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ANALYZE OF INFLUENCE OF BASE OILS AND ADDITIVES EP ON LUBRICATION OF METALLIC SURFACES[1]

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Abstract
Lubricants develop an important role in the operation of various equipments, such as simple applications (appliances) or in special applications (aerospace). They minimize the friction and normally reduce wear, which provides economic losses undesirable. In recent years there has been a great development in the lubricants industry, producing synthetic lubricants that can replace mineral oils, which cause different impacts on the environment. Thus, this study aims to evaluate the influence of base oil and additives to minimize wear of metal surfaces. To achieve this objective, pin on disk sliding wear tests were performed. The alloy used for the pin was the SAE 52100 steel against SAE 1020. The used lubricants were paraffin mineral oil base and synthetic polyalphaolefins with viscosity of 180 cSt. Combinations of bases with sulfur and phosphorus additives to 5% were made. The mechanical load was kept stable (20 N) with the same speed (0.15 m/s) for all tests. The metallic wear was analyzed by optical microscopy and scanning electron microscopy. To assess the volume of worn material was used a profilometer. The combination of EP additive phosphorus-based and oil based polyalphaolefins (PAO) and the combination more effective in reducing wear, resulting in lower volume worn. The main wear mechanism observed was abrasive.
Keywords: Oils; EP additives; Pin-on-disc test.

ANÁLISE DA INFLUÊNCIA DOS ÓLEOS BASE E ADITIVOS EP NA LUBRIFICAÇÃO DE SUPERFÍCIES METÁLICAS

Resumo
Os lubrificantes desenvolvem um importante papel na operação de vários equipamentos, tais como, simples aplicações (eletrodomésticos) ou em aplicações especiais (aeroespacial). Eles minimizam o atrito e normalmente reduzem o desgaste, que acarretam perdas econômicas indesejáveis. Nos últimos anos tem se observado um grande desenvolvimento da indústria de lubrificantes, produzindo lubrificantes sintéticos que podem substituir os óleos minerais, os quais causam impactos sobre o meio ambiente. Assim, este artigo objetiva avaliar a influência do óleo base e aditivos para minimizar o desgaste de superfícies metálicas. Para atingir este objetivo, foram realizados ensaios de desgaste por deslizamento do tipo pino sobre disco. Como corpo-de-prova foi utilizado o aço SAE 1020 e contra-corpo esferas de aço SAE 52100. Foram utilizados óleo mineral parafínico e o óleo sintético polialfaolefina, ambos com viscosidade de 180 cSt. Foram adicionadas às bases 5% de aditivos EP (enxofre e/ou fósforo). A carga aplicada foi de 15 N com velocidade de 0,15 m/s para todos os testes. O desgaste foi avaliado por microscopia ótica e eletrônica de varredura. O volume desgastado foi medido com auxílio de um perfilômetro. Os resultados obtidos demonstraram que a combinação polialfaolefinas e o aditivo a base de fósforo foi mais efetiva na redução do desgaste. O principal mecanismo de desgaste observado foi o abrasivo.
Palavras-chave: Óleos base; Aditivos EP; Teste pino sobre disco.

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1 INTRODUCTION

High cost of tribological deficiencies to any national economy is mostly caused by the large amount of energy and material losses occurring simultaneously on every mechanical device in operation. For a single machine, the losses are small. However, when the same loss is repeated on perhaps a million machines of a similar type, then the costs become very large. In this scenario the lubrication have a special place; the lubricants are interposed between two surfaces in order to improve the smoothness of movement of one surface over another and to prevent damage.(1) The development of lubricants has become an integral part of the development of machinery and its corresponding technologies.(2)

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 rustinhibitors. The addition of an appropriate additive to an oil lubricant improves chemical and physical properties and reduces friction and wear, avoiding surface damage.(3,4)

It is known that wear and friction performance in the boundary lubrication regime is controlled mainly from 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.(5) 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.(3,4)

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.(6) According to Ma et al.(7) the sulfur and phosphorus are considered as “active elements” for ferrous-based equipment and they have been investigated by many researchers.

The synergies among additives may either enhance or diminish the surface durability of steel tribological components in applications. Evans et al.(8) affirm that many varieties of S-P additives have been tested for antiwear and extreme pressure protection of steel surfaces. They explain that, in general, sulfur is found in tribofilms formed under highly loads, thin-film lubrications conditions (boundary lubrication) while phosphorus and oxides are predominant in films formed under more mild conditions.

The effect of various sulfur EP agents was investigated in combination with phosphate ester by Najman, Kasrai and Bancroft.(9) Using XANES analyze they concluded that phosphates reacts more readily with steel to form a tribochemical film that protects the oxide layer from depleting. This results in complete oxidation of the

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sulfur additive to iron sulfate. However, Sulfur did not enhance the AW properties of the oil.

Piekoszewski, Szczerek and Tuszynski[(10)] studied the influence of EP additives on the scuffing propagation and wear intensity, their experiments were carried out in four ball equipment. They conclude 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.

The synergy between N-S additive EP were evaluated by Zhang et al.[(3)] The authors prepared and used as additive a derivative of 2-mercaptobenzothiazole containing N–C–S bonds. The heterocyclic part adsorbed on the metal surface by physical and chemical adsorption during sliding, while S in the compound reacted chemically with the lubricated metal surface. This was beneficial for the formation of a boundary lubricating film and for the improvement of the antiwear and extreme pressure properties of the lubricant.

The tribological performance of P and/or S additives were evaluated by Ma et al.,[(7)] using a four-ball equipment and XPS and XANES analyses. In this investigation surface analysis results indicate that tribofilms are mainly composed of absorbed layer and chemical reactant layer, in which phosphorus exists in the form of adsorbed molecule, phosphate or polyphosphate, and sulfur in the form of alkyldisulfide, sulfide and sulfate. As to the thermal films, phosphate (or polyphosphate) and sulfate are detected as the main components. The anti-wear and friction-reducing performances can be described to the formation of films on the metal surface, and the mechanism of the process of molecules adsorption, new compounds production through tribochemical reactions, film formation and destruction.

Beyond the use of additives, also it is important to consider the correct selection of the lubricant base. For most lubricated applications, the conventional choice is a mineral oil-based lubricant. Mineral oils used as lubricants have well-known properties. When a mineral oil is selected, viscosity and viscosity index (VI) are normally used to characterize the fluid. If a synthetic ester-based lubricant is chosen for an application, for technical and/or environmental reasons, beyond viscosity and VI, thermal conductivity and polarity are some properties considered too.[(11)] There are many different synthetic base oil, but the most commonly used in lubricant formulation are polyalpha olefin (PAO).

Peterson[(11)] in your paper describes some characteristics for PAO, such as: high VI (over 130), low volatility, low polarity, extremely good low-temperature properties and high thermal stability. In this investigation PAO and mineral oil were evaluated.

A comparison between mineral and synthetic oil performance was made by Fu et al.[(12)] They tested the lubricants in pin-on-cylinder apparatus using plasma nitride stainless steel as workpiece. With X-ray images, they concluded that the synthetic oil was superior to the mineral oil especially under high load and high sliding speed.

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. Mineral oil and polyalpha olefin (PAO) were combined with phosphorus and/or sulfur EP additives. Theses lubricants were tested using pin-on-disk equipment. MEV and EDS were used to investigate the wear mechanism and additive presence on metal surface.

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2 EXPERIMENTAL PROCEDURE

Oil and additives performance was evaluated through sliding wear tests.

Materials – material used as specimen to evaluate the oils was plain steel, SAE 1020. Specimens were obtained from drawn bars. The Figure 1 shows a picture and dimensions of specimens. This form was used to keep the wear surface immerse in oil during test. Tested surfaces were polished before the tests up to Ra 0.6 µm.

The other material used to slide against the specimens was 6 mm diameter bearing balls. These balls are made of AISI 52100 steel.

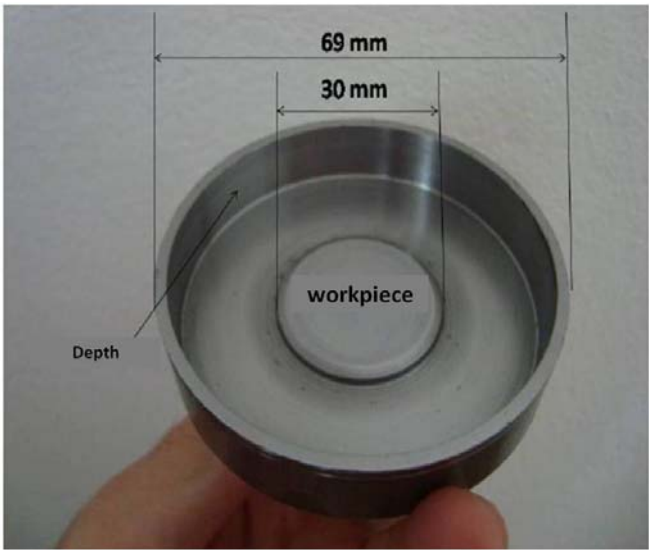

Figure 1 – form of the specimen.

Lubricants – Two oil bases were used, a mineral paraffinic oil and a synthetic polyalphaolefins oil, both with viscosity of 180 cSt. Sulfur (S), Phosphorus (P), and Sulfur plus Phosphorus (P + S), additives were used separately in each oil base. Table 01 shows all mixtures of lubricants and additives used.

It was used 10 ml of lubricant in each test to keep contact region immerse during all test and also, this is the minimum quantity for chemical analysis. After each test, lubricant was gathered in an appropriated recipient for future chemical analysis.

Tabela 1 – lubricants combinations.

Base oil	Additive	Code
Mineral	None	MA
Mineral	P (5%)	MP
Mineral	S (5%)	MS
Mineral	P (2%) + S (2%)	MPS
Sintetic	None	SA
Sintetic	P (5%)	SP
Sintetic	S (5%)	SS
Sintetic	P (2%) + S (2%)	SPS
None	None	Dry

Wear tests – pin on disk sliding wear tests were carried out to evaluate the different types of lubricants. The equipment used in tests is a home made pin on disk showed in Figure 2. Test conditions were the following: 20 N of load, 0.15 m/s of sliding speed and 1000 m of sliding distance, according to ASTM G99-2000.

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Friction force was measured by a load cell and friction coefficient was calculated. Volume of removed material was calculated from the profiles of the wear surfaces after the tests. Each test surface was evaluated in perfilometer equipment and the profiles of the wear tracks were obtained. With the aid of software specially developed for this, volume of removed material was determined.

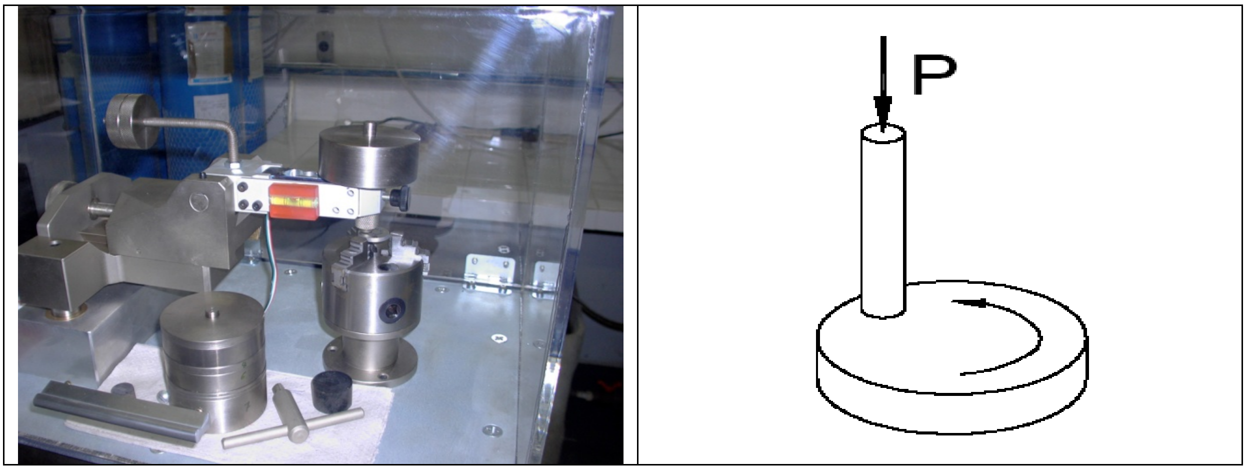

Figure 2 – picture of the pin on disk equipment used in sliding wear tests.

After the tests the wear mechanisms were evaluated in a Scanning Electron Microscopy and the oils were analyzed.

3 RESULTS AND DISCUSSION

Different oil base and additives were evaluated in wear test pin-on-disc. The test condition without lubrication was used as reference in order to analyze the lubrication performance. The Following will be presented and discussed results about worn volume, wear mechanism and lubricant analyze.

3.1 Worn Volume

Assessing the graph of the wear volume (Figure 3 (a)), it is possible to verify the great benefit for wear reduction for all lubricated situations tested. Volume of removed material in dry condition was much higher than any lubricated condition. Comparing only lubricated situations (Figure 3 (b)) is possible to some conclusions about oil base and additives performance. Note when synthetic base was tested without EP additive (SA) lower amount of worn volume was obtained than for mineral oil without EP additive (MA), approximately three times less, indicating better formation of lubricant film. If Sulfur and Phosphorus additives are added, separately, to synthetic base there was little improvement in worn volume. However, for the additives use in mineral base observed other behavior, showing synergy between oil base and additives EP. Probably, this behavior occurred because natural characteristic of the mineral oil to dissolve the additives, according to Carreteiro e Belmiro[13] the main disadvantage of PAO is it’s difficult to dissolve additives. Both the addition of S as P separately in mineral oil provided significant reduction in worn volume.

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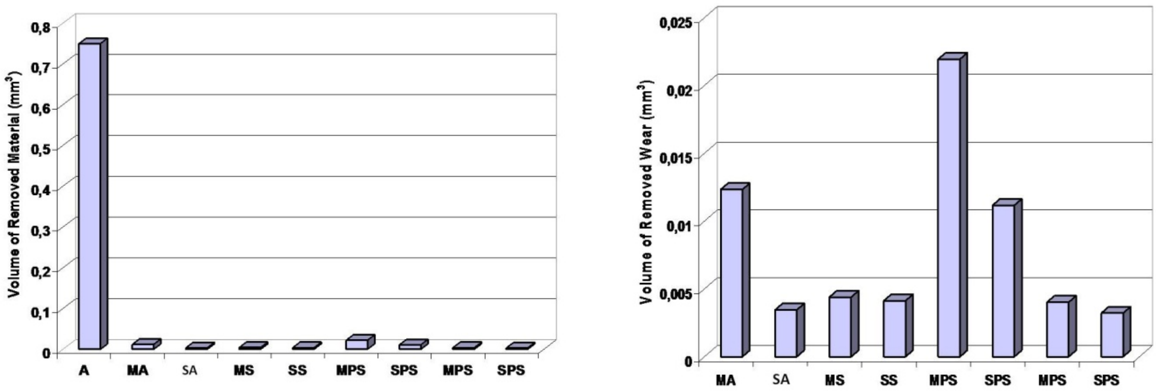

Figure 3 – Volume of removed material in (a) all situations, (b) only lubricated tests.

As it already cited in introduction, the combination of additives S and P can give good or bad results in terms of wear and surface damage. Observing the Figure 1b it is possible to verify that when S and P were added together in oil base there was an increase of values of worn volume. This fact indicate that no synergy between the additives studied (S and P) was observed. Evans et al.(8) also verified by TEM and XPS analyses that when S and P are combined only P form a protect layer, indicating sulfur EP action was limited to break-in phase of the tests.

3.2 Wear Mechanism

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 discs following each test. A selection of micrographs of the worn surfaces is presented in Figures 4 and 5. These show the disc worn surface where the sliding direction is horizontal.

The influence of oil base in wear can be seen in Figure 4 (a) and (b). 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. Therefore it is possible to note another wear mechanisms acting on the surface. Delamination wear was found with mineral oil lubrication. However, this mechanism was not observed for synthetic oil lubrication, where just few signals of abrasive wear could be seen. It is possible to note that even adhesion seems to be present in some situation. In these cases it means that the oils could not to prevent contact of the surfaces completely.

The phosphorus additive effect can be observed on Figure 5 (a) and (b). In these images soft wear marks were found, reducing the wear. Yang and Qunji(14) observed that phosphorus compound to prevent the wear and damage in ferrosystem, and this is associated with the formation of phosphate films with low shear strength on the metal surface.

Comparing the effect of sulfur additive with phosphorus additive (Figure 4 (c) and (d), Figure 5 (a) and (b), respectively) it is possible to observe that when sulfur is added to oil lubricant there is not significant improve in lubricant performance in terms of wear reduction, such as observed in lubricant with phosphorus additive. 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

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was low (15 N), probably the sulfur didn´t react with metal surface and didn´t form the tribofilm (8,15).

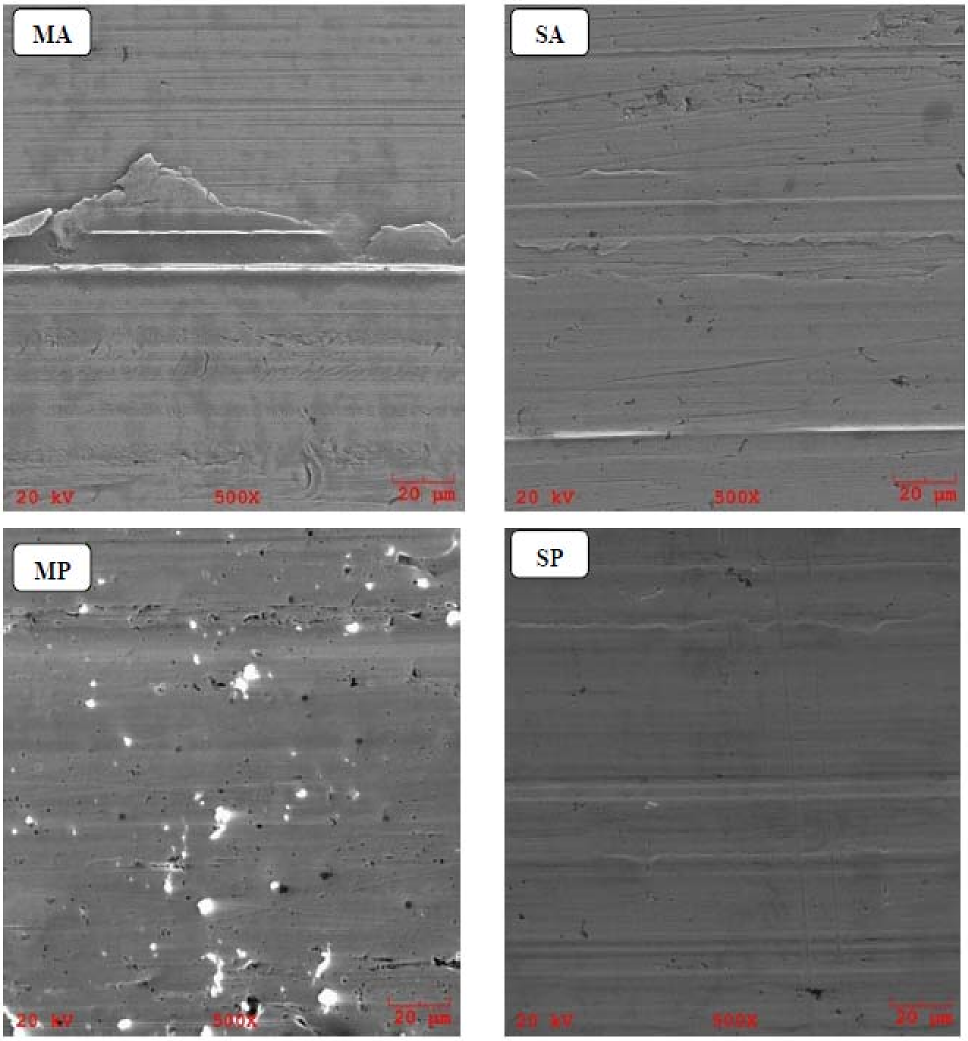

Figure 4 – The worn contact surfaces of the disc obtained by SEM, (a) MA, (b) SA, (c) MP e (d) SP.

The worst performance for lubricated test was observed for lubricant with additives, sulfur and phosphorus. The combination of two additives increase wear for all oil bases studied (Figures 5 (c) and (d)). Sulfur and phosphorus can be classified as chemically active additives, whereby they interact chemically with metals to form a protective film. According to Najman, Kasrai and Bancroft(9) and Waara et al.(15) a possible explanation for this fact is that exists the possibility of competition for surface sites that can lead to the inefficiency of one or more the chemically active additives in the lubricated system. Also, for Han and Masuko,(16) excessive film formation due to very high levels of additive can lead to increased wear through a corrosive mechanism. The main wear mechanism in this situation seems to be abrasion.

The images (Figures 4 (c) and (d)) show more wear on surface that other conditions studied, the abrasive wear was the predominant wear mechanism. According to Hutchings(17) the abrasive wear can increase when lubricant is used. The lubricant difficult the debris adherence on surface lead the hard particle in contact with both surface (pin and disc) increase de wear. But it is possible to realize that other mechanisms are acting too.

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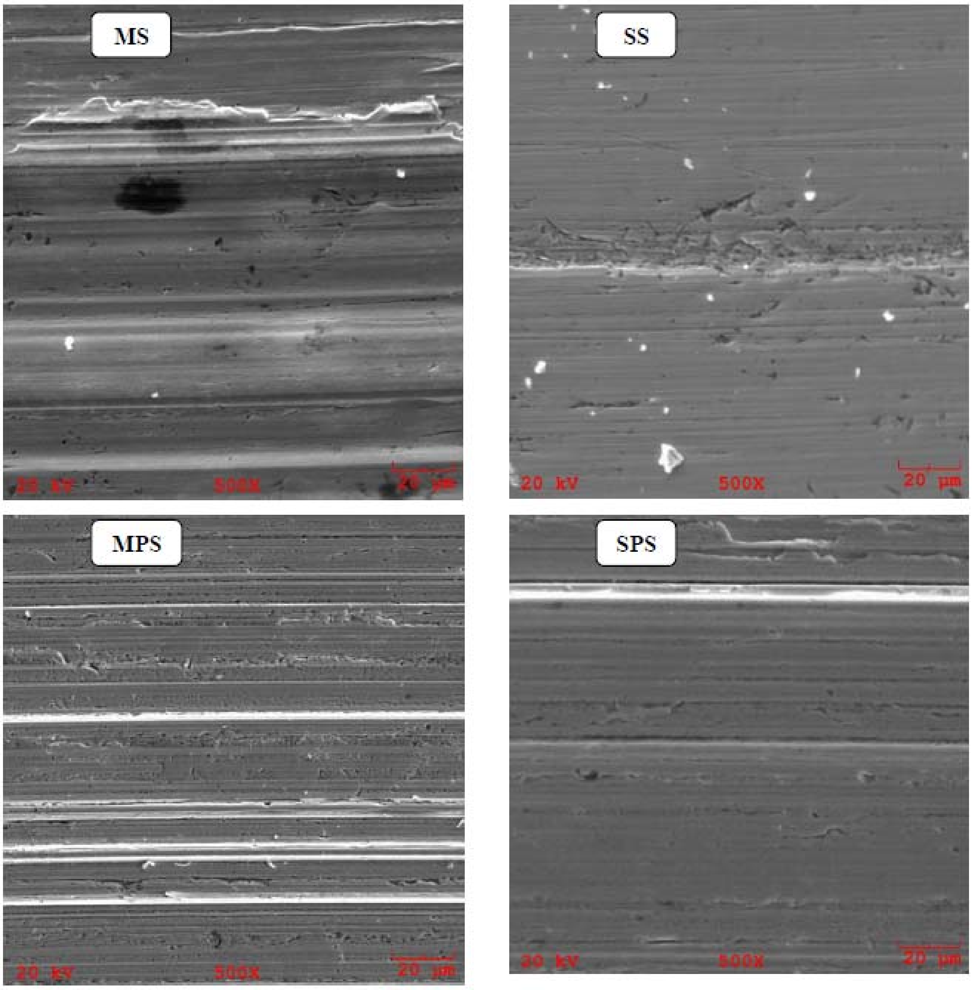

Figure 5 – The worn contact surfaces of the disc obtained by SEM, (a) MS, (b) SS, (c) MPS e (d) SPS.

Follow will be present the lubricant analyze that confirm the comments above.

3.3 Lubricant Analyze

The lubricant analyze have an important role for understanding of lubrication effect on metallic surfaces, evidencing the alteration in function of friction, wear and temperature of sliding process. All formulations tested in this work were analyzed after their use, in order to evaluate this alteration.

Figure 6 shows ferrography analysis for all formulation evaluated. This analyzes show the aspect and size of particles present in lubricant and permit to identify the level of wear. Comparing all images of Figure 6 can confirm the results discussed above about the lubricant ability of wear reduction. The synthetic oil present few particles dissolved indicating lower wear level than mineral oil. The addition of additive kept low presence of metallic particles in lubricant. However, when sulfur and phosphorus are combined in same oil base there was an increase of amount of particles, indicating the high wear observed in the wear analyze above.

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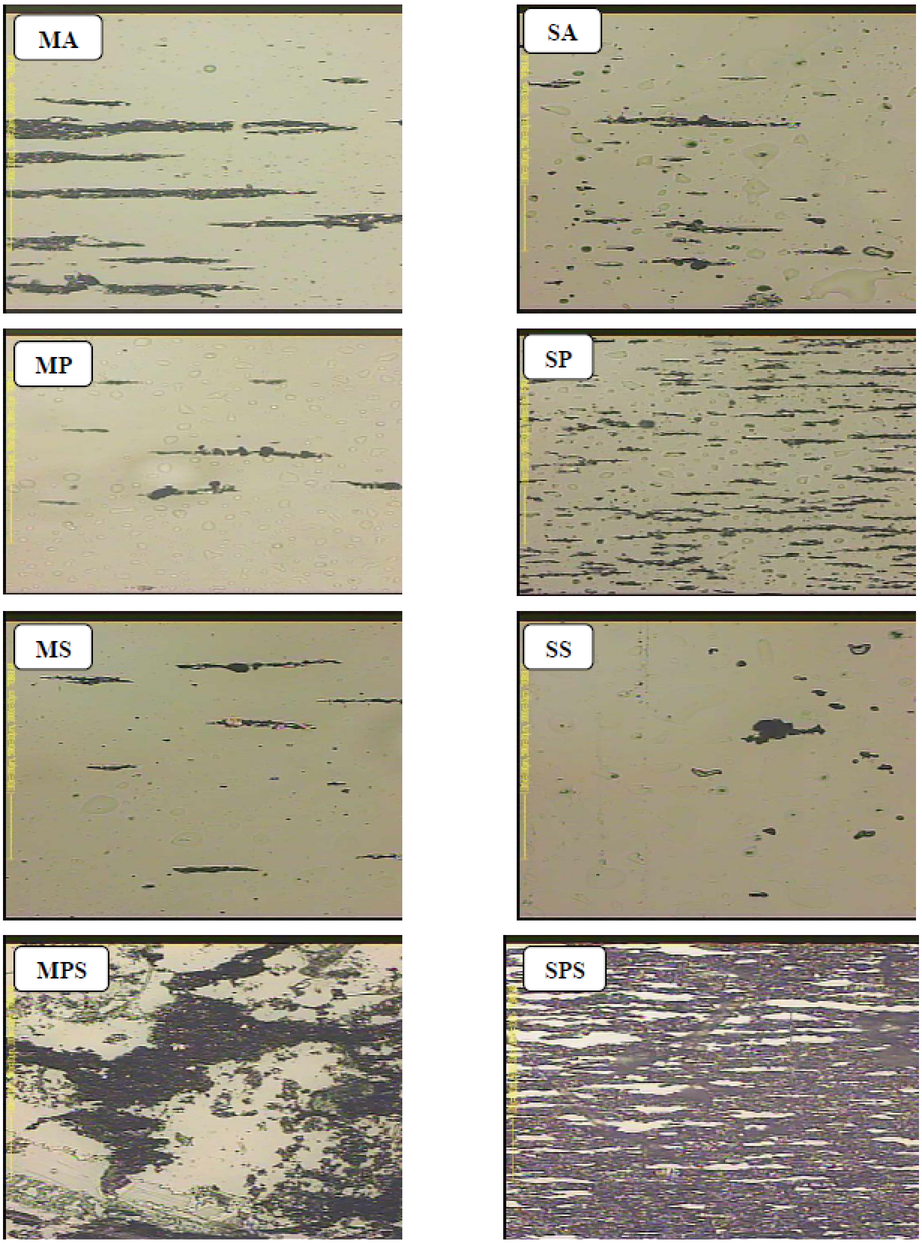

Figure 6 – Ferrography analysis for all formulation evaluated.

4 CONCLUSIONS

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

- Lubrication was effective in reducing wear independent of the oil base and additive used.
- In general, synthetic base had a better performance than a mineral one.
- The EP additives were efficient to improve the oil bases.
- Abrasion was the main wear mechanism in all lubricated tests, but not the only one acting.
- The combination of different EP additives (S and P) provoked increase of wear probably due to competition for surface sites.

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