Tribology Online
Japanese Society of Tribologists

Tribology Online, 3, 3 (2008) 168-172.
ISSN 1881-2198
DOI 10.2474/trol3.168

Additives for Environmentally Adapted Lubricants – Tribo Film Formation

Anders Pettersson[1)], Kassfeldt Elisabet[1)*] and Ichiro Minami[2)]

[1)]Div. of Machine Elements, Luleå University of Technology
SE-97187, Luleå, Sweden
[2)]Dep. of Chemical Engineering, Iwate University
4-3-5 Ueda, Morioka, Iwate 020-8551, Japan
*Corresponding author: elisabet.kassfeldt@ltu.se

(Manuscript received 27 February 2008; accepted 28 March 2008; published 30 April 2008)

Five different anti-wear additives, suitable to formulate environmentally adapted hydraulic fluids, were tested. The used base fluid was a saturated, environmentally adapted synthetic complex ester. The tested materials were steel-steel and bronze-steel. A modified Falex pin and a vee-block tester were used for the tribotests. XPS was used to characterize the surfaces. It was found that the new types of more polar additives work better than the traditional ones, though they can give selective transfer of cupper to the steel pin. To use this type of additives in fully formulated products more investigations have to be performed.

Keywords: tribology, environmentally adapted lubricants, anti wear, additivation boundary lubrication, surface analysis, XPS, ESCA

1. Introduction

New lubricants have to satisfy many demands concerning performance, environmental adaptation and life cycle cost. One way to combine these properties is through the use of synthetic ester base fluids. The molecular structure for synthetic esters can be varied in numerous ways[1)]. Another way to achieve different properties for ester base fluids is the possibility to complexify ester molecules into complex esters. Complexification is done by replacing some of the fatty acids into di-acids, which then form bridges between ester molecules, and the molecular weigh are increased.

One promising group of base fluids for environmentally adapted lubricants is the saturated complex esters[1-3)]. This group of esters could be used to formulate lubricants with excellent high and low temperature stability and good environmental properties. The big challenge faced when saturated complex esters are used is that the additive response is quite different to unsaturated esters and very different to mineral oils and poly-alpha olefins. When using polar base fluids the polarity of the used additives has to be carefully noted.

In this study traditional additives for environmentally adapted lubricants are compared to newly developed additives with larger polarities regarding tribofilm formation capability. Earlier studies have investigated the wear protection and friction performance of these additives[4,5)].

Another phenomenon of note in boundary lubricated bronze contacts is selective transfer. This has been observed in bronze-steel contacts lubricated with synthetic esters[6)].

2. Tested fluids and additives

Fully formulated lubricants are made of one or more base fluids and many different types of additives such as AW, EP, Anti oxidants and corrosion inhibitors. The use of several additives increases the complexity of the task to understand the working principia of the additives. When formulating environmentally adapted lubricants, great care has to be taken concerning the effects of polarity and the synergistic/antagonistic effects between the base fluid and the additive or additive package. To study the effects of different EP and AW additives the use of one and two component blends is useful. In this study no fully formulated lubricants were studied.

2.1. Additives

The chosen additives are both standard state of the art additives for environmentally adapted lubricants and special additives suitable for more polar base fluids; see Table 1 and Fig. 1. The molecular weight for the tested base fluid is about twice as high as for the additives.

The additive abbreviated CM, Methylene -bisdialkyldithiocarbamate, is a sulphur additive with

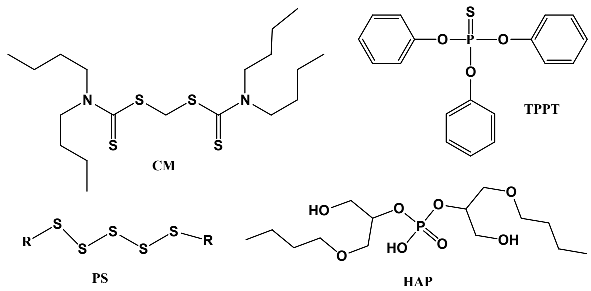

Fig.1 Molecular structure for the used additives

Table 1 Additive data

Notation	Chemical name
PS	Pentasulfie
TPPT	Triphenyl phosphorothionate
CM	[1] Methylene-bis-dialkyldithiocarbamate
HAP	Hydroxyalkyl phosphate
PSHAP	Mixture of PS and HAP

extreme pressure (EP) and anti wear (AW) effects, as well as some anti oxidative effects (AO). TPPT, triphenyl phosphorothionate, is a well-known AW additive that contains both sulphur and phosphor and is known to have some AO effects. The PS additive is a penta sulphide that is commonly used as an EP additive. HAP, hydroxyalkyl phosphate, is a special synthesized phosphorus containing AW additive with greater polarity than other investigated additives. The polarity makes it possible for the additive to access the surface.

2.2. Base fluid and formulated fluids

The tested base fluid is of the saturated synthetic complex ester type; for detailed data about the used base fluid, see part 1 of the study[5].

All the used formulations were additivated to 50 mmol/l concentrations except TPPT with a 100 mmol/l concentration and PSHAP with a mixture of 50 mmol/l of PS and 50 mmol/l of HAP. Fully formulated products normally have a lower concentration of additives than these experiment fluids. The high treat rates were chosen to prevent running out of additives in the tribo-contact during the test.

The HAP additive was prepared by making 0.5 mmol phosphonic acid react with 2.5 mmol of the epoxide in 0.5 ml ethanol. This reaction is spontaneous at room temperature[7]. The HAP additive solution was used to formulate the HAP and PSHAP fluids.

The tested materials in this study were SUJ2 steel and JM3 bronze. SUJ2 is a standard ball bearing steel and JM3 is a tin bronze, for details about the tested materials see part 1 of the study[5]. All the tests were run with a Falex corporation AISI/SAE 3135 steel pin, (HRB 87-91) as counter surface.

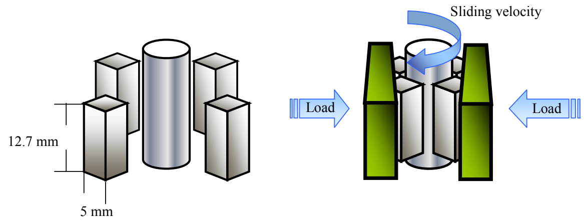

Fig.2 Schematic view of assembled vee block

Table 2 Running conditions, Falex test

Material	Bronze	Steel
Load, [N]	24.5	196.2
Contact pressure, [GPa] (Hertzian)	0.10	0.35

3. Experimental set-up

The tribotests were run in a modified Falex tester. The traditional ASTM D-3233 vee blocks were replaced with assembled vee blocks; see Fig. 2. The dimensions of the 4 vee blocks were 5 × 5 × 12.7 mm and the running conditions are in Table 2.

All tests were performed at a sliding velocity of 0.096 m/s, (290 rpm) and a duration of 10 minutes. The radius of the pin was 6.35 mm.

To ensure that the test specimens' surfaces are clean, a cleaning procedure was performed. The steel blocks were ground with a 2000 grit abrasive paper to bring out a fresh surface layer. The blocks and the pin were then cleaned in an ultrasonic cleaner, 10 minutes with petroleum ether and 10 minutes with acetone. The specimens were dried with hot air before the start of the test and immediately mounted in the test apparatus.

3.1. Surface analysis technology

A surface analysis has to be performed to find out what the surface material consists of. There are many different surface analysis techniques available, but in this study, X-ray Photo electron Spectroscopy (XPS) was chosen. In some scientific disciplines, this technique is also known as ESCA[8-10].

Each element in the specimen has its own unique spectrum. By counting the intensity, the relative quantity of individual elements could be determined[8]. For many materials has the metal oxides and pure metals the spectrum peaks at different energy levels. These effects are called chemical shifts and are one of the biggest advantages of the XPS technique[11,12], making it possible to determine the individual chemical states of a material's surface.

In this study a Perkin-Elmer PHI-5600 XPS instrument was used to analyse the surface. The spot size was 120 μm and a 150 W Aluminium filament was used.

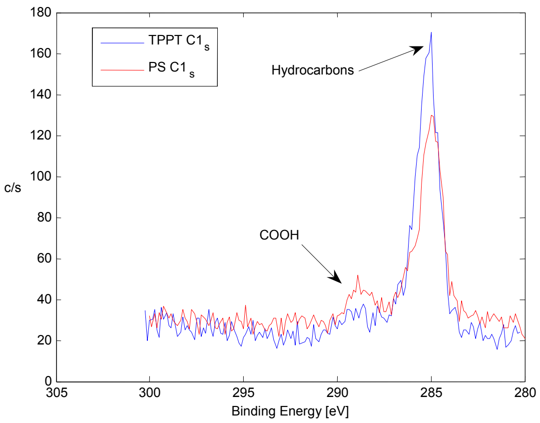

Fig.3 Comparison of $C1_s$ spectrums for TPPT and PS on steel specimens.

A wide scan (1400-0 eV) was initially performed to get an overview of the surface composition. The narrow scans were performed at energy levels for interesting elements.

The narrow scans can be analysed in detail to learn more about the surface. For example, the level of different compounds could be determined. Fig 3 shows the difference in the amount of COOH groups at the surface for two different fluids.

4. Results and discussion

The following results are based on a chosen experiment for each additive and material combination. The surface analysis was performed at one of the four blocks from each Falex test. The analysis spot was carefully chosen to be representative of the test.

4.1. New sample analyze

To find out what the outermost surface layer of the test specimens consists of, an XPS analysis was performed on new test specimens. The clean surface first analysed for both steel and bronze. For bronze, a depth profile measurement was also performed. Material measuring 7 nm was sputtered away in layers and XPS measurements were performed at each level.

On the steel blocks, the outermost surface consists mainly of oxygen and carbon, with a minor content of iron. Some hydroxyl compounds were also present at the surface.

The outermost surface layer on the bronze surface consists of different oxides and some cupper and tin, while deeper into the material the oxygen content is lower and the metal composition is almost the same as the bulk material, see Fig. 4.

The spectrum for tin was studied in detail because tin oxides has a phase shift in the spectrum compared to the pure metal[11,12]. Here, a quite large amount of metal oxides was present at the uppermost layer; see Fig. 5.

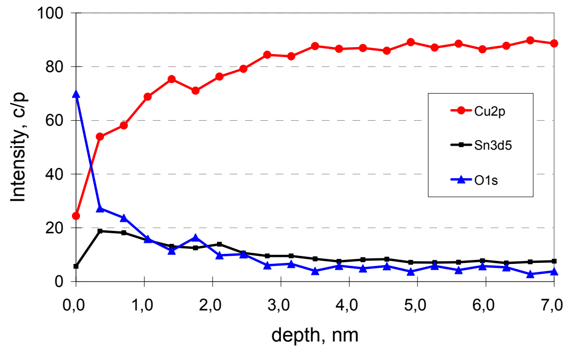

Fig.4 Atomic concentration, depth profile for new bronze specimen.

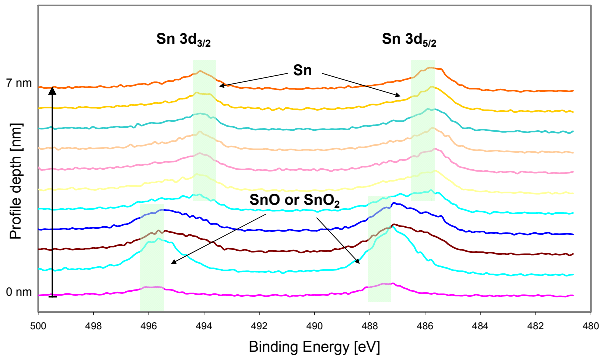

Fig.5 Spectrum intensity for Sn against depth for new bronze specimen, (0-7 nm).

Table 3 Atom concentration on bronze blocks

	Cu	Sn	O	C	S	P
PS	5.84	0.93	18.82	72.15	2.26	-
TPPT	6.22	1.8	28.77	62.73	0.48	0
CM	12.76	1.93	25.13	56.9	3.28	-
HAP	1.51	0.2	38.13	55.09	-	5.07
PSHAP	4.68	0.47	33.92	53.21	4.15	3.57

The spectrum for oxygen shows the presence of a metal- hydroxyl layer on the uppermost layer of the surface for bronze specimens.

4.2. Worn sample analyze

Samples for both steel and bronze for all different additives were tested with XPS. The atom concentration is shown in Tables 3 and 4.

The PS additive gives the highest wear rate for both steel and bronze. On steel, this additive does not produce any detectible sulphur containing tribofilm, whereas on the bronze specimens a sulphur film was detected. It is well-known that active sulphur additives and yellow metals are a disadvantageous combination. Material is removed by oxidative wear.

The TPPT additive containing both sulphur and phosphor gives relatively low wear for both bronze and

Table 5 Atom concentration on steel blocks

	Fe	O	C	S	P
PS	4.6	31.66	63.73	0	-
TPPT	1.61	28.66	66.28	0	3.46
CM	3.53	30.92	65.55	0	-
HAP	1.04	37.78	54.31	-	6.87
PSHAP	0.97	38.34	54.31	0	6.38

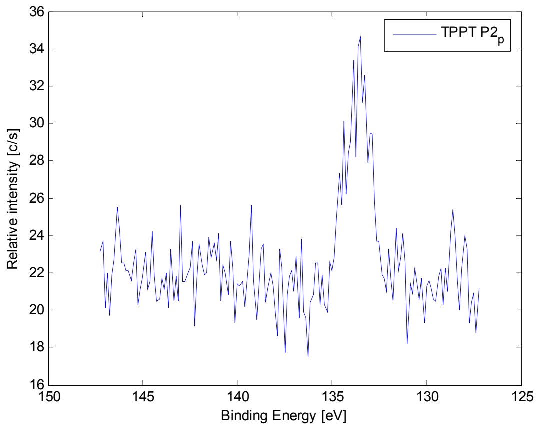

Fig.8 XPS spectrum for P on steel lubricated with TPPT fluid.

steel. A phosphorus tribofilm (probably metal phosphate) was detected on the steel specimens, (see Fig. 6) and a thin sulphur tribofilm was found on the bronze specimens.

The CM additive has a minor effect on friction for both steel and bronze. The wear protection is excellent for steel but bad for bronze. No tribofilm was detected for steel and a relatively thick tribofilm containing sulphur was detected for bronze. Some etching damages and some build-up of oxidized organic matter, carbonates or both are found in the wear track on the steel specimens.

The specially developed HAP additive gives a low wear rate for both steel and bronze. It also produces a thick phosphorus tribofilm for both material combinations and gives low friction for steel and very low friction for bronze. The reaction products seem very aggressive against the steel blocks with etching damages. For bronze, it also gives selective transfer of copper to the pin.

For steel, the PSHAP additive gives an unstable friction and an unstable phosphorus containing tribofilm. The wear track has a spotted look and the tribofilm was worn off and regenerated in the spots. XPS analysis shows that the amount of tribofilm is higher after 2 minutes than after 10 minutes. For bronze, PSHAP gives a low and stable friction and a very thick tribofilm containing a large amount of both sulphur and phosphorus compounds; see Fig. 7 where this additive gives the lowest wear rate for bronze.

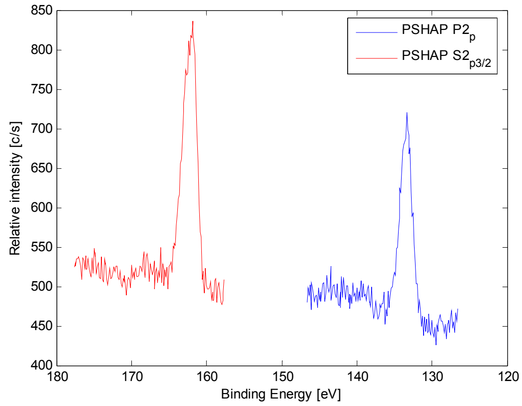

Fig.6 XPS spectrum for P and S on bronze lubricated with PSHAP fluid.

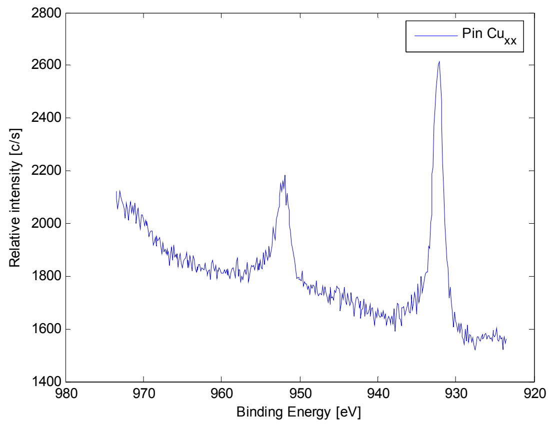

Fig.7 XPS spectrum for pin run against bronze lubricated with HAP fluid.

Table 4 Chemical compisiotion of pin run against bronze lubricated with HAP fluid.

Fe	Cu	Sn	O	C	P
0.72	1.18	0.29	32.87	63.81	1.93

4.3. Selective transfer

The HAP test for bronze showed a visible transfer of copper from the block to the pin. An XPS analysis of the pin was performed to see the content of the surface. The results showed that a layer of copper and tin covered the pin. Phosphorus containing tribofilm on the pin was also slightly detected, (~2 %); see Fig. 8. The amount of iron on the surface of the pin was small.

The atom percentages for the pin from the XPS analysis of the pin are found in Table 5.

5. Conclusions

The result from this investigation shows that the new additives give thick tribofilms at both steel and bronze specimens.

None of the additives give a detectible sulphur tribofilm on steel specimens. There are numerous explanations for this:

- No sulphur containing tribofilm are formed.
- The formed film is continuously removed and regenerated and is too thin to be detected.
- The formed sulphur film is covered by a thick layer of phosphorus film and cannot be detected with the surface sensitive XPS technology.

The PSHAP and HAP fluid gives the thickest tribofilms on both bronze and steel specimens.

This new type of more polar additives shows promising results for the formulation of environmentally adapted lubricants based on saturated esters. More studies about treat rates and synergistic / antagonistic effects of other additives have to be performed.

6. References

[1] Pettersson, A., “High-Performance Base Fluids for Environmentally Adapted Lubricants,” Tribology International, 40, 2007, 638-645.

[2] Pettersson, A. “Tribological Characterization of Environmentally Adapted Ester Based Fluids,” Tribology International, 36, 2003, 815-820.

[3] Randles, S. J., “Esters,” in Synthetic Lubricants and High-Performance Functional Fluids, Edited by L.R.Rudnick and R.L.Shubkin, Marcel Dekker Inc., NY, 1999, 63-101.

[4] Minami, I. and Mori, S., “Antiwear Additives for Ester Oils,” Journal of Synthetic Lubrication, 22, 2, 2005, 105-121.

[5] Pettersson, A., Kassfeldt, E. and Minami, I., “Additives for Environmental Adapted Lubricants -Friction and Wear Protection,” Tribology Online, 3, 3, 2008, 163-167.

[6] Ukonsaari, J. “Wear and Friction of Synthetic Esters in a Boundary Lubricated Journal Bearing,” Tribology International, 36, 2003, 821-826.

[7] Minami, I., Hirao, K., Memita, M. and Mori, S. “Investigation of Anti-Wear Additives for Low Viscous Synthetic Esters: Hydroxyalkyl Phosphonates,” Tribology International, 40, 2007, 626-631.

[8] Briggs, D. and Seah, M. P., Practical Surface Analysis.Vol. 1, Auger and X-ray Photoelectron Spectroscopy, John Wiley & Sons Ltd., Chichester, ISBN: 0-471-92081-9, 1990.

[9] Randell. D. R. and Neagle W., Surface Analysis Techniques and Applications, Thomas Graham House, Cambridge, ISBN: 0-85186-597-6, 1990.

[10] Attard, G. and Barnes, C., Surfaces, Oxford University Press, Oxford, ISBN: 0-19-855686, 1998.

[11] Moulder, J. F., Stickle, W. F., Sobol, P. E. and Bomben, K. D., Handbook of X Ray Photoelectron Spectroscopy, Physical Electronics, Eden Prairie, Minnesota, ISBN: 0-9648124-1-x, 1995.

[12] Brune, D, Hellborg, R. and Hunderi, O., Surface Characterization : A User’s Sourcebook, Wiley-VCH, Weinheim, ISBN: 3-527-28843-0, 1997.