coefficient as a function of fretting cycles for a 1% solution of ZDDP in DEGB at room temperature and at four different adsorption times.

At shorter adsorption times the “induction period”, where a low friction is obtained, is about the same as for the pure DEGB i.e. ca 170 cycles (see Figure 1) at longer adsorption times the induction period becomes substantially longer. This is substantially different than the curves for pure DEGB shown in Figure 1 and indicates that the ZDDP may protect the surface if given time to adsorb on the surface. Figure 6 shows the results obtained for a solution of 1% ZDDP in Hexadecane at room temperature.

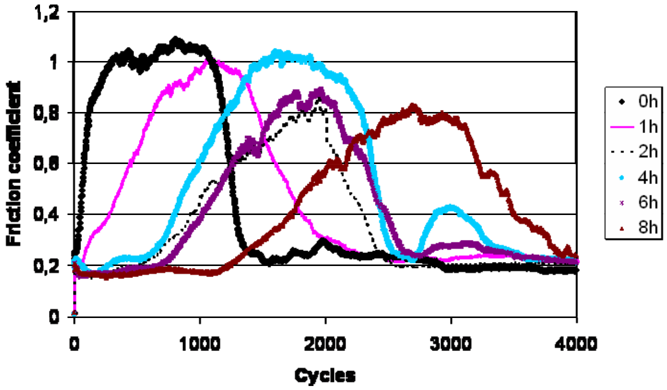

Figure 6. Friction coefficient as a function of fretting cycles for a 1% solution of ZDDP in Hexadecane at room temperature and at four different adsorption times.

The trend is similar as for ZDDP in DEGB viz. at short adsorption times (0h) the result is similar as for the pure base oil (no induction time was observed for pure Hexadecane) but at longer adsorption times a clear induction period where the ZDDP protects the surface emerges, so clearly there is an effect of adding ZDDP. By comparing Figures 5 and 6 it may be noticed that the induction period develops faster when ZDDP is adsorbed from Hexadecane than from DEGB which is expected since ZDDP will have larger problems replacing DEGB on the surface since DEGB is adsorbed stronger on the steel surface than Hexadecane. Energy Dispersive Spectroscopy (EDS) of the wear scars revealed traces of ZDDP in the form of zinc, phosphorus and sulfur, especially at the perimeter of the scars. Figure 7 shows a typical EDS spectrum recorded at the perimeter of a wear scar.

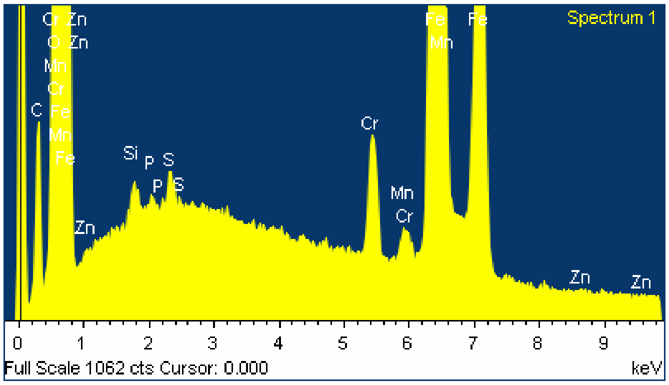

Figure 7. Typical EDS spectrum recorded from the edge of a wear scar. The fretting experiment was conducted at room temperature with 1%ZDDP in hexadecane as lubricant and after 4 hours waiting time.

To illustrate the protective power of ZDDP in fretting wear, an experiment at the same conditions as in Figure 6 (1% ZDDP in hexadecane, room temperature) was carried out but with the difference that the test was suspended after 350 cycles and the surfaces of the flat specimen were examined with optical microscopy and the Wyko surface profiler. Figure 8 shows the surface profiles and the corresponding optical micrographs at four different adsorption times.

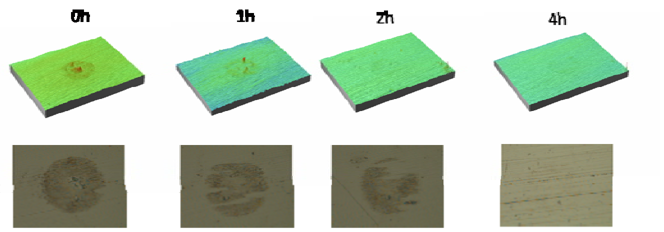

Figure 8. Wear scars measured with the Wyko surface profiler (top) and optical microscopy (bottom) on the flat specimen after 350 fretting cycles at different adsorption times. The lubricant used was a 1% solution of ZDDP in Hexadecane and the experiment was performed at room temperature.

As can be seen both from the surface profiles and the optical micrographs, the wear scars get less severe with increasing time, showing indeed that ZDDP protects the surface from fretting wear under the conditions studied, in agreement with previously reported findings for phosphor and sulfur containing EP/AW additives [4-6].

At 80°C, both the 1% ZDDP in hexadecane and the 1% ZDDP in DEGB showed the same trend viz. at this higher temperature the curves were shifted to the left as compared to at room temperature, i.e. the number of cycles that ZDDP was able to protect the surface decreased. Figure 9 shows the friction curves for 1% ZDDP in hexadecane at 80°C.

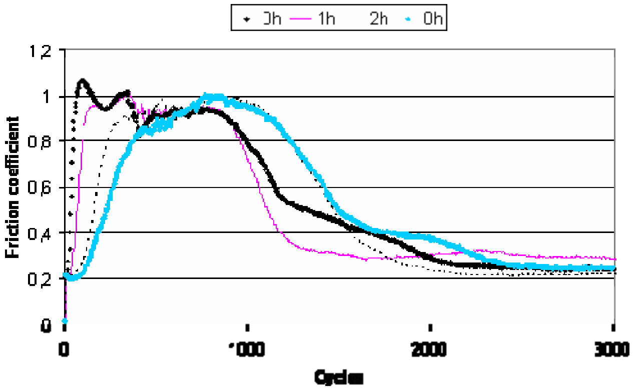

Figure 9. Friction coefficient as a function of the number of fretting cycles determined at different waiting times for hexadecane+1%ZDDP at 80°.

This observed behavior with a decreased efficiency in protecting the surfaces towards wear at higher temperatures (80°C) was unexpected considering that higher temperatures generally favors the formation of protective anti-wear films in sliding contacts, see e.g [8] and references therein, which may suggest that another mechanism could be active during fretting. The results, however, would be consistent with differences observed in the adsorption of ZDDP on iron oxide[9-13]. At low temperatures ZDDP is physisorbed whereas at higher temperatures, ZDDP is chemisorbed (or has started to degrade) on the surfaces. We speculate that either ZDDP is physisorbed in our measurements or, the fretting behavior of physisorbed (which should be dominating at room temperature) and chemisorbed (at higher temperatures) ZDDP is different and in the latter case, the physisorbed ZDDP shows a better capability in reducing fretting wear. We are currently trying to establish whether ZDDP is physisorbed or chemisorbed at higher temperatures in our system.

4. CONCLUSIONS

The effect of ZDDP in fretting wear was investigated. Experiments were carried out at different temperatures, different adsorption times and in two different model base oils with different polarities. It was found that under the conditions studied that ZDDP could reduce fretting wear and longer adsorption times resulted in better protection. The effect of ZDDP decreased with increasing temperature, probably due to different adsorption conditions. Further, it was found that base oil polarity is an important parameter since polar base oils will tend to compete with ZDDP for a place on the surface.

5. ACKNOWLEDGEMENTS

The authors wish to thank SKF for permission to publish this work. The work presented in this paper has been supported by the EC, Sixth Framework Programme, Marie Curie Action (WEMESURF research network entitled: ”Characterization of wear mechanisms and surface functionalities with regard to life time prediction and quality criteria-from micro to nano range” under contract MRTN CT 2006 035589).

REFERENCES

[1] Zhou, Z.R., Vincent, L. “**Lubrication in Fretting – a review**”, *Wear*, 225(2), pp. 962-967, (1999).

[2] Wang, Z.A., Zhou, Z.R, “**An investigation of fretting behavior of several synthetic base oils**”, *Wear*, 267, pp 1399-1404, (2009).

[3] Vingsbo, O., Söderberg, S. “**On Fretting Maps”,** *Wear*, 126(2), pp. 131-147, (1988)

[4] Godfrey, D. “**A study of Fretting Wear in Mineral Oil**”, *Lubr. Eng.*, 12(1), pp. 37-42 (1956).

[5] Law, D.A.; Rowe, C.N., “**Fretting Wear with Powertrain Lubricants**”, *Lubr. Eng.*, 43(8), pp. 616-622 (1987).

[6] Qiu, Y.; Roylance, B.J., “**The Effect of Lubricant Additives on Fretting Wear**”, *Lubr. Eng.*, 48(10), pp. 801-808 (1992)

[7] Naveira-Suarez, A., Grahn, M., Pasaribu, R., Larsson, R. “**The Influence of Base Oil Polarity on the Tribological Performance of Zinc Dialkyl Dithiophosphate Additives**.” Submitted to Tribology International.

[8] Spikes H.A. “**The History and Mechanisms of ZDDP**”, *Tribol. Lett.*, 17(3), pp.469-489, (2004).

[9] Plaza, S. “**The Adsorption of Zinc Dibutyldithiophosphate on Iron and Iron Oxide Powders**“ *ASLE Transactions*, 30(2), pp. 233-240, (1987)

[10] Plaza, S., “**The Effect of Other Lubricating Oil Additives on the Adsorption of Zinc Dibutyldithiophosphate on Fe and γ-Fe_2O_3 powders** “, *ASLE Transactions*, 30(2), pp. 241-247, (1987).

[11] Dacre, B., Bovington, C.H., “**The Adsorption and Reaction of Decomposition Products of Zinc Di-isopropyldithiophosphate on Steel**“, *ASLE Transactions*, 27(4), pp. 252-258, (1984).

[12] Dacre, B., Bovington, C.H., “**The Effect of Metal Composition on the Adsorption of Zinc Di-Isopropyldithiophosphate**“, *ASLE Transactions*, 26(3), pp. 333, (1982).

[13] Wu, Y.L. ; Dacre, B., “**Effects of Lubricant-Additives on the Kinetics and Mechanisms of ZDDP Adsorption on Steel Surfaces**“, *Tribol. Int.*, 30(6), pp. 445. (1997).