Oil contamination and additive effects on the wear and friction of metallic specimens in reciprocating lubricated sliding tests

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Abstract. The present work aimed to characterize the effect of oil contamination and additive presence on the wear and friction in pin-on-plate reciprocating sliding tests. The wear mechanisms in the contact are discussed. The metallic materials used were AISI 52100 steel for round-ended pins and SAE 8640 steel plates. To study the additive effect, two types of paraffin basis oil (viscosity index 100), with and without additives, were used. To verify the contamination effect, the oil of some tests was contaminated with quartz abrasive particles. The tribological tests were performed at 4.2 Hz frequency, 80 N normal load and 100 ºC oil bath temperature, with 100,000 cycles. The results show that the additive effect was related to the tribofilm formation and the oil contamination increased the wear and the friction values. The additive effect was suppressed when contamination was present in the oil.

Key words: contamination, additive, mixed lubrication, reciprocating

1. Introduction

In lubricated systems, friction and wear responses can be significantly influenced by the lubricant characteristics. Literature information shows that the chemical nature of the lubricant changes the friction response of the system. Bowden and Tabor (1964) mentioned the experiments conducted by Hardy, of a monolayer of lubricant deposited on a glass surface, where the friction was measured against a steel ball. He concluded that the friction coefficient decreases with the increase in the number of atoms of the main molecular chain of the lubricant. In another work, Akagaki and Kato (1991) proposed wear maps for lubricated sliding using a paraffinic base oil with two different additives. The wear maps were different for the two additives used, agreeing that different lubricants lead to different tribological performances.

Some systems can have hydrodynamic conditions unable to keep a lubricant film between the sliding surfaces. In such a situation, there is the possibility of metal-metal contact and consequent high wear and friction, which can be avoided with the use of adequate boundary lubricants. In this case, elements of lubricant adsorb on the surfaces, producing protective films with repulsive forces that act in sustaining the applied load, preventing the solid contact and consequently the metallic junctions growth (Hutchings, 1992). The chemical nature of the films depends on the adsorption characteristics of polar groups of the boundary lubricant on the metallic surfaces. The efficiency of the boundary lubricant is related to its qualitative terms "oiliness" and "lubricity". The lubricity of a base oil can be improved by the use of additives, such as fatty acids (Hucthings, 1992). Extreme pressure (EP) additives, such as the ZDDP (zinc dialkyl ditiophosphate), are used to produce protective layers on the highly loaded surfaces. According to Hutchings (1992), EP and anti-wear additives are chemical substances which react with the sliding surfaces in localized areas, forming low shear strength films at the contact regions with severe thermomechanical loading. Most of such additives consists of sulfur and/or phosphorus containing compounds. In this case, Blau (1996) mentioned a mechanism for wear and friction lowering by the use of phosphorus-containing additives, by production of eutectic phosphides at the friction heated spots.

Schumacher and Zinke (1997) named the chemical reaction between the lubricant additive and the solid surface as "tribofragmentation", due to thermal action associated with mechanical energy in the friction zone. In such a mechanism, two steps are considered: the first is the thermal action causing adsorption and the second, the tribo-fragmentation of the adsorbed layer, caused by the mechanical shearing and the contact temperature, resulting in breaking off its molecular arrangement. Consequently, very reactive molecular fragments would be produced, which could develop a layer of ferrous salt. Schumacher and coworkers (1991) mentioned the formation of a layer of ferrous phosphate in case of phosphorus based additives.

Although most investigations describe the occurrence of wear reduction when lubricant additives are used (WANG, CHENG and GUAN, 1995; WAN et al., 1996), it cannot be generalized. Jahanmir (1987) performed lubricated sliding tests at wide range of loads (150 to 3,000 N) and verified that the wear decreased when the lubricant additive was used only for low loads. At high loads, the wear increased and the wear mechanism changed from ploughing to delamination. Therefore, depending on the mechanical loading the tribochemical reactions can cause structural alterations of the materials surfaces.

Another point to be considered in tribological investigations with lubricated systems is the presence of abrasive contaminant. Studies have shown that the presence of contaminant increases both the wear of the contacting bodies and the friction coefficient (MEHAN, 1988). Obviously, this behavior depends on the nature of the materials, as shown by MEHAN, FLYNN and GLAMMARISE (1991). They performed reciprocating block-on-ring tests, with diesel oil at 177 ºC contaminated with Al_2O_3 abrasive. With rings of tungsten carbide and blocks of several coating materials (tungsten carbide, chromium and chromium carbide), it was found that the rings did not suffer changes in the wear while the blocks underwent wear increase, specially with chromium, associated to its low thermomechanical strength.

Concerning abrasive wear and material properties, the importance of hardness has to be pointed out. ODI-OWEI and ROYLANCE (1987) studied the lubricated abrasive wear of materials with different hardness values using a four-ball testing machine with oil contaminated with Al_2O_3 abrasive. The results showed that the contaminant influence depended on the material hardness and the influence was higher for soft materials. In this study, it was observed that the critical load for lubricant film breakdown is lower when contaminant is present, indicating that the presence of the abrasive reduces the integrity of the lubricant film.

The abrasive wear also depends on the hardness relation of the sliding materials and the contaminant. XUAN, HONG e FITCH (1989) used a machine that simulates the contact of journal bearings with three hardnesses of journal materials (Hm_1) and a steel bearing (Hm_2). The lubricant was re-circulated hydraulic oil contaminated with three hardness of abrasives (Ha). Several hardness relations between materials (Hm_1/Hm_2) and material and abrasive (Hm_2/H_a) were tested. They observed that the combination of low values of (Hm_1/Hm_2) and high values of (Hm_2/H_a) resulted in a smaller amount of wear (m_2) and they proposed a mechanism of the abrasive particle action at the contact, schematically presented in Figure 1.

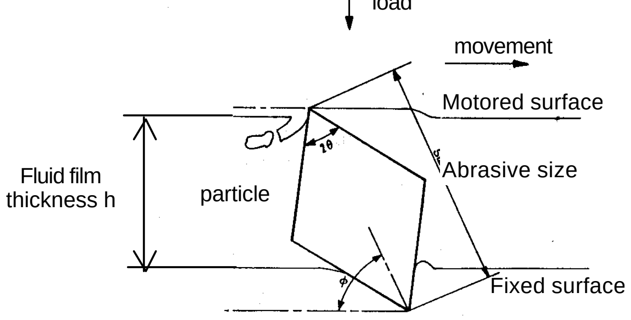

Figure 1: Indentation and cut caused by an abrasive particle in lubricated system (XUAN, HONG e FITCH, 1989).

In this Figure, a fluid film with thickness h separates the solid surfaces. The particle size is in a critical range able to penetrate into the space between the body and the counter-body and cause the abrasion. When the surface hardness difference is high, the particle is able to penetrate into the lower hardness surface and cuts the harder surface. When the difference is small, the particle can either cut both surfaces or be broken, depending on the hardness relationship of the abrasive and the surface materials. However, a critical point is the action of those wear mechanisms, which depends on the uniformity of the particles distribution along the oil film layer. Additionally, it is evident that the wear mechanism also depends on the size and the geometry of the particles (Williams and Hyncica, 1992).

The present study aims at investigating the combined influence of contamination and additives in the lubricant oil on the wear and friction responses of metallic specimens.

2. Materials and methods

The sliding tests were performed in a reciprocating pin-on-plate machine. The normal loading was pneumatically applied on the pin. The contact between the specimens was immersed in an oil bath heated by electrical resistors placed under it. The equipment has electronic sensors to control the normal load, the bath temperature and the oscillation frequency of the plate and to monitor the friction force and the contact potential (electrical resistivity between the metallic specimens).The data were acquired at every 10 s.

Every test was run with a previous step of 1,200 s (0.33 h) for oil heating up to 100 ºC, without loading and at the testing velocity. After the previous step, 80 N load was applied and the test was stopped after 100,000 pin cycles on the plate were completed. Table 1 shows the testing conditions. According with the IRG diagram, which indicates the transition curves among lubrication regimes based on load and velocity values (Gee, Begelinger and Salomon, 1984), the tests were performed under mixed lubrication regime. At least 3 tests were done for each testing condition. Table 2 shows the codification used for the tests.

Table 1: Testing conditions.

Temperature °C	Load N	Frequency Hz	Cycles	Time h	Stroke mm	Mean velocity m/s	Distance m
100	80	4,2	100.000	3,3	32	0,27	3.200

Table 2: Codification used for the tests.

Without additive Without contaminant	Without additive With contaminant	With additive Without contaminant	With additive With contaminant
PP SA	PPc SA	PP CA	PPc CA

The pin material was AISI 52100 bearing steel, 3 mm diameter and 23,8 mm length. The edge of the testing pin surface was rounded with 5,5 ± 0,3 mm radius. The pins are the needle rollers (NRA[1] code) used in the rolling bearings produced by INA Brazil Ltda. The measured hardness was 63 ± 0 HRC (25 kg). Figure 2 shows the top view of the pin surface. Some morphology similar to microcraters can be noticed. The Ra (mean height of asperities) roughness of the pin surface was 0.51 ± 0.05 μm (1.25 mm measurement length).

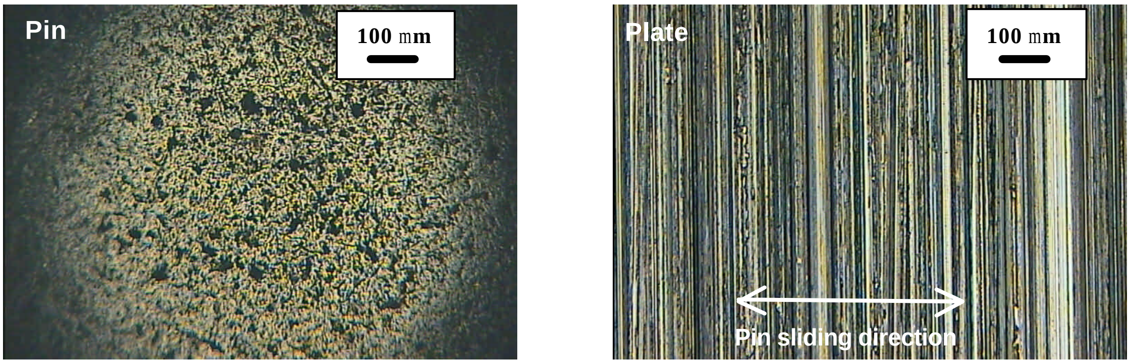

Figure 2: Microscopic observation of the pin testing surface (left) and plate surface (right).

The plate material was SAE 8640, quenched and tempered, 58 mm x 38 mm x 4 mm size and 48 ± 1 HRC final hardness. The plates were ground-finished with 1.3 ± 0.2 μm Ra roughness (Figure 2).

As lubricant, a parafinnic base oil was used with and without additives. The oil with additive was a commercial EGF 100-PS oil (BR Distribuidora), containing less of 3% in mass of additive pack composed by alkyl phosphate, fractions of petroil and sulfured fatty acids with anticorrosive, antirust, antioxidant, anti-wear, extreme pressure (EP) and anti foaming properties[2]. The oil was analyzed by optical spectrometry, which detected the presence of 354 μg/m phosphorus; the analysis by infra-red spectrometry detected the presence of sulfur. The oil without additives was Vitrea 100 designation (Shell). Both oils have the same viscosity index (VI 100) and are normally used for gearbox lubrication.

The material used as abrasive contaminant was quartz (SiO_2), with the average hardness of 1,000 HV and 15 μm average particle size. The abrasive concentration in the oil was 0.5 mg/ml.

3. Results

The worn surfaces of the pins and the plates were observed through optical microscopy. Figure 3 shows the results for PP SA and PP CA tests. It can be observed that the additive in the oil lead to change the wear behavior, especially the surface color. The pin of the PP SA test presented dark gray color, differently from the pin of the PP CA test. Regarding the plates, it can be observed that the original machining lines are still present on the worn area, suggesting a very low intensity of wear in the plates. On the plate of the PP CA test, it is possible to observe the formation of black areas, dispersed at the length of the original machining lines. This fact indicates the occurrence of a tribochemical reaction localized at the asperities. The action in localized areas is characteristic of EP additives in producing low friction tribochemical films (Hutchings, 1992).

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[1] BR019 Catalogue, INA needle rollers, Rolamentos Schaeffler do Brasil, 1998.

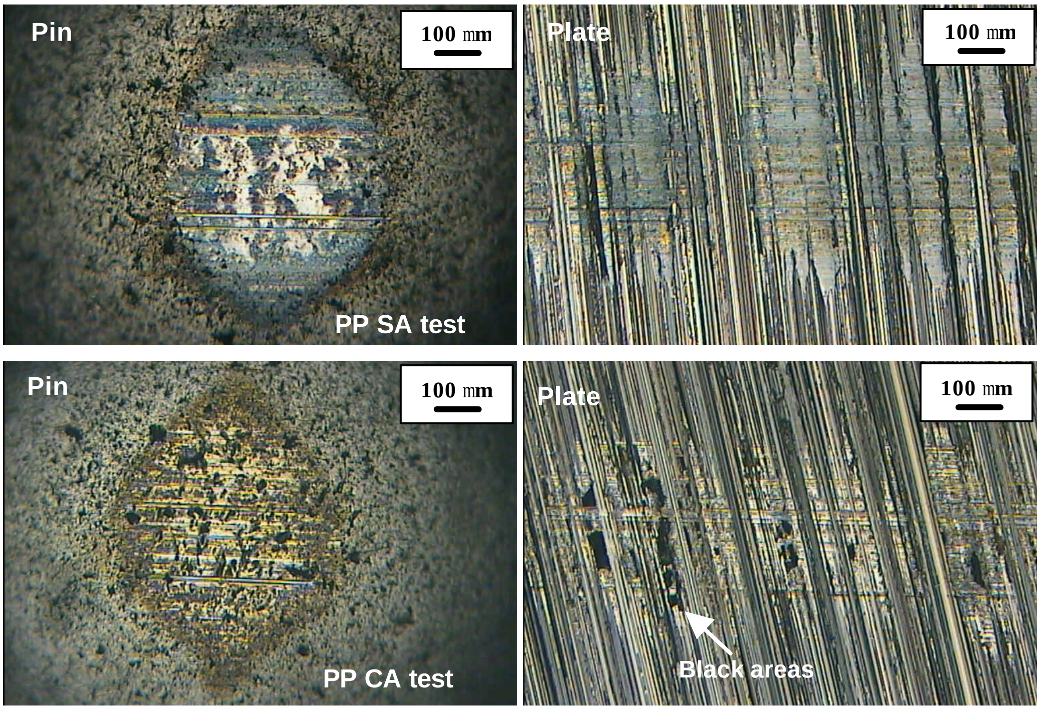


Figure 3: Microscopic morphology of the worn surfaces after sliding tests with non-contaminated oil.

The worn surface of the plate of PP CA test was analyzed by energy dispersive X-ray spectroscopy (EDAX). Figure 4 shows the energy spectrum, where the presence of phosphorus and sulfur are observed.

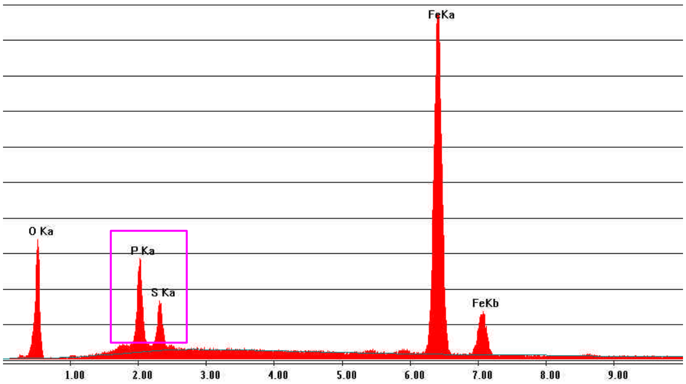


Figure 4: Energy spectrum obtained from EDAX analysis of the black area of the plate of PP CA test.

The results with contaminated oil are shown in Fig. 5. It is possible to observe that the contamination caused an increase in the wear intensity. It also changed the surface appearance of the pins, compared to those observed in Fig. 3. The worn area of the pins in Fig. 5 shows scratching interposed to shiny areas, well evident in the pin of the PP CA test, indicating the occurrence of a mechanism similar to polishing of metalographic preparation, caused by the abrasive contaminant.

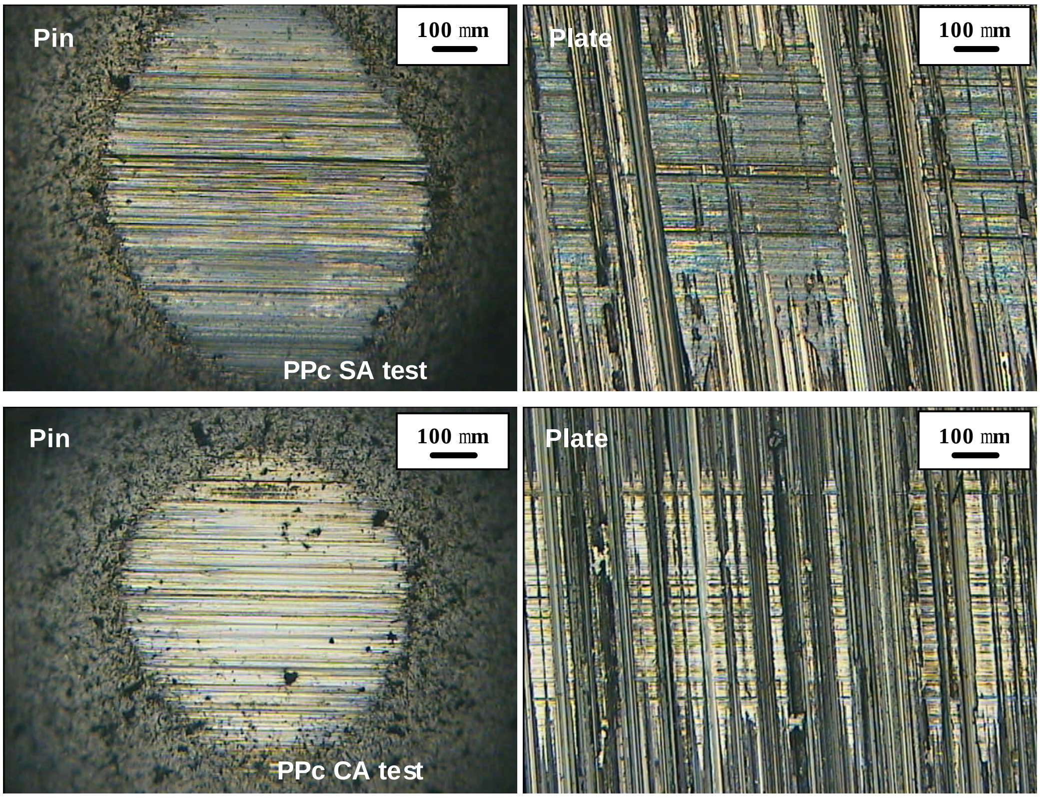


Figure 5: Microscopic morphology of the worn surfaces after sliding tests with contaminated oil**.**

The oil contamination effect can be also observed comparing the plate worn area of PP CA and PPc CA tests. It is noticed that the contaminant presence in the oil suppressed the formation of dark areas. Additionally, the worn area of the corresponding pins increased with oil contamination, even when the additive was present in the oil. Both facts indicate that the tribochemical effect of the oil additives was significantly reduced when the oil was contaminated with abrasive. On the other hand, the comparison among the pin worn areas in Fig. 5 shows a positive effect of the additive in wear reduction.

Figure 6 shows the comparative results of the worn areas measured on the contacting surface of the pins. The significant effect of the oil contamination is observed. This Figure also presents the average values of the friction coefficient; they have any apparent influence of neither the oil contamination nor the additive presence in the oil. Although it is not significant, a slight trend to increased friction coefficient values can be seen in the oil contaminated tests.

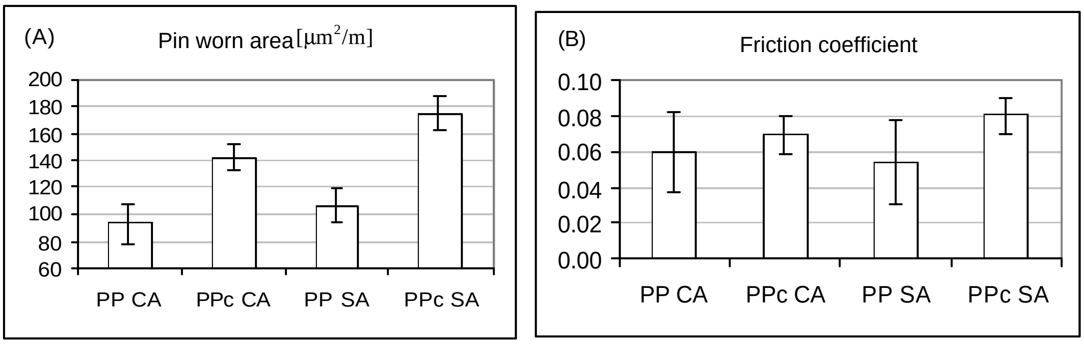


Figure 6: (A) Pin worn area resulting from the tested conditions. (B) Friction coefficient; bars refer to the mean values of the data acquired at the last 50 minutes test.

Some discussion can be considered regarding the positive effect of the oil contamination on the wear increase. A possible action of small abrasives originated in the contact from crushing of larger particles was previously described by Mehan, Flynn and Glammarise (1991). In this case, the dependence of the wear efficiency on the abrasive-metal friction and on the abrasive angularity is evident, since both factors can affect the rate of rolling motion of the abrasives between the pin and the plate surfaces, changing the wear mechanism from cutting to ploughing.

Another possible effect is related to the abrasive incrustation on the plate surface, because the plate hardness was lower (48 HRC ~ 480 HV) than both the abrasive (~ 1,000 HV) and the pin (63 HRC ~770 HV). The incrusted abrasive could cause abrasion with a mechanism similar to those occurring during metalographic polishing. However, it was not observed evidences of particles incrustation on the plates by the surface analyses performed by scanning electron microscope.

On the other hand, since the original surface of the plates presented very high Ra roughness value, the abrasive particles could settle at the valleys of the asperities. Figure 7 shows a groove from the original surface that could actuate as an "anchor" site for the particles at the contact interface.

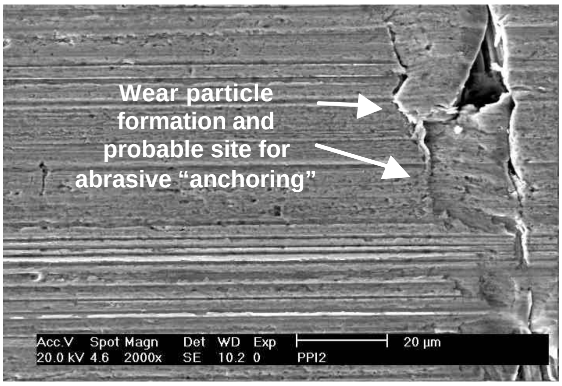
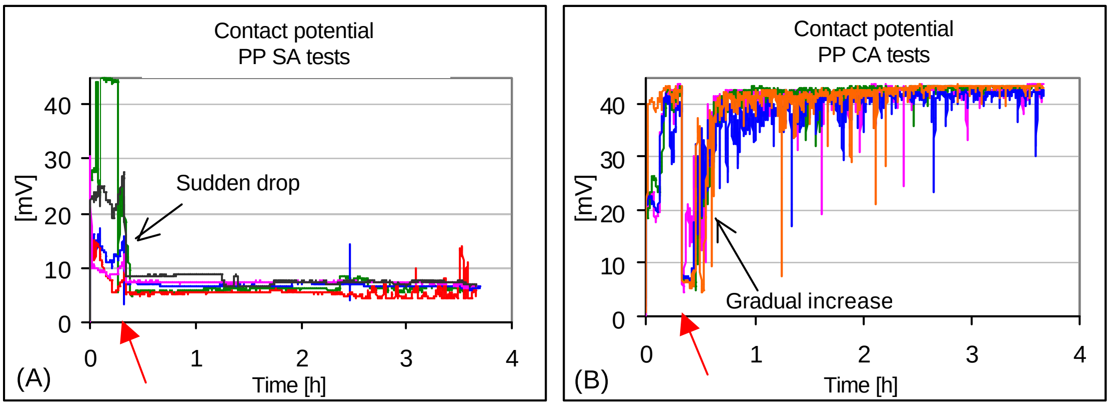


Figure 7: Microscopic appearance of the plate worn stroke (central), evidencing the formation of possible regions for abrasive "anchoring". Secondary electrons image.

The contact potential was measured during the tests to verify metal-metal contact occurrence. According to Hutchings (1992), the continuous monitoring of the contact potential can give information about the presence and thickness of oxide layer or, in elastohydrodynamic lubrication, about the lubricant film thickness. Some authors use the electric contact resistance for evaluation of the lubricant additives performance for protective film formation (So et al., 1993). In the used equipment, the potential value varies from 0 to 45 mV for closed circuit (metal-metal contact) to open circuit (electrically insulated). In the tests, an insulating film can occur either by an oil film that physically separates the surfaces or by tribolayer formation in the surfaces.

Figure 8 shows the contact potential behavior for PP SA and PP CA tests.



The red arrow indicates the instant of normal loading

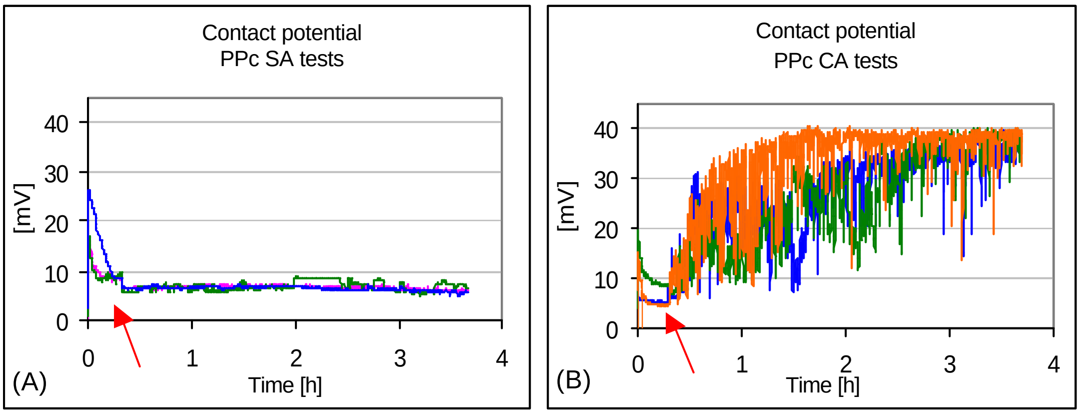
Figure 8: Contact potential behavior of the tests (A) PP SA and (B) PP CA.

From Fig. 8, it was not observed 0 mV values in all the tests, which indicates absence of metal-metal contact. This can be related to the occurrence of film at the contact interface. Such a film can be fluid (due to hydro or elastohydrodynamic effect) or of boundary type (due to chemical adsorption).

The comparison between the two graphs in Fig. 8 shows that the potential behavior was clearly distinct for the two oils. In the non-additived oil tests (Fig. 8A), a sharp drop in the potential is observed just at the loading application instant, and this low value is kept to the end of the test. On the other hand, the potential in the additived oil tests (Fig. 8B) indicated that the contact interface became gradually isolating just after the loading application.

It has to be mentioned that in all tests presented in Fig. 8 the testing conditions were identical, i.e., the loading, the materials of the bodies and the base oil were the same. Therefore, the physical separation of the surfaces in terms of oil film thickness should be similar in all the tests, at least during the first sliding cycles, when both the contact geometry and surface roughness were still close to the original ones. The only difference between the tests was the additive presence; thus, it is possible to infer that the difference among the graphs in Fig. 8 indicates the potential measurement is sensible to detect the tribochemical reactions effect of the oil additives on the metallic surfaces. Therefore, the dark areas on the asperities of the plate of the PP CA test (Fig 5) could be attributed to tribochemical film. Regardless of the contact potential differences among the tests, the results with both oils did not show significant difference on the wear (Fig. 6), demonstrating that tribochemical reaction did not significantly affect the wear behavior.

It is important to mention that the comparison among contaminated and non-contaminated tests needs careful analysis, because the contact potential can be influenced by the electrical nature of the contaminant material. In the tests, the abrasive used is electrically insulating. Figure 9 shows the contact potential behavior of PPc SA and PPc CA tests; the behaviors are quite similar to those presented in Fig 8.



The red arrow indicates the instant of normal loading

Figure 9: Contact potential behavior of the tests (A) PPc SA and (B) PPc CA.

On the other hand, comparing Fig. 8B and Fig. 9B, it can be observed that the oil contamination shifts the potential values down. It is possible that the tribochemical film was pulling out while it was being formed in the contacting surfaces, caused by the abrasive contaminant action. As a result, the potential showed to be shifted down.

Comparing Fig. 8A and Fig. 9A for the non-additived oil tests, it is not observed potential changes caused by oil contamination; both curves showed low level in the values. The low limit values might correspond to an insulating property of physical separation produced by oil film between the contacting bodies and is not affected by the abrasive contaminant. However, such insulation does not seem to be produced by fluid film, since its occurrence should increase contact potential during the test due to the gradual increase in geometrical conforming. The insulating characteristic might have occurred due to the effects of either boundary lubricant or oxidation.

4. Summary and conclusions

1. The influence of contaminant and additive presence in the oil on the wear and friction responses in reciprocating pin-on-plate sliding was investigated.
2. The occurrence of a tribochemical reaction caused by the additive in the oil was observed. The worn surface appearances were also influenced by the action of tribochemical reaction, although there were no significant influences observed in both dimensional changes and friction coefficient values.
3. The contaminant presence in the oil increases the pin wear. The abrasive particle action on wear mechanism due to particles “anchoring” in the plates asperities seems to be the cause of increase in the wear rate. A slight trend in friction coefficient increase was observed in the test with contaminated oil.
4. A negative synergetic effect was observed in the contaminated oil tests in the presence of additive, due to tribochemical effect being reduced by the presence of the contaminant.

5. Acknowledgements

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6. References

AKAGAKI, T.; KATO, K., Effects of additives on wear mode and morphology of wear debris generated in the lubricating sliding of steel, **Wear** 143, p.119-135, 1991

BLAU, P.J., **Friction Science and Technology**, Marcel Dekker, 398p., 1996

BOWDEN, F.P; TABOR, D., **The friction and lubrication of solids – Part II**, Oxford University Press, 544p., 1964

GEE, A.W.J.; BEGELINGER, A.; SALOMON,G., Failure mechanisms in sliding lubricated contacts, In: **Mixed lubrication and lubricated wear, Proceedings of the 11th Leeds-Lyon Symposium**, England, p.108-116, 1984

HUTCHINGS, I.M., **Tribology: friction and wear of engineering materials**, Edward Arnold, Great Britain, 273p., 1992

JAHANMIR, S., Wear reduction and surface layer formation by a ZDDP additive, **Journal of Tribology**, Transactions of the ASME, Vol.109, p.577-586, 1987

MEHAN, R.L., The wear of selected materials in mineral oil containing a solid contaminant. **Wear** 124, p.65-85, 1988

MEHAN, R.L.; FLYNN, P.L.; GLAMMARISE, A.W., Evaluation of piston ring materials in oil containing an abrasive using a ring-on-block test machine. **Wear** 147, p.41-57, 1991

ODI-OWEI, S.; ROYLANCE, B.J., Lubricated three-body abrasive wear-contaminant condition versus bounding surface material hardness, **Tribology International**, Vol.20, n.1, p.32-40, 1987

SCHUMACHER, R., ZINKE, H., Tribofragmentation and antiwear behavior of isogeometric phosphorus compounds, **Tribology International**, Vol.30, n.3, p.199-208, 1997

SCHUMACHER, R.; ZINKE, H.; LANDOLT, D.; MATHIEU, H.J., Improvement of lubrication breakdown behavior of isogeometrical phosphorus compounds by antioxidants, SO, H.; LIN, Y.C.; HUANG, G.G.S.; CHANG, T.S.T. Antiwear mechanism of zinc dialkyl dithiophosphates added to a paraffinic oil in the boundary lubrication condition. **Wear**, Vol.166, n.1, p.17-26, 1993ET AL, 1993

XUAN, J.L.; HONG, I.T.; FITCH, E.C., Hardness effect on three body abrasive wear under fluid film lubrication, **Journal of Tribology**, Transactions of the ASME, Vol.111, p.35-40, 1989

WANG, F.; CHENG, Y.; GUAN, D., On the tribological behavior and surface analysis of a sliding PSZ ceramic-steel pair, **Journal of Tribology**, Transactions of the ASME, Vol. 117, p.548-52, 1995

WAN, Y.; PU, Q.; XUE, Q.; SU, Z., Antiwear and extreme pressure characteristics of 2-mercaptobenzoathiazole derivative as the potential lubricating oil additive, **Wear** 192, p.74-7, 1996

WILLIAMS, J.A., HYNCICA, A.M., Mechanisms of abrasive wear in lubricated contacts, Wear 152, p.57-74, 1992