

FORMULATION OF LUBRICANTS WITH DIFFERENT BASE OILS AND EP ADDITIVES

Salete Martins Alves, saletealves@ect.ufrn.br

Science and Technology School and Postgraduate Mechanical Engineering Department of Federal University of Rio Grande do Norte. Campus Universitário, Lagoa Nova, Natal/RN, Brazil. Zipcode 59072-970

Marcos Vinicyus de Araújo Oliveira, vinicyus_marcos@hotmail.com

Jonhny Poulyeston Paulo Ribeiro, johnny.p.p.r@hotmail.com

João Marcos Silva Lins, joao-marcos2005@hotmail.com

Science and Technology School, Federal University of Rio Grande do Norte. Campus Universitário, Lagoa Nova, Natal/RN, Brazil. Zipcode 59072-970

Aline Cristina Mendes de Farias, alinecmfarias@ufrnet.br

Postgraduate Mechanical Engineering Department, Federal University of Rio Grande do Norte. Campus Universitário Lagoa Nova, Natal/RN, Brazil. Zipcode 59072-970

Abstract. *The increased development of lubricants from renewable sources came as a result of a series of government measures and increased public awareness regarding concerns about the environment. Nowadays, there is a broader range of lubricating oils' bases, which includes mineral oils, synthetic oils, re-refined oils and vegetable oils. Among them, the most used are the mineral ones which, by having sulfur, nitrogen compounds and a number of metals in their chemical composition, are highly toxic and non-biodegradable, causing constant threat to water supplies and ecology. Aiming at a sustainable and innovative alternative, lubricants environmentally friendly, also called lubricants of the future, must show high-performance properties, high biodegradability and to contain additives which do not harm the environment. Therefore, the study's goal is to evaluate the substitution of lubricants' base, from mineral to synthetic, and its combination with extreme pressure additives (EP) allowing less wear on metal surfaces in contact and which are appropriate to the environment. To achieve this goal, different formulations of lubricating oils were prepared, blending base oils and EP additives, and the additives' percentages studied were 0 % and 5 %. Three EP additive were studied: ZDDP, Active sulfur and compound of bismuth and polysulfides. The formulated lubricants were characterized according to some physical properties. The density, viscosity and viscosity index were evaluated. The friction and wear characteristics were studied using HFRR test. 10N of normal load was applied and the sliding velocity was 40 mm/s. Through the results of these tests, it was concluded that replacement of mineral oil by synthetic oil is viable. Also, synthetic oils are more stable at high temperatures. In relation EP additives was observed that they show different behavior in film formation, friction and wear. The best performance was obtained by synthetic oil (PAO) combined with compound of bismuth and polysulfides as EP additive.*

Keywords: mineral oil, PAO, EP additives, lubricity

1. INTRODUCTION

The lubricants have an important paper in the reduction of friction and wear in many cases; for example, the relative movement of two bearing surfaces is only possible if a lubricant is used. Thus, the development of lubricants has become an integral part of the development of machinery and its corresponding technologies (Mang and Dresel, 2007).

However its importance, since the middle of the 1970s the environmental impact of lubricants, both in their manufacture and use, has attracted increasing attention (Bartz, 1998). For most lubricated applications, the conventional choice is a mineral oil-based lubricant, but from an environmental point of view, mineral oil based lubricants are not readily biodegradable and contain many kinds of additives; many of which are known to be toxic or otherwise harmful to the environment (Petterson, 2007; Waara *et al*, 2001).

According to Petterson (2007) the lubricants of the future have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than commonly used lubricants today. Normally one has to be content with the fact that the lubricant is environmentally acceptable, this is that it affects the environment only to a less pronounced degree. Under this point of view, all aspects of impairment between the production of the lubricant, its application and its disposal have to be taken into account. Often there is an agreement to define lubricants as environmentally acceptable if they cover the requirements shows in Tab. 1 proposed by Bartz (1998).

The Lubricant formulations usually contain a variety of additives of different chemical functionality to meet many service requirements. These additives include friction modifiers (FM), extreme pressure agents (EP), antiwear (AW), antioxidants (AO), detergents–dispersants, and rust inhibitors. The addition of an appropriate additive to an oil lubricant improves chemical and physical properties and reduces friction and wear, avoiding surface damage (Zhang *et al*, 1999;

Unnikrishnan *et al*, 2002). The choice of additives and oil base should be careful, the biodegradability and toxicity of each component need to be evaluated.

Table 1. Aspects of environment impairment by lubricants (Bartz, 1998).

At production environmentally neutral
- Low energy consumption, no waste materials, no emissions
If possible using regenerable resources
- No depletion of resources, no greenhouse effect
Physiologically harmless
- Non toxic, not cancerous, etc.
Without toxic decomposition substances
- Non bio-accumulative potential
Eco-toxicological acceptable
- Non water endangering, no water miscible, lower density than water
After usage fast biologically degradable
- No toxic or unpleasant decomposition products
No disposal problems
- Possibility of simple recycling processes

According to Pettersson (2007) the lubricants of the future have to be more environmentally adapted, have a higher level of performance and lower total life cycle cost (LCC) than commonly used lubricants today. To be able to formulate these lubricants, the properties, if the base fluids, have to be well known and, they can be divided into three groups, i.e., physical, chemical and film formation properties.

Base oil could be of different types: mineral, synthetic and vegetable oil. Mineral oils are produced from crude oil. They have well-known properties as viscosity and VI (viscosity index). Since thirties many different synthetic base oils have been invented, but the most commonly used in lubricant formulation are polyalpha olefins (PAO); other synthetic oils used in lubricant applications are polyalkylene glycols (PAG), phosphate esters, and polyisobutylene (PIB). However, cost limits the use of synthetic oil, where the cost of them relative to a mineral one is high; i.e., the relative cost varies from 2-3 times up to over 500. But, it is very important to evidence the PAO characteristics, such as, high IV, extremely good low-temperature properties and high thermal stability (Pettersson, 2007). A relative evaluation and rating of different important aspects of lubricant oil is given in Tab. 2.

Table 2. Relative comparison and rating of different oils (Bartz, 2001).

Evaluation: 1 – Excellent; 2 – Very good; 3 – Good; 4 – Moderate; 5 – Poor.	Mineral oils	Polyalpha olefines	Polyalkylene- glycols	Polyolesters	Vegetable oil
Viscosity Temperature Behavior (VI)	4	2	2	2	2
Low Temperature Behavior (pour point)	5	1	3	2	3
Oxidation Stability	4	2	3	2	3
Thermal Stability	4	4	3	2	4
Solubility of additives	1	2	4	2	3
Lubricating properties, load carrying capacity	3	3	2	2	1
Toxicity	3	1	3	3	1
Biodegradability	4	3/4	1/2	1/2	1
Price relation against mineral oil	–	3-5	6-10	4-10	2-3

It is known that wear and friction performance in the boundary lubrication regime is controlled mainly by the lubricant additives which form tribofilms in the contacting surfaces, but surface treatments and coatings have an important role to play in providing an improved performance or they can, in fact, eliminate the benefits of the additives. Knowing the details of how surfaces and additives react is paramount in understanding how to achieve optimal lubrication in the boundary (and mixed) regimes (Neville *et al*, 2007). The film formation depends on the nature and chemistry of additives added to the lubricant oil. The additives and lubricants can usually form a boundary lubricating film on the lubricated surface by physical adsorption, chemical adsorption, and tribochemical reaction, during the friction process (Zhang *et al*, 1999; Unnikrishnan *et al* 2002).

Also, in conditions of boundary friction, such properties depend greatly on the tribological effect of their active elements (sulphur, phosphorus, nitrogen, chlorine, etc.). The required functional action is achieved by appropriate balance. Investigations that can optimize the composition and expand the areas of application of additive packages are of considerable scientific and practical interest. One of the modern developments in this field is the systematic

characterization of the performance of additives with different elements, alone and in combination, in order to promote their scientific selection. The effect of a particular additive depends on its chemical nature, and its concentration (Stanulov et al, 1998). According to Ma et al (2009) the sulfur and phosphorus are considered as “active elements” for ferrous-based equipment and they have been investigated by many researchers.

Piekoszewski et al. (2001) studied the influence of EP additives on the scuffing propagation and wear intensity; their experiments were carried out in four ball equipment. They concluded that under extreme pressure conditions chemical reactions of active compounds of AW and EP additives (based on ZDDP and S–P compounds, respectively) with the steel surface as well as diffusion of sulfur and phosphorus take place. Also, due to chemical reactions and diffusion probably inorganic compounds of S and P are created. Their good antiseizure properties mitigate the scuffing propagation and reduce wear intensity.

In this work, some combinations between different oil base and EP additive were evaluated in order to identify the better formulation to minimize the wear on metallic surface and environmental impacts. Mineral oil and polyalpha olefin (PAO) were combined with different EP additives. These lubricants were tested using HFRR equipment, where the lubricant lubricity could be analyzed. SEM were used to investigate the wear mechanisms and film lubricant formation on metal surface.

2. EXPERIMENTAL

2.1 Oil samples

The oil blends containing different additives and oil base were prepared. Mineral oil and Polyalphaolefin (PAO) were used as oil base. There additives EP were studied and some characteristics are presented in Tab. 3. The EP additives were added to each oil base in rates of 0 and 5 % (in volume). Table 4 shows all blends of lubricants studied and their density, viscosity and viscosity index. The density was measured by pycnometer and viscosity was determined by rheometer (Brookfield RS 2000) at 40 °C and 100 °C.

Table 3. Description of EP additives studied.

ADDITIVES EP
EP1: Zinc dialkyldithiophosphate (ZDDP) – it has in its composition 3,5% of sulfur; 1,9% of phosphor and 2,1% of zinc.
EP2: Additive base on metalorganic compounds of bismuth and polysulfides (17% of bismuth and 7% of inactive sulfur).
EP3: Additive EP with high active sulfur containing.

Table 4. Some characteristics of lubricants blends.

Blend number	Oil base	EP additive	Density (g/cm³)	Viscosity (cSt) at 40 °C	Viscosity Index
1	Mineral – 100%	None	1.38	28.06	174.54
2	Mineral – 95%	EP1 – 5%	1.43	24.51	184.80
3	Mineral – 95%	EP3 – 5%	1.55	26.93	179.01
4	Mineral – 95%	EP2 – 5%	1.46	23.46	186.70
5	PAO – 100%	None	1.28	51.84	155.24
6	PAO – 95%	EP1 – 5%	1.42	30.27	179.40
7	PAO – 95%	EP3 – 5%	1.45	30.23	179.05
8	PAO – 95%	EP2 – 5%	1.51	29.07	180.04

2.2 Friction and wear test

The friction and wear performances of oil blends were evaluated using the HFRR (High Frequency reciprocating rig) as shown in Fig. 1. The HFRR method is a ball-on-disk test to measure the friction and wear under boundary lubrication conditions using a highly stressed ball-on-disk contact. A hard steel ball (570 – 750 HV) of 6.0 mm diameter reciprocates on a softer steel disk (190 – 210 HV) of 10 mm diameter under the fully submerged oil condition at normal load of 10 N and a 1 mm stroke length at a frequency of 20 Hz for 60 min. Both ball and disk were made of AISI 52100 steel. The oil temperature was kept at 50 °C. The wear scars of the ball (WSD – wear scar diameter) were determinate by optical microscope at 100 times magnification and disk wear were analyzed by SEM. The friction coefficient was measured by a piezoelectric force transducer and the formation of electrically insulating films at the sliding contact was measured by the ECR (electron cyclotron resonance) technique. Both ball and disk were cleaned by ultrasonically agitated bath of acetone and toluene before and after the HFRR test.

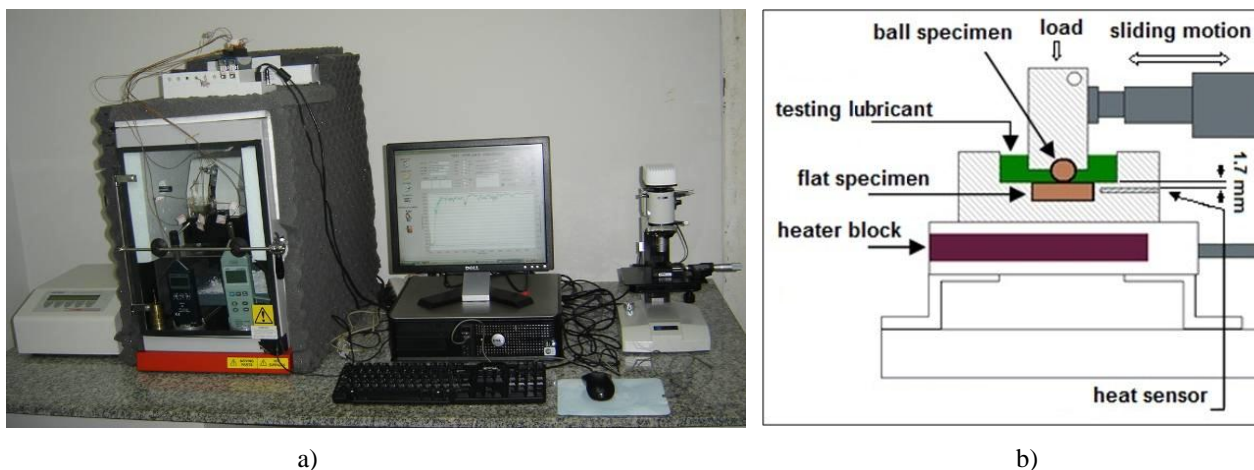


Figure 1. HFRR test: a) picture of equipment used in tests and b) schematic diagram of HFRR.

3. RESULTS AND DISCUSSION

Different oils base and additives were evaluated using HFRR test. Test condition with oil mineral and PAO without additive was used as reference in order to analyze the influence of EP additive on wear of metallic surface. The following will be presented and discussed results about friction coefficient, wear scar diameter (on ball) and wear mechanism (on disk).

3.1. Friction coefficient and film formation

The formation of electrically insulating films was measured using during HFRR test by means of the ECR. The surface coverage, caused by generation and removal of surface films, was measured under boundary lubrication conditions with a steel ball sliding against a steel disk. Figure 2 shows the film formation behavior of the lubricants studied. The film formation is strongly influenced by oil base and EP additive. When oil mineral base without additive was used there was a film formation, but a not very expressive percentage, and the synthetic oil (PAO) formed more film and showed more fluctuations during the test. Also, when active sulfur (EP3) and compounds of bismuth and polysulfides (EP2) were added to oil base as EP additive, observed that film insulating film formation was not significant. However, the ZDDP promotes film formation for both mineral oil and PAO. The higher percentage of film formation was observed for blend of PAO and ZDDP.

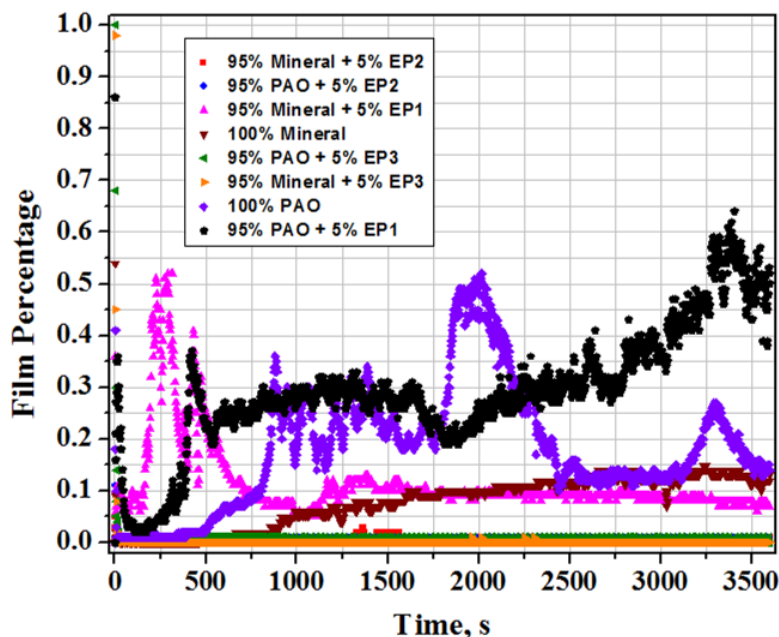


Figure 2: Film formation as measured by ECR.

Figure 3 shows the variation of friction coefficients with run time for various blends lubricant. The friction coefficient for most of blends exhibits few fluctuations during the test. The high values of friction coefficients were observed to oil base without EP additive, both mineral oil and PAO, and for blends where ZDDP (EP1) were added. According to McQueen *et al* (2005) the friction coefficient corresponds well with the film formation as shown in Fig. 2. The films covering the rubbing surfaces affect the surface roughness and structure. Thus, the friction behavior shows a corresponding response to the film formation between the contacts under the boundary lubrication conditions. Once the friction behavior is different for three EP additives studied added a same base, for example mineral oil, this fact suggests that the boundary films formed in the EP1, EP2 e EP3 oils are not same and formed by different mechanisms. The low friction coefficients are produced by both oil bases blended with EP2 additive.

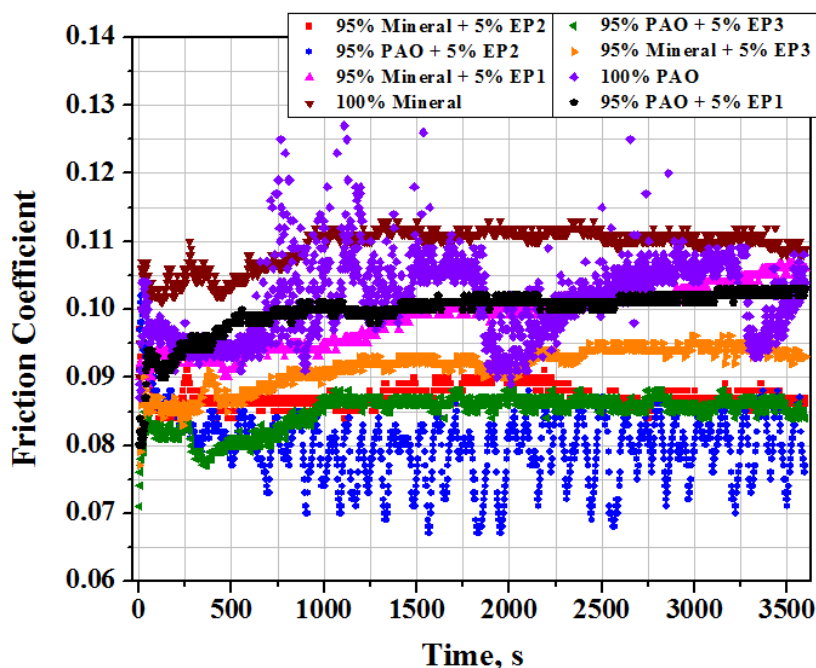


Figure 3. Friction behavior of lubricant blends.

3.2 Wear

The worn volume values indicated that different wear mechanisms are acting in the contact. A scanning electron microscopy was used to examine the surfaces of the disks following each test. A selection of micrographs of the worn surfaces is presented in Fig. 4. This figure shows the ball scar measured by optical microscopy with 100 x magnification. These show the disk worn surfaces and their sliding directions by arrows.

The influence of oil base in the wear can be seen in Fig. 4 (a) and 5 (a). These images show the worn surface when mineral oil and synthetic oil were used as lubricant, respectively, without add of EP additives. In both situations there are abrasive signals and it seems to be the main wear mechanism, but for mineral oil the wear was more severe. Therefore it is possible to note another wear mechanisms acting on the surface. According to Hutchings (1992) the severe wear can be associated to debris formation and detached from the surface, the rolling of debris particles between sliding surfaces is the cause of severe wear. This mechanism can be observed for lubricants number 2 and 4, where ZDDP was used as EP additive (Fig. 4 (b) and 5 (b)). Fan et al (2008) observed that ZDDP apparently increases the friction coefficient (see item 3.1), which probably is due to the high shear strength or the surface roughness of the film formed by ZDDP. Also, Li and So (2008) concluded in their work that at a low sliding speed, the surface film is mainly a physisorbed film at temperatures below 50°C and no protective film is formed in conditions such as, high contact pressure, large relative hardness between two rough surfaces or a low concentration of ZDDP at high temperature.

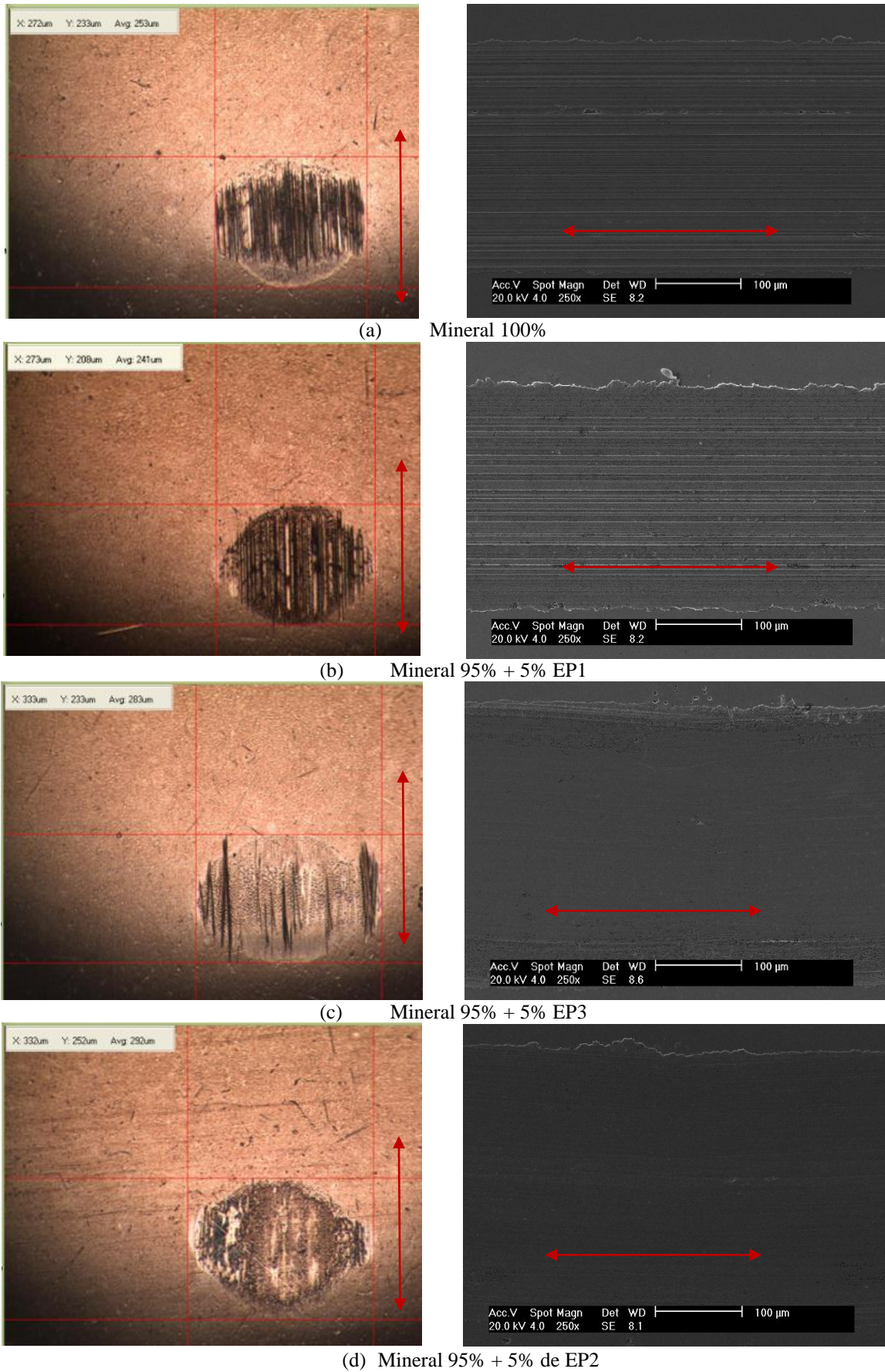


Figure 4. Wear scar of ball (first column) by optical microscopy and the worn contact surfaces of the disk (second column) by SEM when mineral oil with and without EP additive was used.

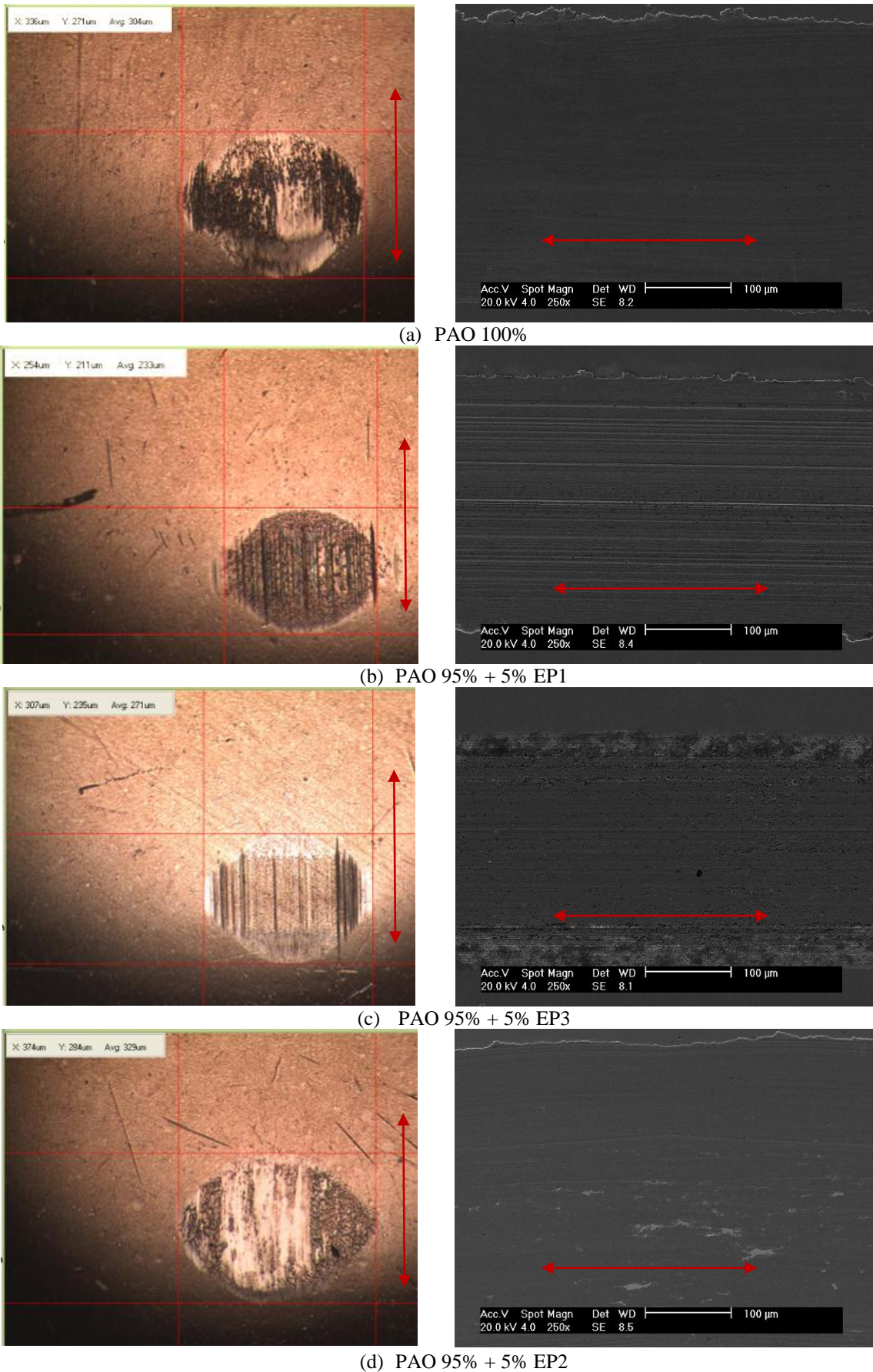


Figure 5. The worn contact surfaces of the disk (second column) and wear scar of ball (first column) when synthetic oil (PAO) with and without EP additive was used.

Comparing the effect of active sulfur additive (EP3) with compounds of bismuth and polysulfides (EP2) (Fig. 4 (c) and (d) and Fig. 5 (c) and (d), respectively) it is possible to observe that when EP3 is added to oil lubricant PAO there is not significant improve in lubricant performance in terms of wear reduction, such as observed in lubricant with EP2 additive. Some explanations for this observation can be: (1) Probably the EP3 additive was not dissolved by PAO according to Carreteiro et al (2006) the main disadvantage of PAO is it's difficult to dissolve additives. Both the addition of EP1 as EP2 separately in mineral oil provided significant reduction in worn; (2) this fact can be explained by sulfur reactivity with metals surface. Normally, sulfur formed tribofilms under highly loaded (high temperatures), as in this work the load applied was low (10 N), probably the sulfur didn't react with metal surface and didn't form the tribofilm (Evans et al 2007; Waara et al, 2001).

4. CONCLUSIONS

According to the test results the following conclusions could be taken:

- Insulating film formation was effective when ZDDP was used as EP additive, but the active sulfur (EP3) and compounds of bismuth and polysulfides (EP2) additives didn't promote the film formation.
- The friction behavior is different for three EP additives studied, probably they formed film by different mechanisms. The low friction coefficients are produced by both oil bases blended with EP2 additive.
- Abrasion was the main wear mechanism in all lubricated tests, but not the only one acting.
- Severe wear was observed for mineral oil base without EP additive and for blends with ZDDP additive.
- In general, synthetic base had a better performance than a mineral one.

5. ACKNOWLEDGEMENTS

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