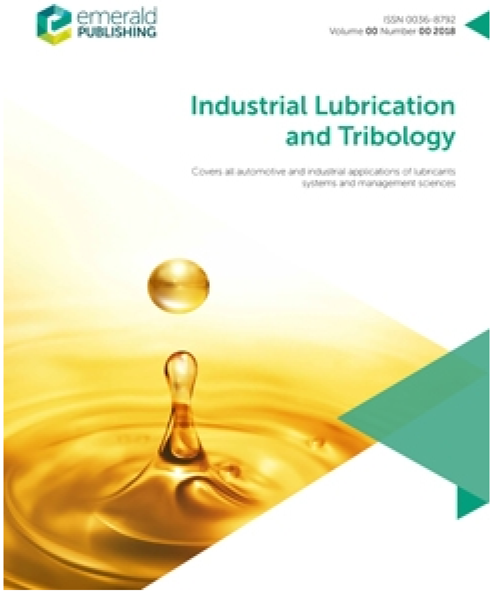

Tribological behavior of oils additised with a phosphonium-derived ionic liquid compared to a commercial oil

Journal:	*Industrial Lubrication and Tribology*
Manuscript ID	ilt-05-2020-0179.R1
Manuscript Type:	Original Article
Keywords:	phosphonium-derived ionic liquid, Additive, antifriction, antiwear

Abstract

Purpose
The purpose of this work is to study the antifriction, antiwear and tribolayer formation properties of the trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ionic liquid (IL) as additive at 1 wt% in two base oils and their mixtures, comparing the results with those of a commercial oil.

Design/methodology/approach
The mixture of the base oils used in the formulation of the commercial oil SAE 0W20 plus the IL was tested under rolling/sliding and reciprocating conditions to determine the so-called Stribeck curve, the tribolayer formation and the antifriction and antiwear behaviors.

Findings
The use of this ionic liquid as additive in these oils does not change their viscosity; improves the antifriction and antiwear properties of the base oils, making equal or outperforming these properties of the SAE 0W20; and the thickness and formation rate of the tribolayer resulting from the IL-surface interaction is highly dependent on the type of base oil and influence on the friction and wear results.

Originality
The use of this ionic liquid allows to replace partial or totally commercial antifriction and antiwear additives.

Keywords: phosphonium-derived ionic liquid; additive; antifriction; antiwear.

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1. Introduction

The ionic liquids (ILs) are being used for over 40 years in different applications (Li Chum *et al.*, 1975; Wilkes *et al.*, 1982). These molten salts have properties that make them ideal for using in lubrication: non-flammability, high thermal stability, high conductivity, high polarity, ashless character and miscible in organic compounds (Bermúdez *et al.*, 2009; Blanco, *et al.*, 2011; Somers *et al.*, 2013; Viesca *et al.*, 2010; Ye *et al.*, 2001). The metal surface-IL interaction leads to a tribolayer formation on the surface contributing to better both antifriction and antiwear performances (Blanco, *et al.*, 2011; Otero, *et al.*2014; Viesca *et al.*, 2013) .

All the above-mentioned good lubricating properties of the ILs increased the interest for testing them as neat lubricant or as additive. The first works studied ILs with fluorine-containing anions (Battez *et al.*, 2009; Chen *et al.*, 2009; Liu *et al.*, 2002; Mu *et al.*, 2005; Phillips and Zabinski, 2004), but these anions produced corrosive and toxic products in presence of water, making possible their use only in free-water conditions. Despite the excellent properties of ILs as lubricant, their industrial application as base stock is limited by their high cost compared to synthetic- and mineral-based oils (Somers *et al.*, 2013). However, numerous studies have been carried out about their use as additive in lubricants and it has been observed that small quantities of IL improve significantly tribological behavior of the base oil (Zhou *et al.*, 2009).

The current commercial availability of phosphonium-derived ILs has promoted their testing in various applications (Fraser and MacFarlane, 2009) and shown their better performance as neat lubricant than imidazolium-based ILs and conventional oils (Liu *et al.*, 2006; Minami *et al.*, 2008, 2010). The better miscibility of these ILs in non-polar oils has led to test them as lubricant additive (Barnhill *et al.*, 2014; González *et al.*, 2016; Hernández Battez *et al.*, 2017; Otero, *et al.*, 2014; Qu *et al.*, 2014; Totolin *et al.*, 2014; Zhou *et al.*, 2014).

Previous works reported the physical-chemical properties and tribological behavior of the phosphonium-derived IL $[P_{6,6,6,14}][(iC8)_2PO_2]$ as additive in both a mineral oil (González *et al.*, 2016) and a polyalphaolefin (González *et al.*, 2019). When the $[P_{6,6,6,14}][(iC8)_2PO_2]$ was used as additive in mineral and synthetic oils improved antifriction behavior under rolling/sliding motion compared to $[P_{6,6,6,14}]$[BEHP] counterpart and mixtures containing ZDDP (zinc dithiophosphates). Meanwhile, the $[P_{6,6,6,14}][(iC8)_2PO_2]$ behaved worse as additive than ZDDP in friction results under reciprocating motion, the former equalled or outperformed the antiwear behaviour of the latter when the IL concentration was 0.5 or 1 wt%.

This work is focused on the performance of the $[P_{6,6,6,14}][(iC8)_2PO_2]$ as additive to a mixture of two non-polar oils which are used as base stock in the formulation of the commercial oil SAE 0W20. This research is important for lubricant industry in order to determine the feasibility of replacing partial or totally the ZDDP used in the aforementioned commercial oil.

2. Methodology

2.1 Base oils and ionic liquid

The polyalphaolefin (PAO 4) and the hydrocracked mineral oil (YUBASE) used as base oils and the commercial low viscosity engine oil SAE 0W20 were kindly provided by Repsol S.A. The trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}]$ $[(iC8)_2PO_2]$) was obtained from IOLITEC GmbH.

For preparing the mixtures, 1 wt.% of the IL was added to each oil, reaching a phosphorous concentration of 700 ppm (below the limit of 800 ppm in motor oils). Besides, a blend of 37 vol.% of YUBASE and 62 vol.% of PAO 4 was also additised with 1 wt.% of the IL to be compared with the SAE 0W20 (formulated with the same blend of YUBASE and PAO 4).

2.2 Viscosity measurements

A Stabinger Viscometer SVM3001 was used for measuring viscosity of all lubricant samples from 20 to 100 ºC and then calculate the viscosity index.

2.3 Tribological tests

The friction behavior of all lubricant samples was studied through two type of tests in a ball-on-disk configuration with a Mini-Traction Machine tribometer (Fig. 1), which permit controlling ball and disk independently (rolling/sliding motion). The steel specimens used were a ball (AISI 52100, Ra ≈ 0.01µm, 19.05 mm-diameter) and a disk (AISI 52100, Ra ≈ 0.01µm, 46 mm-diameter). The ball-on-disk contact was lubricated with 10 mL of lubricant and the cleaning procedure employed with the specimens was the same to that described in (González *et al.*, 2019). The first type of test (Stribeck curve determination) was performed at 50% of slide-to-roll ratio (SRR), speed range of 2000-10 mm/s, 0.95 GPa of maximum pressure, and temperature range of 40-100 ºC. Electrical contact resistance (ECR) and friction coefficient were measured during tests. The second type of test was made using the technique employed by (Kapadia *et al.*, 2007) for measuring the tribolayer formation due to the lubricant-surface reaction. The tests were performed at 0.66 GPa of maximum pressure, 150 mm/s of speed, 50% of SRR, 100 ºC of temperature and 60 min-duration.

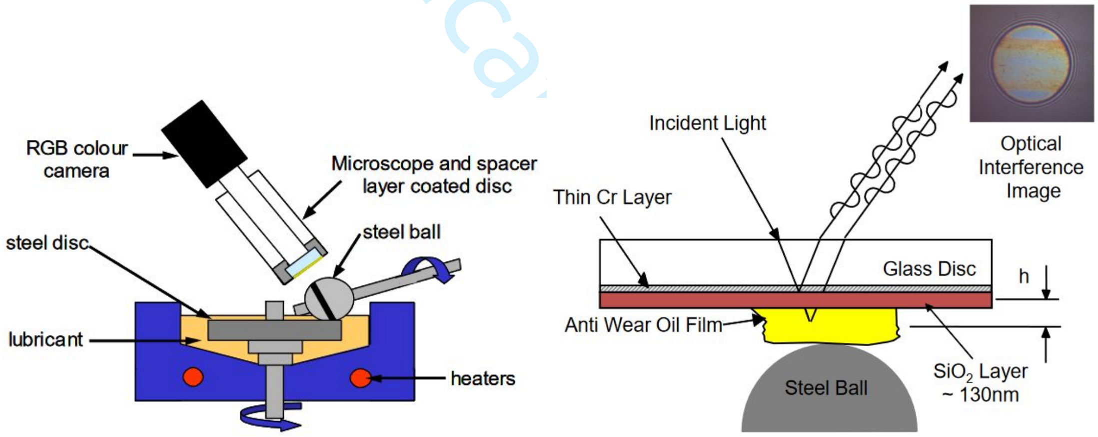

Fig. 1. Mini-Traction Machine: ball-on-disk set-up (left) and tribolayer measurement configuration (right). Courtesy from PCS-Instruments.

Additionally, tribological tests under reciprocating motion were made in a UMT-3 tribometer (Fig. 2). The test condition used in this case was: 60 min-duration, 60 N-load (equivalent to 1.91 GPa of maximum pressure), 15 Hz of frequency, 4 mm of stroke length, room temperature and relative humidity of 20-30%. The volume of lubricant sample used was 4 mL. As upper specimen was used a steel ball (AISI 52100, 63 HRC of hardness, 9.5 mm-diameter, Ra ≈ 0.01µm) and as lower specimen was used a steel disk (AISI 52100, machined from annealed rod, with 190–210 HV$_{30}$ of hardness and Ra < 0.02 µm). During the tests, friction coefficient was determined, and confocal microscopy was used after tests for measuring wear on the disk surface. At least three tests were conducted for each lubricant sample. The cleaning procedure of the specimens before tests was the same used in (González *et al.*, 2016).

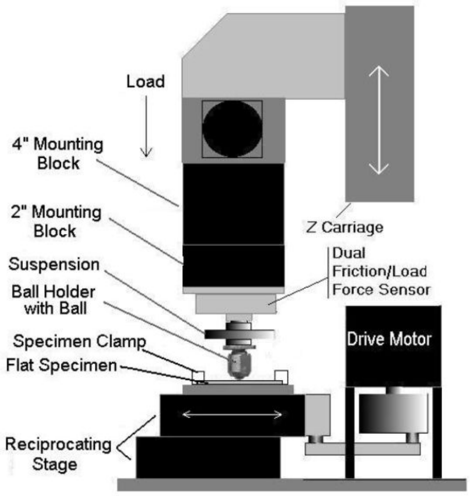

Fig. 2. Configuration of the UMT-3 tribometer.

2.4 Surface characterization

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were utilized after reciprocating tests in order to study the worn surface regarding both wear mechanisms and chemical composition.

3. Results and discussion

3.1 Viscosity

Fig. 3 shows that the commercial oil (SAE 0W20) has the highest viscosity values at all temperatures. The rest of lubricant samples show similar viscosity values from 40 ºC onwards. Due to the low concentration used, the addition of the IL hardly modifies viscosity of the base oils. Taking into account that the commercial oil SAE 0W20 is formulated using a mixture of YUBASE and PAO 4 as base stock, the additive package used is responsible for its higher viscosity.

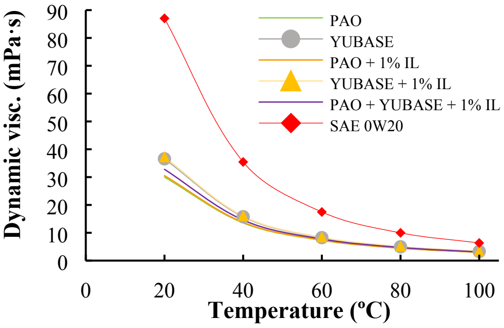

Fig. 3. Viscosity and density properties versus temperature.

3.2 Tribological tests

Fig. 4 shows the friction and ECR behaviors against speed and temperature of all lubricant samples during the rolling/sliding tests. The friction behavior against a wide range of speed is a simple technique to obtain the Stribeck curve varying only one variable (load, viscosity or speed). Friction decreased under elastohydrodynamic lubrication regime (high speed values) with temperature increase. These results are connected with the reduction of viscosity at increasing temperature and the consequent decrease in the lubricant film thickness. Due to film thickness is dependent on viscosity, the lower friction showed by the IL-containing mixtures at 40 and 60 ºC regarding the SAE 0W20 is quite related to the above-mentioned viscosity results (Fig. 3). The change from elastohydrodynamic to mixed lubrication regime took place at higher speeds with temperature increase due to the greater viscosity decrease, which counteracts the influence of the speed on the lubricant film thickness reducing it and leads to more asperities contact between surfaces. Under mixed lubrication regime, the friction results are also controlled by the formation/destruction process of the tribolayer formed from the IL-surface interaction. Regarding the ECR results, it is also observed how higher temperature and/or lower entrainment speeds leads to thinner lubricant film thickness, greater asperities contact and hence lower ECR and higher friction values. In general, the highest ECR values were found under elastohydrodynamic lubricant regime, where the lubricant film thickness avoids the asperities contact.

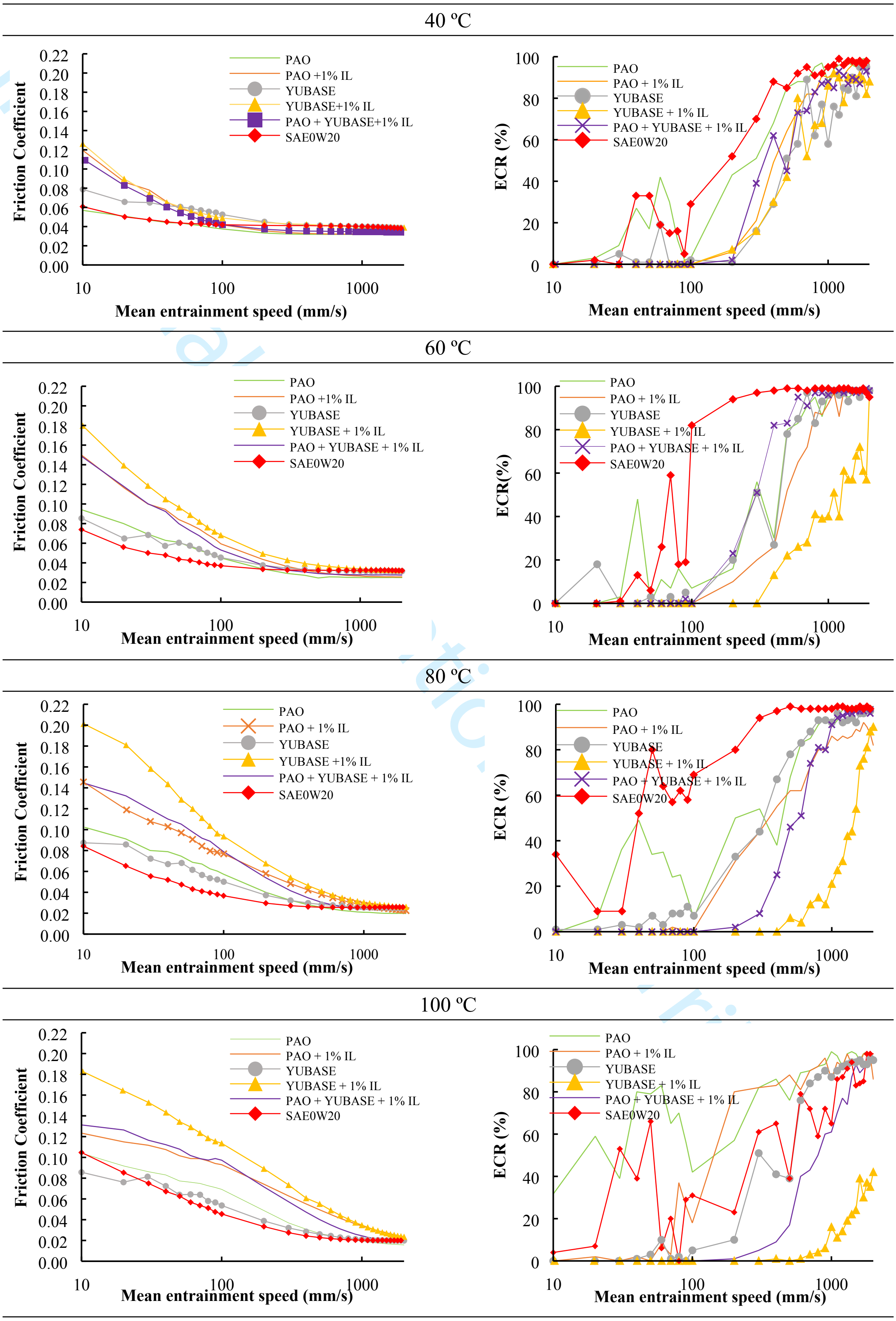

Fig. 4. Stribeck curves and ECR behaviors under different temperatures.

In addition, the measuring of tribolayer formation (Fig. 5) indicated a clear influence of the oil used. For the mixture of PAO 4 + 1 wt.% IL, it was noted a rapid tribolayer build up, with the thickest tribolayer measured after 60-min test. This result correlate with the high reactivity of this IL reported in previous works (González *et al.*, 2016, 2019). However, it seems that the YUBASE interferes in the tribolayer formation process when YUBASE + 1 wt.% IL was used, resulting in the thinnest tribolayer formed. For the mixture of YUBASE + PAO 4 + 1 wt.% IL, the tribolayer thickness formed was greater than that from YUBASE + 1 wt.% IL, but far away from the tribolayer formed when only the PAO 4 was used as base oil. Moreover, the SAE 0W20 shows a tribolayer formation rate almost constant, with a significant final thickness, although smaller than that from the PAO 4 + 1 wt.% IL. The interference images obtained during tribolayer formation tests is shown in Fig. 6.

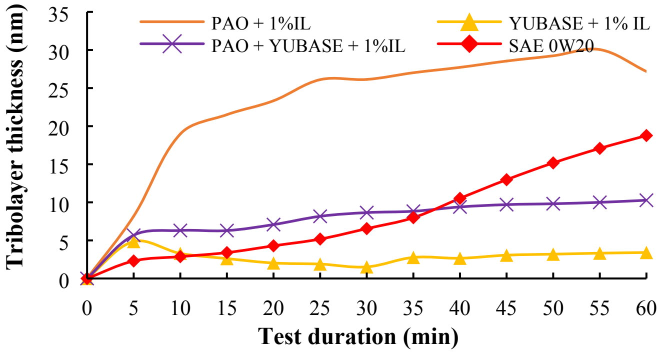

Fig. 5. Thickness of the tribolayer formed on the ball surface during tests.

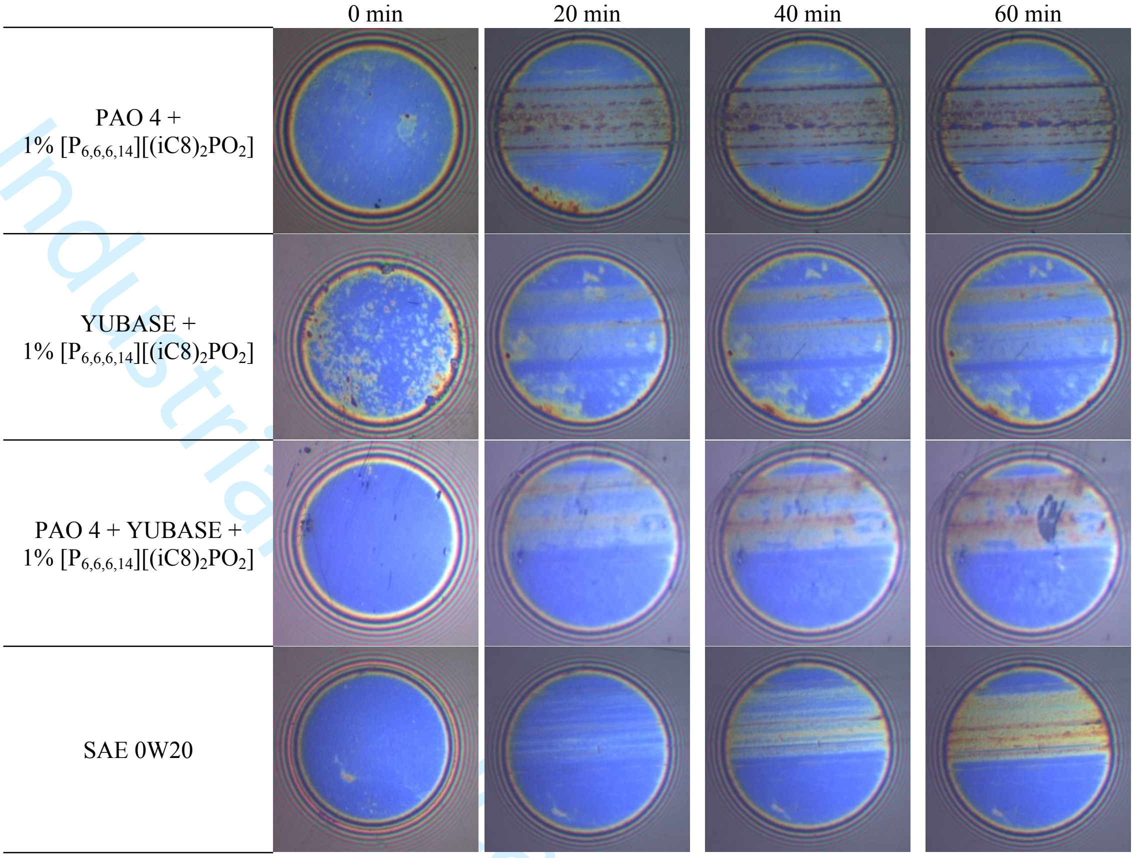

Fig. 6. Interference images of tribolayer formation on the surface of the ball during tests.

Fig. 7 shows the friction evolution during the 60-min tests and the wear volume measured on the surface of the disk. Excepting pure PAO 4 and YUBASE, the remaining lubricants showed a relatively stable or decreasing friction coefficient with time. The blend of PAO 4 +1 wt.% IL showed the lowest friction values, especially during the first half of the test, which can be connected with the rapid tribolayer formation showed by this mixture. In general, the additivation with the IL led to a decrease in friction compared to pure oils. In addition, a remarkable reduction in wear (comparable to that with SAE 0W20) was found with the additivation with the IL compared to the use of pure oils. This is also in accordance with the reactivity observed for this ionic liquid and its capacity of surface tribolayer formation.

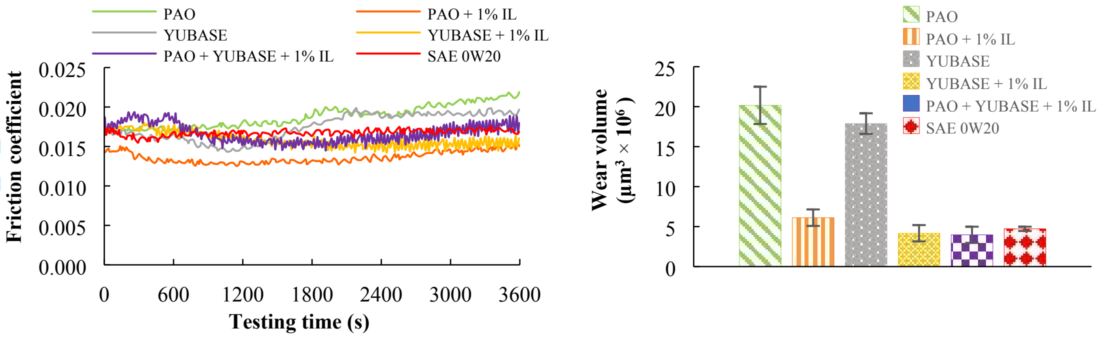

Fig. 7. Friction and wear from reciprocating tests.

3.3 Surface characterization

The SEM-EDS analysis shows how the wear track on the surfaces lubricated with pure oils are bigger than those in which the IL has been used as additive, Fig. 8. Plastic deformation was found at the edges of the wear track with a predominant adhesive wear mechanism in all cases. A difference morphology of the wear track can be noted when PAO 4 + 1 wt.% IL was used likely due to its higher capacity to form a tribolayer. In the EDS analysis, only the constituent elements of the AISI 52100 steel could be detected, with the exception of the surfaces lubricated with SAE 0W20 where typical elements included in the additive package (Zn, S, etc.) were also detected.

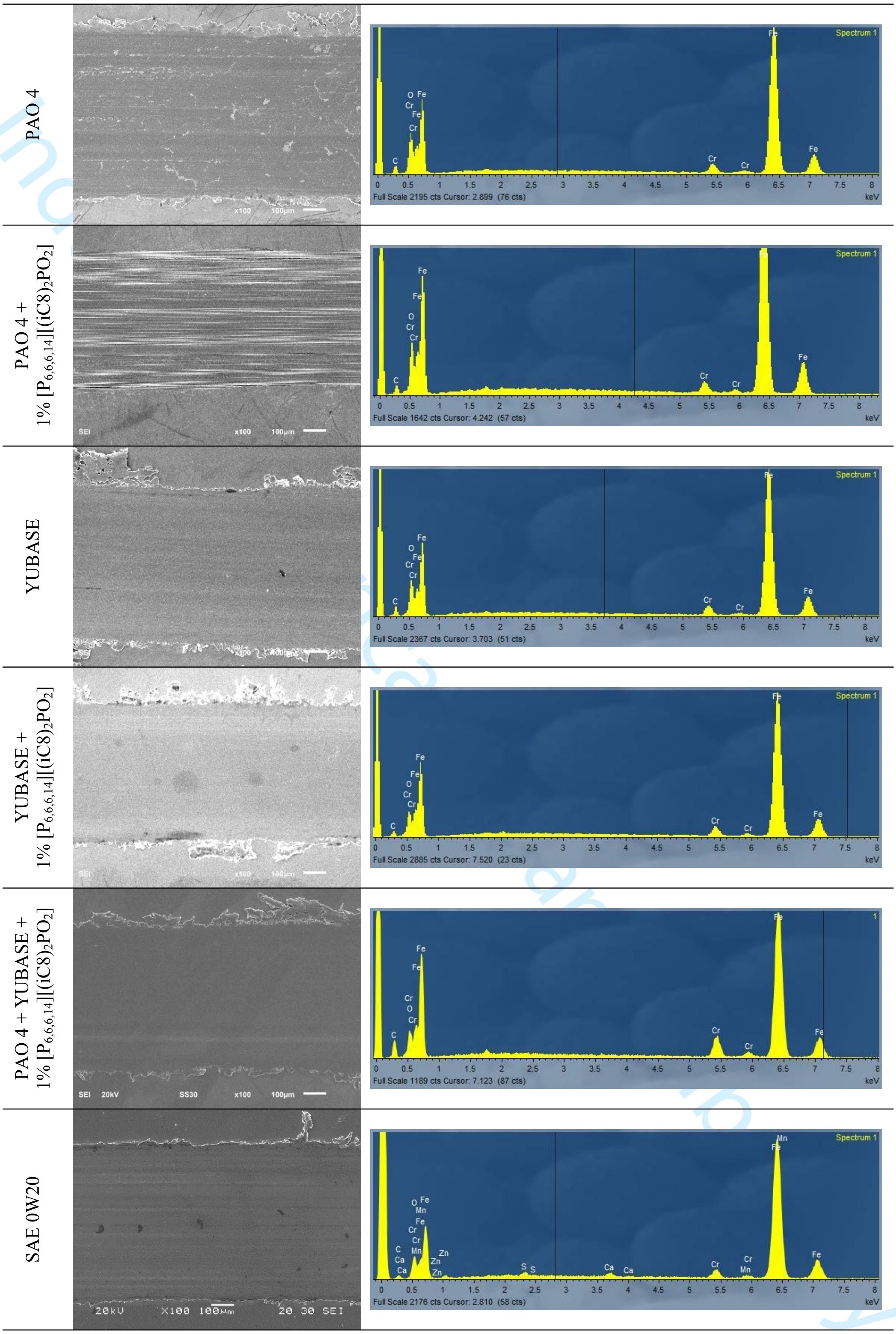

Fig. 8. SEM-EDS analysis after reciprocating tests.

4. Conclusions

The tribological performance of the trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][(iC8)_2PO_2]$) used as additive in two non-polar oils was compared to the commercial oil SAE 0W20. The main conclusions arose from this work are:

- The addition of $[P_{6,6,6,14}][(iC8)_2PO_2]$ at 1 wt.% concentration practically does not change viscosity of the base oils.
- The use of $[P_{6,6,6,14}][(iC8)_2PO_2]$ as an additive hardly changes friction under rolling/sliding motion but under reciprocating (sliding) motion reduces significantly both friction and wear.
- The formation rate of tribolayer from the IL-surface interaction is highly dependent on the base oil used and influence positively in friction or wear reductions.
- The use of $[P_{6,6,6,14}][(iC8)_2PO_2]$ as additive improves the antifriction and antiwear behavior of the base oils, achieving antiwear results comparable to that of the commercial oil SAE 0W20.

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