Manuscript Number: JET719R1

Title: Effect of lubricant additives in rolling contact fatigue

Article Type: Paper

Corresponding Author: Dr. Clotilde MINFRAY, Ph.D.

Corresponding Author's Institution: Ecole Centrale de Lyon

First Author: Mathilde MEHEUX, Ph.D.

Order of Authors: Mathilde MEHEUX, Ph.D.; Clotilde MINFRAY, Ph.D.; Fabrice VILLE, Ph.D; Thierry Le MOGNE, Engineer; Antonius A LUBRECHT, Professor; Jean-Michel MARTIN, Professor; Henri-Paul LIEURADE

Abstract: Lubricant formulations for manual gear box applications are optimized for gear contacts although rolling element bearings are lubricated with the same fully formulated oil. This may cause fatigue related damage to these bearings. Several explanations can be considered, but this work focuses on the effect of additives contained in the lubricant.

Rolling contact fatigue tests were performed on a twin-disc machine (TDM). Artificial dents generated by a Rockwell penetrator were made on the faster surface in order to accelerate the fatigue phenomena. Then, pure rolling and 6.7 % slip (SRR) tests were performed with the different lubricants (pure base oil, fully formulated oil and base oil with detergent and anti-foam). Fatigue life results and spalling morphologies are compared.

For the sample obtained with the fully formulated oil and 6.7% of SRR, crack analysis was performed. Using Focus-Ion-Beam Technique (FIB), a spalled sample was milled to reveal a cross-section of a crack. SEM images were taken and EDX analyses along the crack were performed. Additive elements are detected up to the crack tip. AES depth profiling was also performed in the tribofilm generated on the disc surface. The role of additives in rolling contact fatigue is discussed in the light of these results.

Effect of lubricant additives in rolling contact fatigue

M. MEHEUX[1]*, C. MINFRAY*[2]*, F. VILLE*[3]*, Th. LE MOGNE*[2]*, A. A. LUBRECHT*[3]*, J. M. MARTIN*[2]*, H. P. LIEURADE*[1]

[1] *CETIM, Pôle Fatigue des Composants Mécaniques, 52, avenue Felix Louat, SENLIS Cedex 60304*

[2] *Université de Lyon, Ecole Centrale de Lyon, LTDS, CNRS UMR5513, F69134*

[3] *Université de Lyon, INSA-Lyon, LaMCoS, CNRS UMR5259, Villeurbanne F69621*

Abstract:

Lubricant formulations for manual gear box applications are optimized for gear contacts although rolling element bearings are lubricated with the same fully formulated oil. This may cause fatigue related damage to these bearings. Several explanations can be considered, but this work focuses on the effect of additives contained in the lubricant.

Rolling contact fatigue tests were performed on a twin-disc machine (TDM). Artificial dents generated by a Rockwell penetrator were made on the faster surface in order to accelerate the fatigue phenomena. Then, pure rolling and 6.7 % slip (SRR) tests were performed with the different lubricants (pure base oil, fully formulated oil and base oil with detergent and anti-foam). Fatigue life results and spalling morphologies are compared.

For the sample obtained with the fully formulated oil and 6.7% of SRR, crack analysis was performed. Using Focus-Ion-Beam Technique (FIB), a spalled sample was milled to reveal a cross-section of a crack. SEM images were taken and EDX analyses along the crack were performed. Additive elements are detected up to the crack tip. AES depth profiling was also performed in the tribofilm generated on the disc surface. The role of additives in rolling contact fatigue is discussed in the light of these results.

Keywords: Rolling Contact Fatigue, lubricant additives, FIB/EDX, AES

1. Introduction

The gear box is considered a key element of the car design because it adjusts engine and wheel speed. In the case of manual gear boxes, the main components are gears, bearings and synchronizers. Lubricant formulations are optimized for gear contacts although rolling element bearings (REBs) are lubricated with the same fully formulated oil. REB fatigue related damage (spalling) seems to be influenced by the lubricant [1-2]. The industrial aim is to increase the REB life, limit maintenance operations (oil change), while maintaining good precision in gear shifts, low noise, and low energy loss. Currently, bearing damage originates mainly from surface defects and less from inclusions in steel. Those surface originated spalls can be triggered by different parameters: pressure, friction, surface defects, roughness and lubricant. Details on these four points are given below.

Concerning contact conditions in REBs (EHL conditions), the contact pressure can reach 4 GPa, much higher than the pressures found in gears (<1 GPa). Moreover, the presence of a defect, possibly a dent or an asperity, can locally increase the contact pressure significantly [3].

The slide-to-roll ratio SRR (SRR= sliding speed/mean rolling speed) value is close to zero in bearings and much higher for gears (up to 60%-80%). If the SRR is increased, the friction at the interface increases as well as the energy dissipation. A reduction in viscosity results and the EHL film thickness is reduced.

Roughness will induce local pressure increase and perturbations in the EHL film thickness.

Although the previous parameters are important, this work will focus mainly on the possible effect of lubricant formulation on rolling contact fatigue. A transmission gear box lubricant contains various additives in addition to the base oil, such as antiwear, extreme-pressure, detergent, dispersant, anti-foam, corrosion inhibitors, viscosity modifiers etc…

As reported in Fig.1, the formulated lubricants possibly contribute to the damage of mechanical parts at two locations: on the top of friction surfaces and as soon as a crack is formed, inside the crack (on the crack faces). The effect of lubricant additive elements on Rolling Contact Fatigue (RCF) has been considered by various authors [4-5] but no clear conclusions were found. Therefore the current work focuses on this point. The base oil also affects the RCF. Possible mechanisms are listed below without further investigation: i) viscosity variation of the base oil induces variation of the EHL film thickness [6-8], ii) if the lubricant enters the crack, this modifies the RCF behaviour [9-12], iii) hydrogen originated from hydrocarbon species embrittles the steel especially at the crack tip [13], iiii) the Rehbinder effect [14].

Let us now focus on lubricant additive effects on RCF at the top of the friction surfaces (first case in Fig.1). This could disrupt the running-in process; for example by preventing the formation of early surface initiated cracks. For certain contact conditions, tribofilms consisting of additive elements, are generated in the contact. Usually, these films are created under pure sliding conditions but it is also possible for milder SRR ratios [15]. If a tribofilm is generated (around 100 nm thick), it will contribute to an increase of the whole separation of the friction surfaces [16] (tribofilm + EHL film thickness) reducing contact severity. Other authors [17-18], on the contrary, propose that the tribofilm roughness modifies the lubricant feed, reducing the EHL film thickness. Another possible effect of the tribofilm, if formed before cracks appear, is to act like a sticking plaster limiting crack propagation. Finally, lubricant additives effect on RCF at the top of friction surfaces is mainly due to tribofilm generation and its action on both crack initiation and propagation can be considered.

For the second case (lubricant action inside cracks), the lubricant additive is going to have an effect mainly on crack propagation, as soon as the lubricant enters the crack or if additives are present in gas phase.

Finally, the effect of additives contained in the formulated lubricant on both crack initiation and propagation is not clearly elucidated. Is it a positive or negative influence? Does the tribofilm generated in the contact area play a key role? Do the additives enter the crack? This work presents elements of comprehension about additive effects on Rolling Contact Fatigue (RCF).

2. Experimental details

The experimental methodology (Fig. 2) couples fatigue experiments with physico-chemical analysis of the top friction surface and the crack faces. Further details are reported in the following paragraph.

Lubricants

Three lubricants are used in this work: the mineral base oil (BO), a fully formulated lubricant (base oil with five additives: Htot), and the base oil with only antifoam and detergent (Hdet). The mineral base oil is from group III with a viscosity at 80°C of 12.6 cSt, a viscosity pressure coefficient at 80°C of 20 GPa^{-1} and a density of 806.6 kg/m^3.

Concerning additives, an overbased calcium sulfonate is used as detergent and a succinimide as dispersant. For extreme pressure and antiwear performance, an organic polysulfide and organothiophosphate additive are used. Each additive is blended at concentration between 1 wt% to 3 wt%. An anti-foam additive is also added. The following elements are present from the additives: Phosphorus, Sulphur, Calcium, Nitrogen, Oxygen and Carbon.

Twin Disc Machine fatigue tests

Rolling contact fatigue tests are performed on a twin disc machine (TDM).

TDM test discs have a radius of 35 mm in each direction resulting in a circular contact. The discs are made of AISI 52100 steel (58 to 61 HRc) with a surface roughness Rms ≈ 0.05 μm. Four artificial dents, generated with a Rockwell penetrator, are made on the faster surface in order to accelerate the fatigue phenomena [19].

Table 1 shows the operating conditions used in this study and Table 2 shows the Hertzian contact parameters evaluated using two smooth discs. The maximum Hertz pressure is much higher around the dent than the smooth surface pressure reported in Table 2. The EHL film thickness has been calculated using the Hamrock-Dowson formula for circular contacts [6]. It is 270 nm which gives a λ ratio of 2.2 (outside the dented area).

The test stops automatically when a defect is detected on the smooth disc using a magnetic sensor.

Two parameters are investigated in this work. First, the influence of lubricant additives as mentioned above: pure base oil (BO), fully formulated oil (Htot) and base oil with detergent and antifoam (Hdet). Then, the effect of the slide-to-roll ratio is also studied. Pure rolling and 6.7 % slip (SRR) tests are performed with the different lubricants. Every test is repeated three times. Fatigue life results and spalling morphologies are compared.

AES analyses and FIB + EDX analyses

For the sample obtained with the fully formulated oil and 6.7% SRR, an additional analysis is performed.

First, all samples were cleaned by solvent washing (n-heptane) in order to remove the remaining oil.

Then, AES (Auger Electron Spectroscopy) depth profiling is performed inside the tribofilm generated at the top of the disc, in the contact area (flake). The electron gun used for AES analysis was a Field Emission Gun (FEG1000-Thermo) working at 5 keV. The lateral resolution during AES is around 1 µm. The analyzed area is 18000 µm² for the spall. The analyser used is a Thermo ESCALAB 220i. This spectrometer was calibrated with the photopeak Au4f7/2 at 84.0 eV +/- 0.2 eV. Sputtering was performed with an ion gun EXO5 (Thermo) working at 2 keV, with Argon ions, and with a differential pumping of the sputtering source. The etched zone was of 2 x 2 mm².

To investigate the composition of the crack faces, Focus-Ion-Beam (FIB) is used as a nano-machining technique to reveal the crack faces (Fig. 3). SEM images and energy dispersive X-ray spectrometry *(*EDS) analyses along the crack were performed, in order to detect additive presence.

3. Fatigue life results

Fatigue life results after pure rolling tests with the base oil alone (BO), the fully formulated lubricant (Htot) and the lubricant with detergent (Hdet) are reported in Fig. 4.a. The average fatigue life for the BO, Htot and Hdet are respectively 18±4 Mc, 15±4 Mc and 5.3±0.5 Mc. The average fatigue life values are comparable for the BO and Htot lubricants, the life is much lower for the detergent (fatigue life reduced by 3 compared to BO). Fig. 4.b and 4.c show optical images of the damaged surfaces for the different lubricants on both discs. Different damage morphologies are found for the test with detergent (Hdet) compared to BO and Htot .

Concerning the rolling-sliding contact fatigue experiments (6.7 % SRR), results are shown in Fig. 5.a. The overall fatigue life is reduced compared to the pure rolling conditions. For the different lubricants the fatigue life is 3.5±2 Mc for BO, 2.5±1 Mc for Htot and 2.7±0.4 Mc for Hdet which are very close. Looking at the optical pictures of the smooth discs (Fig. 5.c), significant spalls are found on these pieces. Their size exceeds the contact zone (around 2 * 2 mm² compared to 1.7 mm contact width). Slight differences are found in spalls (size for example) according to the lubricant. On all surfaces (smooth and dented discs Fig 4. b and c) and with each lubricant, a tribofilm of about 250 μm width is optically detected in the centre of the contact area. The location of this film seems related to the position of dents. This zone is called “dent area” in the following sections.

4. Analytical results

An additional analysis was performed on the spall of the smooth disc obtained under rolling-sliding conditions (6.7% SRR) with the fully formulated lubricant. A flake retrieved in the lubricant is analyzed by AES spectroscopy and especially the tribofilm generated in the dent area. Next, EDX analyses were performed inside the spall on the smooth disc. A FIB cross-section of a crack was also carried-out and followed by an EDX analysis.

Flake analysis

Figure 6.a, shows an optical image of the retrieved flake. An AES spectrum obtained in the middle of the track, in the tribofilm area, is also presented in Fig. 6.b. It is obtained after a slight etching with argon ions. The contamination (adventitious carbon) is removed and information coming mainly from the inside of the tribofilm is obtained. Phosphorus (P_{LMM} peak), Calcium (Ca_{LMM} peak), Oxygen (O_{KLL} peaks) and Iron (Fe_{LMM} peaks) are the elements detected. A small amount of carbon (C_{KLL} peak) is found but no sulphur (S_{LMM} peak). Oxygen and Calcium are detected in significant amounts (considering peak height and auger sensibility factors) suggesting chemical bounds between those elements. A CaO form can be considered. Even if only a small amount of carbon is detected, the presence of $CaCO_3$ can not be excluded. Actually, Cizaire et al. [20] have observed that ion sputtering or electron beam impact can reduce $CaCO_3$ to CaO and CO_2. In our case, if $CaCO_3$ was present in the sample (coming from the detergent) it would have been modified during the analysis process in CaO

and CO_2. It could explain why carbon is poorly detected. Little literature is found concerning Auger peak shift for $CaCO_3$ and CaO [21].

Another option is the presence of phosphate in the tribofilm. Phosphorus is detected as well as oxygen, and the oxygen peak is around 505-507 eV [22]. So the presence of mixed iron and calcium phosphate is possible.

Finally, the tribofilm obtained in the dent area could consist of a mixed iron and calcium phosphate and/or calcium carbonate and/or metallic oxide.

Its thickness has been estimated in [23] by AES depth profiling and could exceed 40 nm. On the flake but outside the tribofilm area (but still inside the contact area), a very thin film is found (around 10 nm) consisting of similar elements. It is likely to be an adsorbed additive layer

Spall analysis

Next the spall, corresponding to the retrieved flake, is studied (Fig. 7 and 8).

Various EDX spectra are recorded inside the spall. Iron and Chromium are found and attributed to the steel. Oxygen and carbon can originate from the lubricant or air contamination. Phosphorus, Sulfur and Calcium are characteristic additive elements present in the lubricant.

Fig 7.c shows the atomic percentages attributed to these elements knowing that the remaining percentages are attributed to Fe and Cr. The Sulfur quantity is about twice the Phosphorus value. Calcium is found in even smaller quantities as Phosphorus. Looking carefully at the EDX images of Sulfur (Fig. 8), higher amounts are found on the left side of the spall.

Because Phosphorus, Calcium and Sulfur are detected inside the spall, a certain reactivity of the additive elements can be deduced. But the reaction could have occurred during the immersion of the flake in the lubricant and not during the damage process.

Crack analysis

To investigate the additive reactivity during the damage process, analyses of cracks which were not exposed to the lubricant are necessary. This was possible using a FIB sample preparation presented previously (cross section cf. Fig 3).

The length of the considered crack is about 40 µm and its maximum width (near the surface) is 2 µm. EDX analyses are performed along this crack (fig 9 and 10). First of all, in order to get a steel reference, measurements are performed outside of crack. Characteristic elements of the steel are found such as Iron, Chromium and Silicon (Fig 9.a). Aluminum and Gallium originate from the sample preparation process.

When analyzing the inside of the crack (Fig 9.b), peaks attributed to Phosphorus, Sulfur and Calcium are clearly found in addition to the reference elements. Among all detected elements, steel characteristic ones represent 71 at%, oxygen about 21 at% and 2 at% are related to elements from the preparation process. About 6 at% remaining are elements originating from additives. The elemental balance along the crack, between Phosphorus, Sulfur and Calcium is shown in Fig. 10.

Calcium and Phosphorus vary in a very similar manner. On the contrary, the Sulfur amount seems to increase towards the crack tip.

Phosphorus, Sulfur and Calcium possibly originate from the antiwear, the extreme pressure and the detergent molecules. The fact that these elements are detected in the FIB cross-section shows that the additives are present and react inside the crack.

5. Discussion

First of all, under rolling contact fatigue conditions, the detergent, when used alone, seems to reduce fatigue life. Concerning BO and Htot lubricants at 6.7% SRR, very small differences in the fatigue life results are found. The mineral base oil has probably a dominant negative influence on fatigue life, partially masking the additive effect. Another hypothesis is that both negative and positive effects of lubricant additives occur in the formulated lubricant.

When looking carefully at the fatigue damage under rolling-sliding conditions (6.7% SRR) with Htot, evidence of additive activity has been found. The reactivity of these molecules should be considered at two levels, as suggested in Fig. 1: i) through the generation of a tribofilm in the dent area (only rolling-sliding conditions) and ii) through the presence of additive elements (Phosphorus, Sulfur, Calcium) in the crack (for pure rolling and rolling-sliding conditions).

Concerning the possible effects of the generated tribofilm on rolling-contact fatigue damage, different hypotheses can be considered. First, we need to know if tribofilms are generated before or after crack initiation. Studies on tribofilm generation on an MTM machine [15, 24] suggest that a tribofilm is fully formed in less than 5 hours, which is much shorter than the fatigue life. Meheux et al. have performed tests at 5% SRR (0.89 GPa Hertzian pressure, 80°C, 100 mm/s entrainment speed) with the same fully formulated lubricant like the one used in this paper. As soon as the tribofilm is generated, two antagonist effects can be considered. The crack propagation could be limited by the tribofilm, acting like a sticking plaster as it was reported by [25] (Fig. 11). In that paper (Fig. 11), the tribofilm was generated under pure sliding conditions with a lubricant containing 3% of ZDDP. Because different lubricant and contact conditions are used, the tribofilm studied in this paper has a different composition (possibly a mixture of calcium phosphate and/or calcium carbonate and/or metallic oxide) and could have different mechanical properties. Another effect of the tribofilm could be related to the increase in friction coefficient it induces. This is reported in Meheux et al. [15] condering tests on an MTM machine with the same fully formulated lubricant. The conditions are close to the ones used in this study even if it is difficult to know exactly the increase of contact pressure induced by the dents for TDM experiments. If an increase of friction coefficient occurs in the dent area, which is known to be the location of crack initiation, this can further contribute to initiation or accelerate propagation.

As soon as cracks are open to the lubricant under pure rolling or rolling sliding conditions, lubricant and so additives can enter the cracks, depending on size and contact conditions. Olver [12] shows evidence of oil seepage inside a crack. In this study, evidence of additive seepage in a crack of about 40 μm length and a maximum width of 2 μm is given. Crack faces are fresh metallic surfaces and so they are chemically reactive. Sulfur, Phosphorus and Calcium are detected inside the crack. Sulfur is found everywhere and especially at the tip of the crack. On the spall, a larger amount of sulfur was found in the area which was last exposed to the lubricant. All this, suggest a first reaction of sulfur with fresh metallic surfaces. This sulfur can stem from the extreme-pressure, the antiwear and the detergent additives. By the way, the chemical reaction between sulfur and iron is known to be very rapid [25] as is the case for example in an asperity contact. As soon as Sulfur has reacted on the crack faces, other elements can react such as Calcium which is present in the detergent and Phosphorus which is contained in the anti-wear additive. The contact conditions between crack faces are not well known but should be quite severe. Using EDX, only elemental information is obtained, so no chemical bonds can be detected. Hence, it is not possible to distinguish adsorbed additives from tribofilm. But the presence of additive elements inside the crack is demonstrated and this should affect the crack propagation velocity.

6. Conclusion

The effect of lubricant additives in rolling contact fatigue is investigated in this paper. Pure rolling and rolling sliding (6.7 % SRR) conditions are imposed using three lubricants: a mineral base oil, a fully formulated lubricant and a mineral base oil with detergent and anti-foam. Four dents are placed on the faster surface to accelerate the fatigue phenomenon. The following conclusions can be made:

- Under pure rolling conditions, the lubricant containing detergent and antifoam exhibits a significantly lower fatigue life compared to the other lubricants. The damage observed on both surfaces for Hdet differs from the two other lubricants.
- Under rolling-sliding conditions, fatigue life is much shorter than under pure rolling conditions. No clear difference between base oil, totally formulated lubricant and base oil with detergent are found, for the fatigue life and fatigue damage.
- In case of rolling-sliding conditions with the fully formulated lubricant, a tribofilm is found in the dent area. This tribofilm was analyzed by AES and seems to consist of mixed iron and calcium phosphate and/or calcium carbonate and/or metallic oxide.
- In case of rolling-sliding conditions with the fully formulated lubricant, additive elements such as Sulfur, Phosphorus and Calcium are detected inside the crack, all the way up to the crack tip (length 40 µm – maximum width 2 µm).

Finally, additive activity is shown through the generation of a tribofilm in the contact area and the presence of additives inside the cracks. Their respective effects on rolling contact fatigue, which can be positive or negative, were discussed.

This is the first time that direct evidence of lubricant additive activity inside cracks is shown.

Acknowledgements

The authors would like to thank the following companies for their support and discussions: CETIM, Lubrizol, SKF, TIMKEN, SNR, Rollix, TOTAL. The FIB cross section was performed at SERMA Technologies (France).

References

[1] **O'Connor, B.** The Influence of Additive Chemistry on Micropitting, *Gear Technology*, 2005, **22**, 34-41.

[2] **Nixon, H.** and **Zantopulos, H.** Lubricant additives, friend or foe, what the equipment design engineer needs to know, *ASLE Lub. Eng.*, 1995, 815-822.

[3] **Couhier, F.** « Influence des rugosités de surface sur les mécanismes de lubrification du contact elasto-hydrodynamique cylinder-plan », *PhD thesis*, INSA Lyon, France, 1996.

[4] **Olver, A.,** and **Benyajati, C.** The effect of oil additives on micropitting, Proc. of the 30th Leeds-Lyon Symposium of Tribology, Lyon France, 2-5 September 2003, paper 43/2004, pp. 601-610 (Tribology series Elsevier).

[5] **Torrance, A.A. Morgan, J.E.** and **Wan, G.T.Y.** An additive's influence on the pitting and wear of ball bearing steel, *Wear*, 1996, **192** (1-2), 66-73.

[6] **Hamrock, B.** and **Dowson, D.** Isothermal Elastohydrodynamic lubrication of point contacts. Part I: theoretical formulation, *ASME J. of Lubr. Tech.*, 1976, **98** (2), 223-229.

[7] **Hamrock, B.** and **Dowson, D.** Isothermal Elastohydrodynamic lubrication of point contacts. Part II: Ellipticity parameter results, *ASME J. of Lubr. Tech.*, 1976, **98** (3)**,** 375-383.

[8] **Hamrock, B.** and **Dowson, D.** Isothermal Elastohydrodynamic lubrication of point contacts. Part III: fully flooded results, *ASME J. of Lubr. Tech.*, 1977, **99** (2), 264-276.

[9] **Way, S.** Pitting due to rolling contact, *Trans. Am. Soc. Mech. Eng., J. Appl. Mech.*, 1935, **2**, A49-A58.

[10] **Kaneta, M.** and **Murakami, Y.** Effects of oil hydraulic pressure on surface crack growth in rolling/sliding contact. *Tribology International*, 1987, **20** (4), 210-217.

[11] **Bower, A. F.** The Influence of Crack Face Friction and Trapped Fluid on Surface Initiated Rolling Contact, Fatigue Cracks, *ASME J. of Trib.*, 1988, **110**, 706-711.

[12] **Olver, A. V**., **Tiew, L. K., Medina, S.** and **Choo, J. W.** Direct Observations of a micropit in an elastohydrodynamic contact. *Wear*, 2004, **256**, 168-175.

[13] **Kino, N.** and **Otani, K.** The influence of hydrogen on rolling contact fatigue life and its improvements, *JSAE Review*, 2003, **24**, 289-294.

[14] **Savenko, V. I.** and **Shchukin**, **E. D.** New applications of the Rehbinder effect in tribology. A review, *Wear*, 1996, **194** (1-2), 86-94.

[15] **Méheux, M., Minfray, C., Ville, F., Le Mogne, T., Lubrecht, A.A., Martin, J.M.** and **Lieurade, H.P.** Influence of slide-to-roll ratio on tribofilm generation, *Proceedings of the Institution of Mechanical, Engineers, Part J: Journal of Engineering Tribology*, 2008, **222**, 325-334.

[16] **Fowles, P., Jackson, A.** and **Murphy, W.R.** Lubricant chemistry in rolling contact fatigue - The performance and mechanism of one antifatigue additive, *ASLE Transactions*, 1981, **24** (1), 107-118.

[17] **Taylor, L., Dravta, A.** and **Spikes, H.** Friction and wear behavior of Zinc Dialkyldithiophosphate additive: Part I: friction and morphology of ZDDP reaction films, *Tribology Transactions*, 2003, **46** (3), 303-309.

[18] **Taylor, L.** and **Spikes, H.** Friction and wear behavior of Zinc Dialkyldithiophosphate additive: Part II: Influence of ZDDP reaction films on EHD lubrication, *Tribology Transactions*, 2003, **46** (3), 310-314.

[19] **Coulon, S., Ville, F.** and **Lubrecht, A. A.** Experimental investigations on Rolling Contact Fatigue for dented surfaces using artificial defects, Proceedings of the 31st Leeds-Lyon Symposium on Tribology - Life cycle tribology, Leeds UK, 7-10 September 2004, pp. 691–702 (Elsevier Science, Amsterdam).

[20] **Cizaire, L., Martin, J. M., Gresser, E., Truong Dingh, N.** and **Heau, C.** Tribochemistry of overbased calcium detergent studied by ToF-SIMS and other surface analyses., *Tribology Letters*, 2004, **17** (4), 715-721.

[21] **Eisenlohr, L., Meteva, K., Gabrovsek, F.** and **Dreybrodt, W.** The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H_2O-CO_2 solutions, *Geochimica et Cosmochimica Acta*, 1999, **63** (7/8), 989-1002.

[22] **Minfray, C.** « Réactions tribochimiques avec le dithiophosphate de zinc », *PhD thesis*, Ecole Centrale de Lyon, France, 2004.

[23] **Méheux, M.** « Influence des additives de lubrification sur la formation de tribofilms, le coefficient de frottement et la durée de vie en fatigue des roulements », *PhD thesis*, Ecole Centrale de Lyon, France, 2009.

[24] **Fujita, H.** and **Spikes, H.** The formation of Zinc Dithiophosphate antiwear films, *Proceedings of the Institution of Mechanical, Engineers, Part J: Journal of Engineering Tribology*, 2004, **218** (4), 265-277.

[25] **Minfray, C., Le Mogne, T., Lubrecht, A.A.** and **Martin**, **J.-M.** Experimental simulation of chemical reactions between ZDDP tribofilms and steel surfaces during friction processes, *Tribology Letters*, 2006, **21** (1), 67-78.

Table 1: TDM operating conditions

Temperature (°C)	80
Load (N)	5120
Mean entrainment speed (m/s)	11
Maximal duration (h)	111.1/20 Mc
Slide to roll ratio (%)	Near 0 or 6.7

Table 2: TDM contact conditions and EHD film thickness. Lambda ratio is the ratio of the minimum film thickness to the combined surface roughness

Maximum Hertz Pressure (GPa)	3.2
Contact radius (µm)	835
Elastic deformation (µm)	40
Minimum EHD film thickness (nm)	270
EHD film thickness in contact center (nm)	470
λ	2.2

List of figure captions:

Figure 1: Scheme of possible actions of the formulated lubricant (base oil + additives) on rolling contact fatigue (initiation and propagation of cracks)

Figure 2: Experimental methodology uses in this study

Figure 3: Focused Ion Beam (FIB) sample preparation for crack visualisation (cross section) on the follower sample of the TDM test performed with 6.7% sliding with totally formulated lubricant (Htot)

Figure 4: Rolling contact fatigue results performed on TDM near 0 % sliding, contact pressure of 3.2 GPa: a) fatigue life results, b) optical images of dented discs after test (BO and Htot), c) optical images of smooth disc after test (BO and Htot)

Figure 5: 6.7% sliding fatigue results performed on TDM at a contact pressure of 3.2 GPa: a) fatigue life results, b) optical images of driver discs after test (BO and Htot), c) optical images of follower discs after test (BO and Htot)

Figure 6: a) Scheme of samples and optical image of a flake retrieved in the fully formulated lubricant (Htot) after the test under rolling sliding conditions (6.7% SRR) b) AES spectrum obtained in the tribofilm area of the flake (dent area) after TDM test with Htot and sliding (6.7% SRR)

Figure 7: a) SEM images and b- c) EDX analyses on a spall of the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

Figure 8: a) SEM images and b) EDX analyses (sulphur image) on a spall of the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

Figure 9: SEM images of a crack cross section obtained by FIB and related EDX analyses: a) outside of the crack (steel reference) b) crack tip. Analyses are performed on the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

Figure 10: SEM image of a crack cross section obtained by FIB (cf. Fig 3) and EDX analyses along the crack. Analyses are performed on the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

Figure 11: TEM image of a ZDDP tribofilm obtained under pure sliding condition from [23]. The tribofilm was generated on a Cameron-Plint tribometer, under cylinder-on-flat configuration with a load of 350 N, a speed of 0.1 m/s, a stroke length of 7 mm and a cylinder diameter of 6 mm. Both cylinder and flat are made of steel. The lubricant used is a polyalphaolefine base oil blended with 3% of ZDDP (zinc dialkyldithiophosphate) additive. The Hertzian contact pressure is estimated at 0. 85 GPa

Figure 1: Scheme of possible actions of the formulated lubricant (base oil + additives) on rolling contact fatigue (initiation and propagation of cracks)

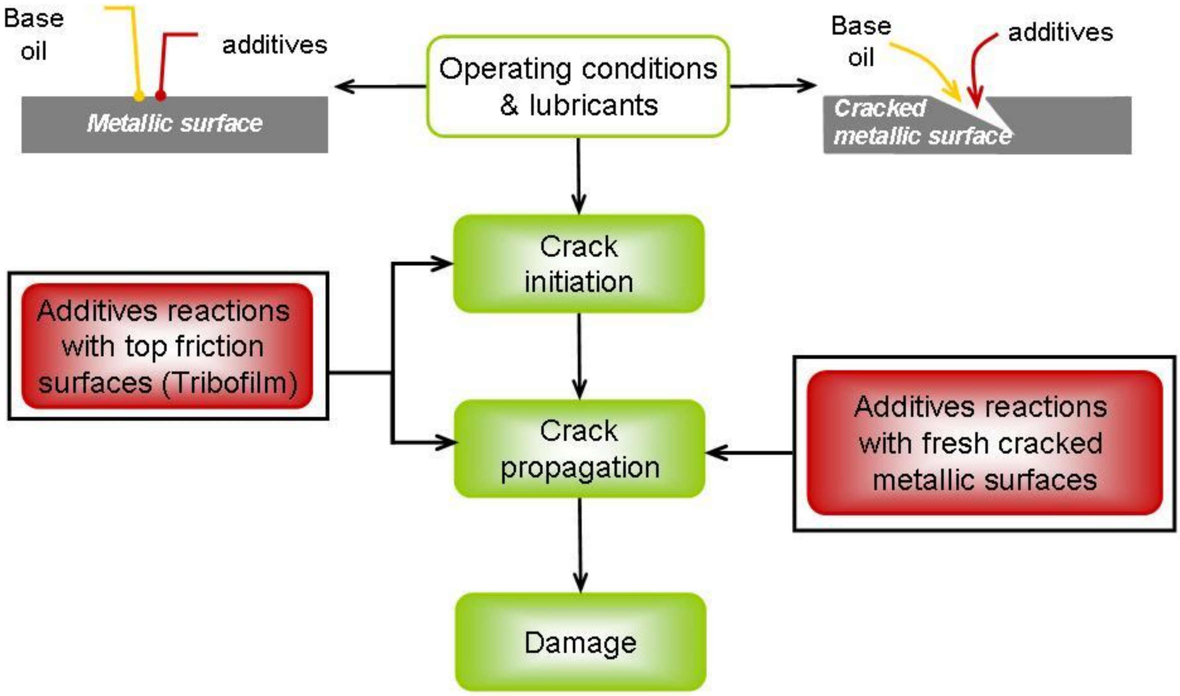


Figure 2: Experimental methodology uses in this study

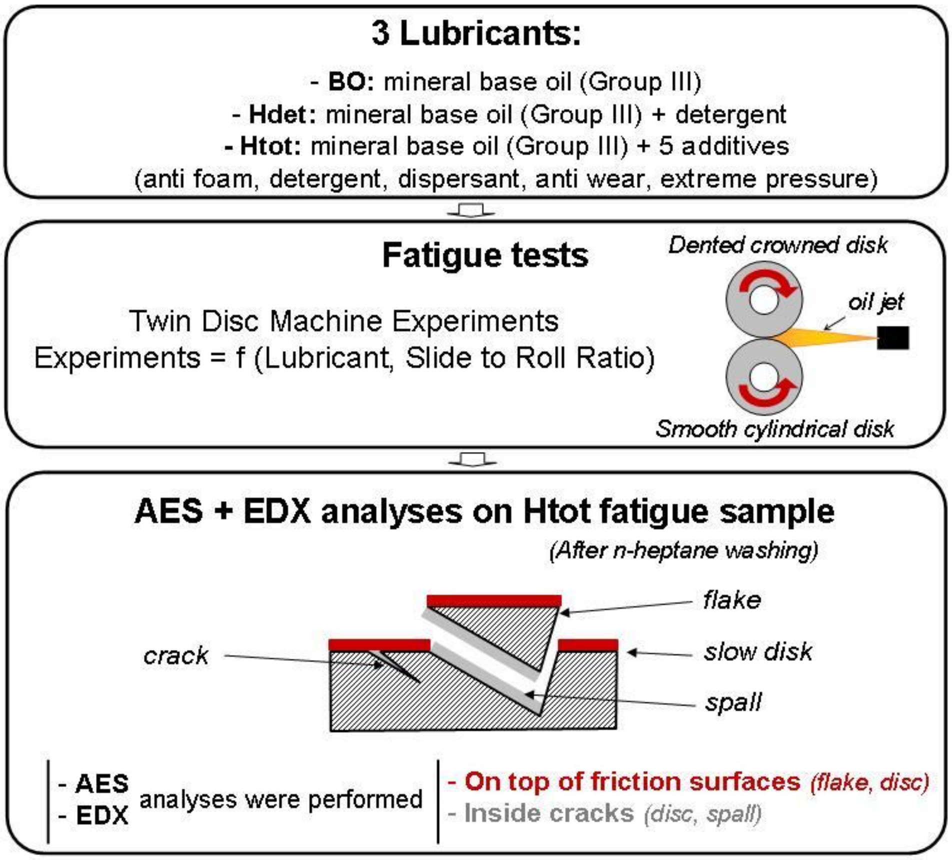


Figure 3: Focused Ion Beam (FIB) sample preparation for crack visualisation (cross section) on the follower sample of the TDM test performed with 6.7% sliding with totally formulated lubricant (Htot)

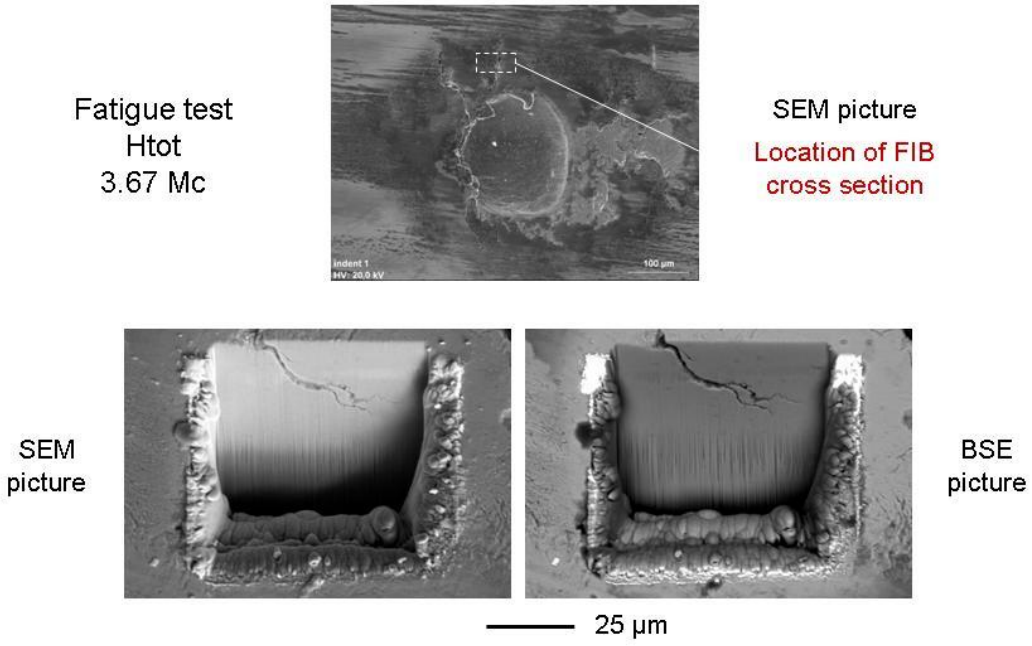


Figure 4: Rolling contact fatigue results performed on TDM near 0 % sliding, contact pressure of 3.2 GPa: a) fatigue life results, b) optical images of dented discs after test (BO and Htot), c) optical images of smooth disc after test (BO and Htot)

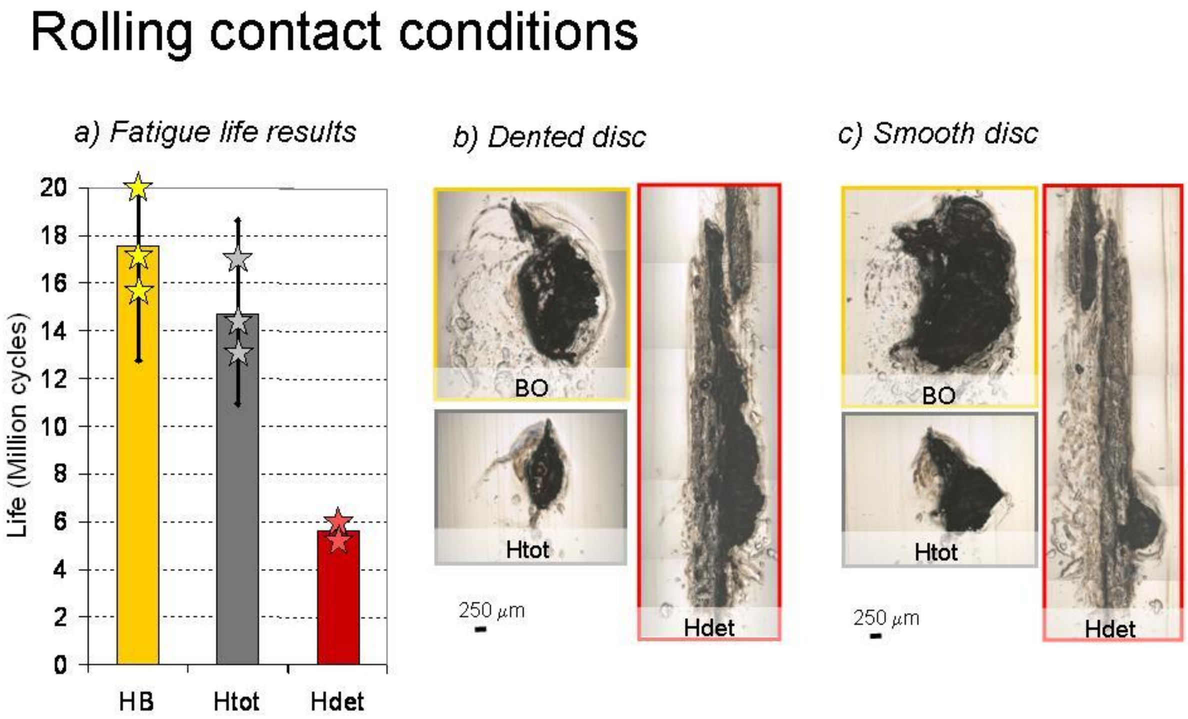


Figure 5: 6.7% sliding fatigue results performed on TDM at a contact pressure of 3.2 GPa: a) fatigue life results, b) optical images of driver discs after test (BO and Htot), c) optical images of follower discs after test (BO and Htot)

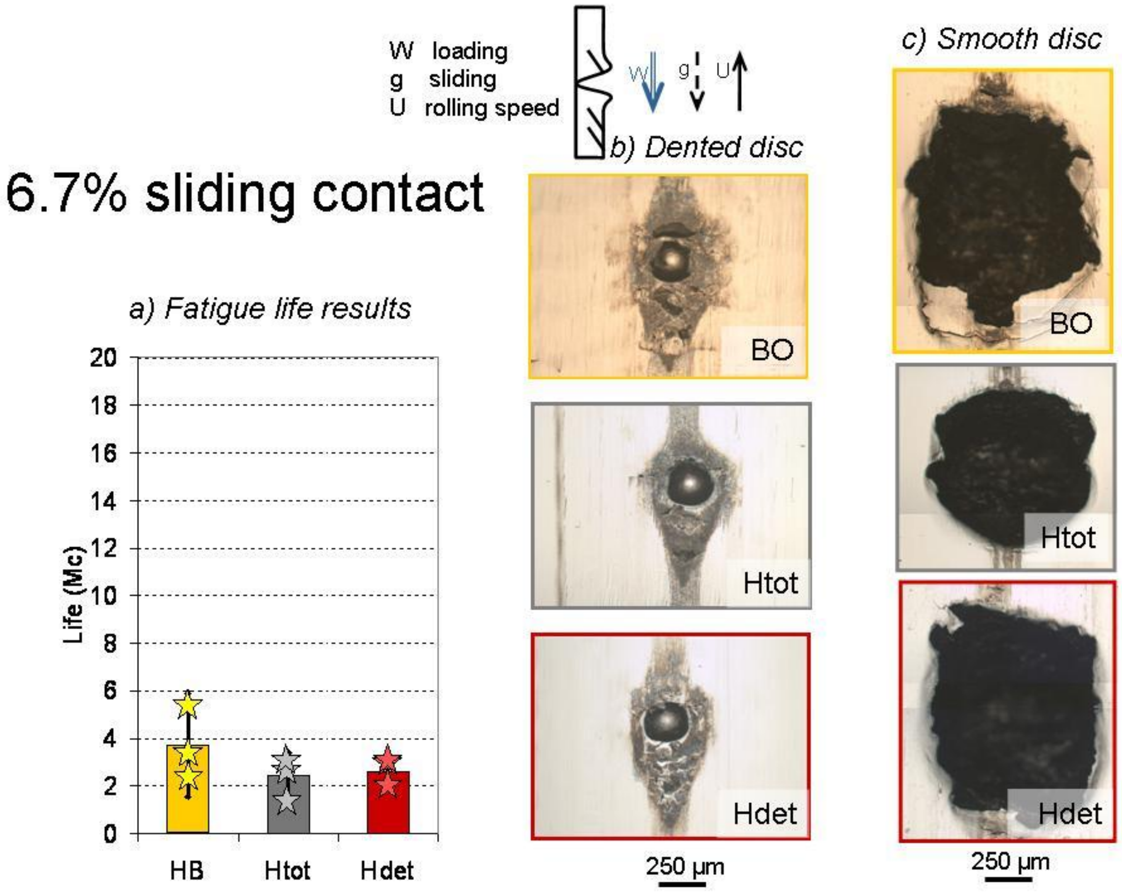
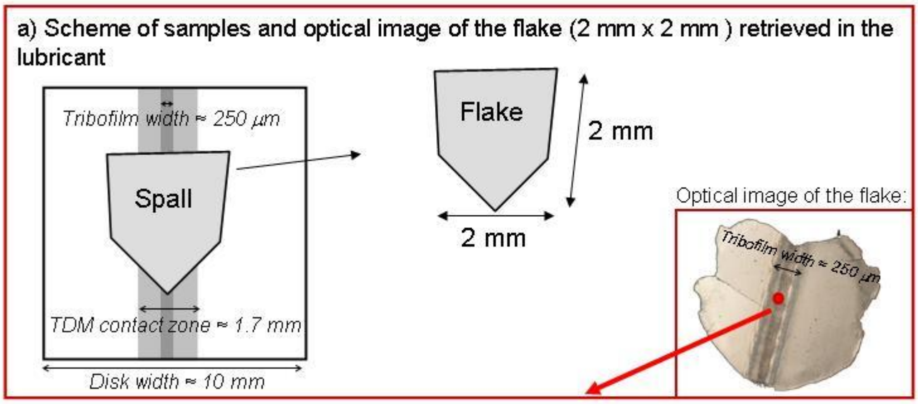


Figure 6: a) Scheme of samples and optical image of a flake retrieved in the fully formulated lubricant (Htot) after the test under rolling sliding conditions (6.7% SRR) b) AES spectrum obtained in the tribofilm area of the flake (dent area) after TDM test with Htot and sliding (6.7% SRR)


a) Scheme of samples and optical image of the flake (2 mm x 2 mm) retrieved in the lubricant

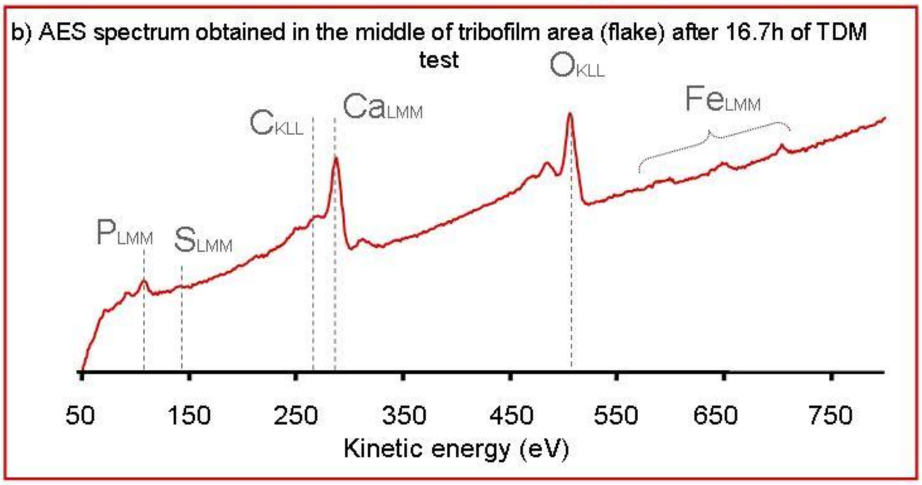

b) AES spectrum obtained in the middle of tribofilm area (flake) after 16.7h of TDM test

Figure 7: a) SEM images and b- c) EDX analyses on a spall of the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

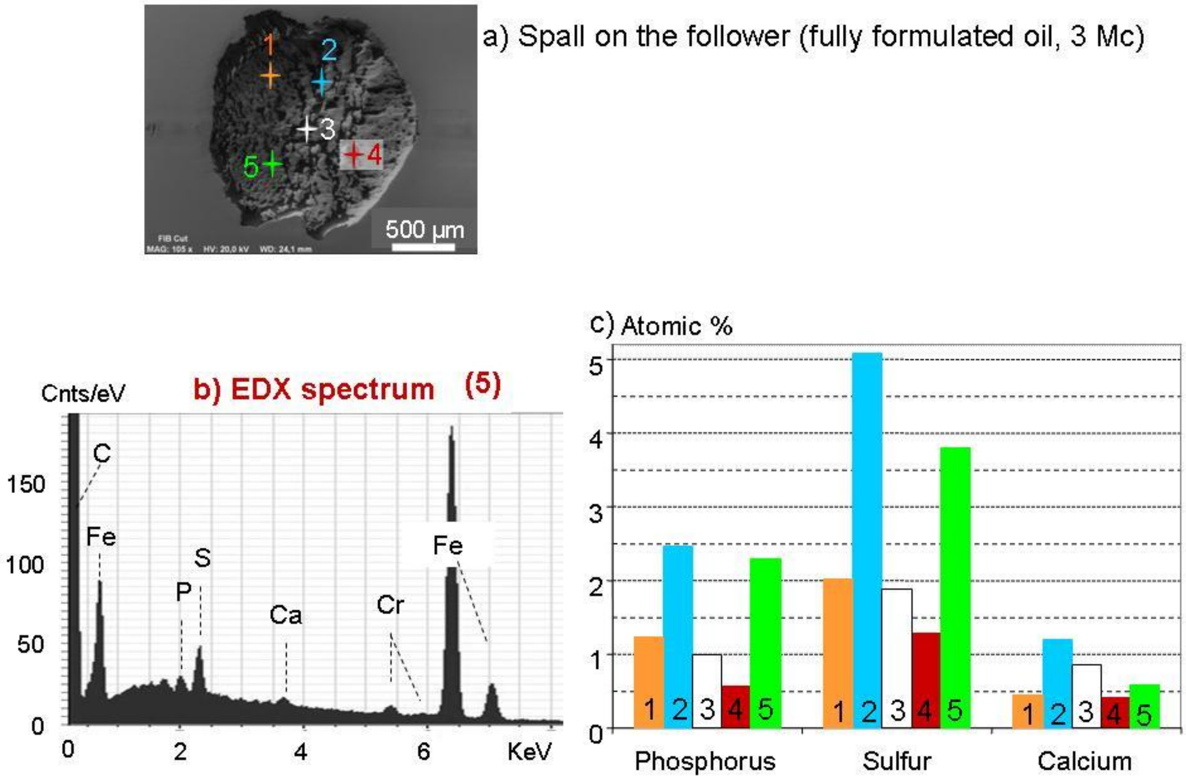


Figure 8: a) SEM images and b) EDX analyses (sulphur image) on a spall of the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

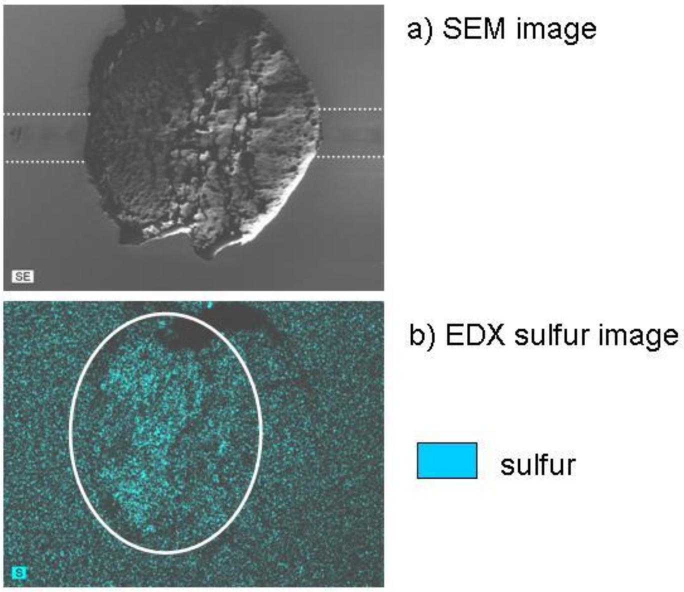


Figure 9: SEM images of a crack cross section obtained by FIB and related EDX analyses: a) outside of the crack (steel reference) b) crack tip. Analyses are performed on the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

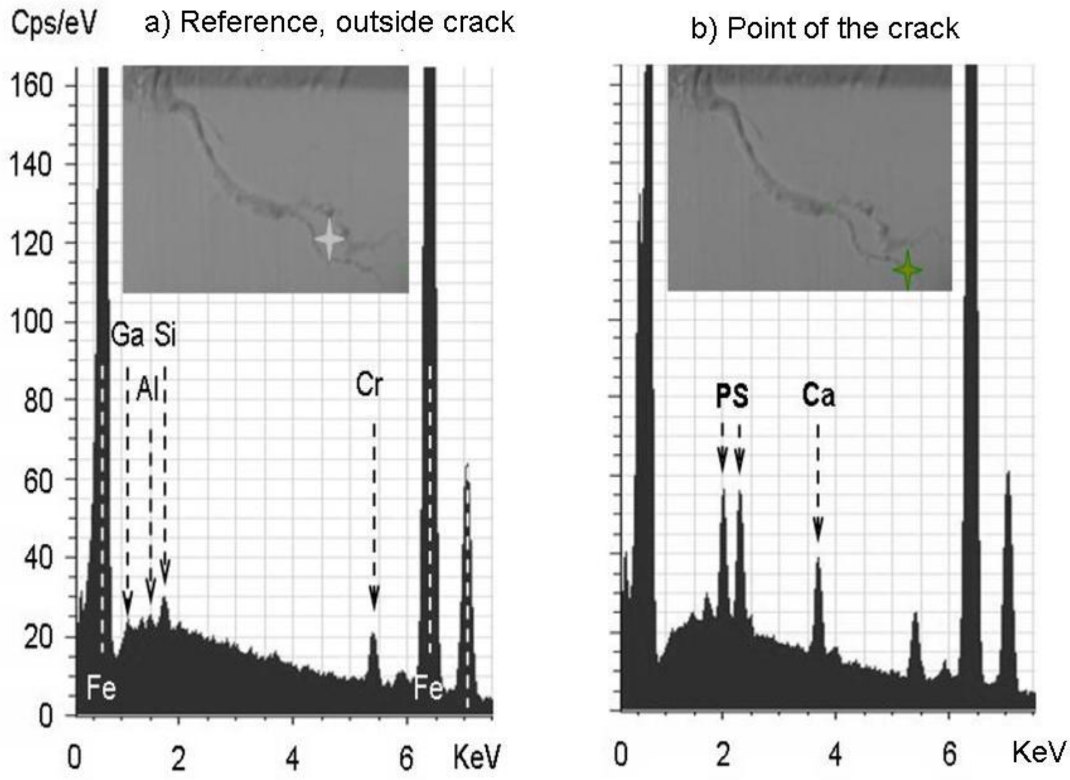


Figure 10: SEM image of a crack cross section obtained by FIB (cf. Fig 3) and EDX analyses along the crack. Analyses are performed on the follower disc after the rolling sliding test (6.7% SRR) with the fully formulated lubricant (Htot)

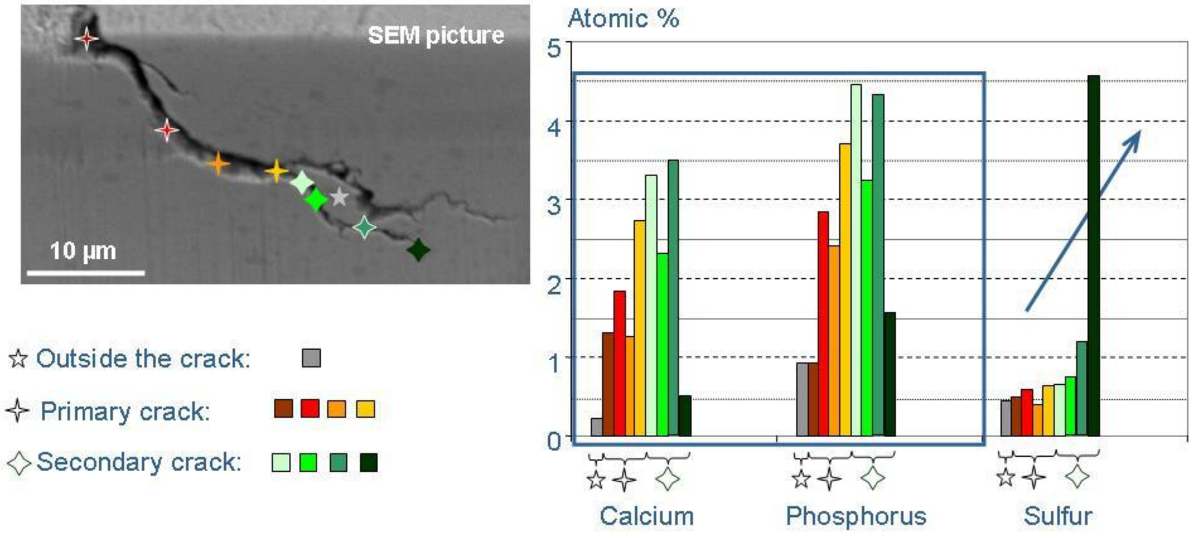
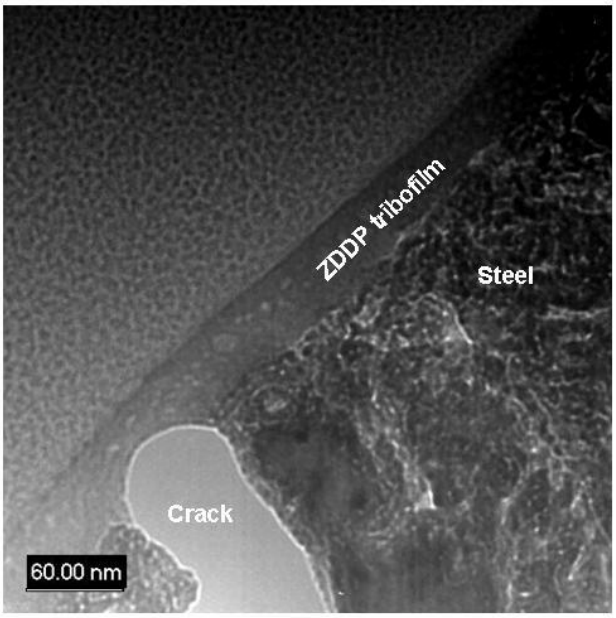


Figure 11: TEM image of a ZDDP tribofilm obtained under pure sliding condition from [23]. The tribofilm was generated on a Cameron-Plint tribometer, under cylinder-on-flat configuration with a load of 350 N, a speed of 0.1 m/s, a stroke length of 7 mm and a cylinder diameter of 6 mm. Both cylinder and flat are made of steel. The lubricant used is a polyalphaolefine base oil blended with 3% of ZDDP (zinc dialkyldithiophosphate) additive. The Hertzian contact pressure is estimated at 0. 85 GPa



***Revision Notes - list of changes and response to referees**

Reviewer #1: The paper constitutes yet another addition to a long string of publications devoted to rolling contact fatigue (RCF) in the presence of a lubricating medium. Although researchers in the past did not have an access to advanced surface analysis instruments but, nevertheless. were able to reveal essential causes for lubricated RCF. In view of that the current paper merely provides more details concerning elemental composition of surface film within the crack but not anything else, which could be considered as fundamentally novel. Also, one reading the paper gets impression that at the end of the day what has been found is rather inconclusive and fatigue damages observed could be equally well explained by "hydraulic pressure" mechanism postulated more than half the century ago. As submitted the paper does not require any amendments and modifications. Results are properly presented and the quality of illustrations at the professional level. Therefore, there is no formal objection to its publication.

The authors would like to thank you for your remarks and comments.

Reviewer #2: The authors studied Effect of lubricant additives in rolling contact fatigue, which will be a good guidance for others to design and study the similar works. This paper contains interesting and applied results in the gears. However, the work would be excellent if some mistakes were revised and some explanations were given.

1. Please give a detailed diagram of the working principle of the specimens, and a complete sample size.
Figure 2 was modified to make "the working principle of the specimens" clearer.
Figure 6 was modified to give precision on complete sample size.

2. Please give a reason, why did you choose a fully formulated lubricant, base oil and base oil with only antifoam and detergent not base oil with extreme pressure and/or antiwear additives.
The idea was as a first step to identify the effect of additives in condition closed to the application. That is why we choose to work first with a fully formulated lubricant.

Then, concerning tests with only one additive per lubricant:
According to conclusions of this paper related to the totally formulated lubricant, calcium and sulphur are found in the crack. All additives containing those two elements will be interesting to be studied separately. As you suggest, it is the case for detergent containing calcium, and for extreme-pressure and antiwear additives containing sulphur. We decided to study first the effect of detergent which seems to be more significant.

3. A fixed additive concentration has to be added, it is very important.
Because of confidentiality, only bracket values of additive's concentration were added in the paper.

4. Please explain "the oil film thickness" and how to measure oil film thinkness?
By "oil film thickness" we mean the EHL film thickness. It was calculated using the Hamrock-Dowson formula for circular contacts (cf. page 5 and table 2). We use the word "oil" in order that there is no confusion between the EHL film in the contact and the "solid" tribofilm generated on friction surfaces.
The EHL film thickness was only calculated and not measured.

We have replaced “oil film thickness” by “EHL film thickness” in the entire document.

5. The result is not clear, you should analyze flake of different oils lubricated conditions.
The purpose of this study was to identify if additives can reach inside the crack and act on crack propagation and so on fatigue life. That is why we concentrated on the procedure to realise the fatigue tests, the FIB milling at the right place to access to the inside crack and the analyses (AES, XPS…). So of course, other tests are missing, but we clearly demonstrate that additives can go inside the cracks and act on fatigue life by modifying friction between crack leaps and so propagation.
We plan to continue these analyses with different additives.

6. References should be changed according to"Journal Engineering Tribology" form.
Corrections have been done

EDITORIAL CHECKLIST

When preparing your manuscript would you please attend to the following points.

A ILLUSTRATIONS:
A1. Ensure that you have provided original illustrations.
A2. Check the quality of line drawings (Please ensure that any shaded illustrations must be defined with variant lines to avoid poor quality reproduction).
A3. Check the font size for labelling of illustrations - is this appropriate for reduction of the figure for reproduction in the journal?
A4. Check the quality of any photographs and half-tones.
A5. Ensure that you have written permission to reproduce (in all media) any figures for which you are not the copyright holder
A6. Extract the illustrations from the text and supply on separate sheets.
A7. Provide a separate list of figure captions.

B ABSTRACT, KEYWORDS AND MAIN BODY OF THE TEXT:
B1. Type the manuscript (including references) in double line spacing across the page. This aids both editor and typesetter in efficient and accurate production.
B2. Check that the abstract provides an accurate synopsis of the paper.
B3. Check that the keywords are appropriate for information retrieval purposes.
B4. Check that the style of writing is in the third person throughout.
B5. Number your section and sub-section headings.

C UNITS, EQUATIONS AND NOTATION:
C1. Check your use of units and convert to SI where necessary.
C2. Include a list of notation, in alphabetical order (lower case precedes capitals, Roman precedes Greek).
C3. Clarify the presentation of the equations and mathematical symbols:
C3(a) clarify Greek Characters.
C3(b) explain unusual symbols required.
C3(c) make the matrices bold upright, vectors bold italic if possible.
C3(d) clarify ambiguities in display equations, caused by use of solidus (the division slash /)

D REFERENCES:
D1. Check the references and ensure that they contain:
D1(a) Names and initials of all authors (if not more than three)
D1(b) title of paper or chapter

D1(c) source
D1(d) year, volume, pages or paper number
D1(e) publisher and/or sponsor (for books, conference, proceedings etc.)
D2. Ensure that the references follow the Vancouver sequential numbered style.