Wear 334-335 (2015) 67–74

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Ionic liquids as tribological performance improving additive for in-service and used fully-formulated diesel engine lubricants

M. Anand [a,b,*], M. Hadfield [a], J.L. Viesca [b,a], B. Thomas [a], A. Hernández Battez [b,a], S. Austen [c]

[a] Faculty of Science and Technology, Bournemouth University, Poole, UK
[b] Department of Construction and Manufacturing Engineering, University of Oviedo, Asturias, Spain
[c] Royal National Lifeboat Institution, Headquarter, Poole, UK

ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form
19 January 2015
Accepted 27 January 2015

Keywords:
Ionic liquids
Antiwear
Lubricant additives
Boundary lubrication
Surface analysis

ABSTRACT

In recent years, several papers have been published that investigate the potential use of ionic liquids (ILs) as additives in lubricants. However, corrosive attack of ILs on lubricated metal surfaces and low miscibility of ILs in the non-polar oils are major obstacles to maintaining an optimum lubrication performance level. High miscibility and no corrosive behaviour of Trihexyltetradecyl phosphonium bis(2,4,4-trimethylpentyl) phosphinate and Trihexyltetradecyl phosphonium bis(2-ethylhexyl) phosphate, as lubricating oil additives have recently been described in literature. This article presents work on using these phosphonium based ILs as an additive in the fully formulated diesel engine lubricants. This approach could allow the used lubricants to recover their tribological performance for further use at the end of service life. This extension of service life has the potential to generate significant economic and environmental benefits. Also it will add to the much needed knowledge about the effect of interaction between ILs and existing additives in engine-aged lubricants on the tribological performance of ring-liner tribo-system of diesel engines. Results revealed an improvement in friction and antiwear performance of used lubricant by addition of both ILs. However an increase in wear was noted for new (fresh) and in-service lubricant samples. An interesting interference between existing lubricant additives and added ILs in a boundary film formation process has been observed.

1. Introduction

Within Internal Combustion (IC) engines high friction and wear losses are known to take place in ring-liner contact at top dead centre (TDC) near the top ring reversal point of cylinder liners. Both sliding surfaces rely on the formation of a protective boundary film in the contact zone by the anti-wear additives present in engine lubricants. The prolonged use of lubricants in engine environment leads to additives depletion [1] thus affecting the fuel efficiency and service-life of engine. Ionic liquids (IL) could serve as a potential solution to the problem of depleting additive content due to lubricant ageing in engines.

In recent years, several papers have been published that investigated the potential use of ionic liquids (IL) as additives in lubricants [2–11]. Corrosive attack of ILs on lubricated metal surfaces [12,13] and low miscibility of ILs in the non-polar oils [14,15] are major problems in order to maintain an optimum lubrication performance level. Although, some engine suitable non-corrosive ILs can overcome the miscibility issue by using them in their neat form as a lubricant [12,16]. But at present, using small quantity of ILs as additive, rather than in bulk as neat lubricants, for engine applications seems to be an economical option due to the higher cost of ILs. It should be noted, however, that the multiple-recycling of ILs after use could reduce the overall cost of employing ILs [17] in real applications. Thus is another cost effective aspect for investigation by the lubricant industry.

Yu et al. [14] and Qu et al. [15] recently described the high miscibility and no corrosive behaviour of two phosphonium based ILs as lubricating oil additives. In the current work, authors of this article present their contribution on using the same phosphonium based ILs as additives in engine-aged lubricants. This could allow the aged lubricants to recover their tribological performance for further use at the end of service life. This extension of service life has the potential to generate significant benefits in terms of fuel economy, engine reliability and also by reduced oil consumption and drainage into the environment. Also most of the previous research on phosphonium ILs is carried out as neat lubricant, and as an additive in either base oil or new (fresh) engine oil [3,13–15,18,19]. Therefore current work will add to the much needed knowledge about the effect of interaction between ILs and existing additives in engine-aged lubricants on the tribological performance of ring-liner tribo-system.

* Corresponding author at: Faculty of Science and Technology, Bournemouth University, Poole, UK. Tel.: +44 7438259072.
E-mail address: m.anand8@yahoo.com (M. Anand).

http://dx.doi.org/10.1016/j.wear.2015.01.055

Tribological bench testing is a cost effective and quick way for screening potential candidate materials and lubricants during their development stage prior to full-scale engine testing. Therefore, initial bench experiments are performed to assess the tribological behaviour of these Oil-IL blends containing 6% volume ILs, benchmarked against the original engine-aged oil. Mineral Base Oil and new engine oil, both with and without ILs, were also tested for comparison. The investigation also involved an Electrical Contact Resistance (ECR) method to understand the tribo-film formation process. Energy Dispersive X-ray Microanalysis (EDX) and X-ray photoelectron spectroscopy (XPS) analysis of worn surfaces were employed to extract useful information about tribo-chemical reactions taking place during the sliding process.

2. Experimental details

Trihexyltetradecyl phosphonium bis(2,4,4-tri-methylpentyl) phosphinate, referred here as IL1, was purchased from Sigma-Aldrich. Whereas, Trihexyltetradecyl phosphonium bis(2-ethylhexyl) phosphate, referred as IL2, was purchased from Iolitec. Both ILs were mixed in 6 vol% proportions with lubricating oil samples collected from the heavy duty 4-stroke diesel engine (MAN D2840LE401, power output ~850 hp) installed in Trent Class Lifeboats operated by the Royal National Lifeboat Institution (RNLI). The oil samples were collected at different service intervals such as 135 and 196 h which are termed as In-service Oil whereas the one collected at 315 h was termed as Used Oil since its standard oil analysis showed it unsuitable for further service. The engine oil used by RNLI is a commercially available fully-formulated mineral-based SAE 15W40. Mineral Base Oil and new 15W40 engine oil, both with and without ILs, were also tested for comparison purpose. ILSAC GF-5 limits the phosphorus content in engine lubricants between 600 and 800 ppm, to prevent poisoning of emission control system alongside providing optimum wear protection. Calculations based on molecular weight and amount of ILs added to the oils as additive, resulted in the net increase in phosphorus content of oils by 4337 ppm (for IL1) and 4163 ppm (for IL2). However, the aim of this research is to assess the interaction between the ILs and existing additives in aged engine oils, therefore a higher amount of ILs is employed. Also a previous study by Jun Qu et al. [3] used lower concentration (1 wt%) of phosphonium IL as an additive but in PAO base oil with total phosphorus content of 1000 ppm. Their study demonstrated promising tribological performance for piston ring-cylinder liner contact. Therefore, the future work with lower concentration of ILs will help in understanding the interaction between ILs and existing additives in aged engine oils, while keeping the phosphorus content within the limits of GF-5 legislation.

Table 1
Characteristics for the different lubricants and ILs in this study.

Lubricant	Viscosity (cSt) at 40 °C	Viscosity (cSt) at 100 °C	Fe (ppm)
Mineral Base Oil	43.4 [a]	6.4 [a]	–
New Oil	106.10	14.34	1
In-service Oil (135 h)	100.30	13.66	27
In-service Oil (196 h)	102.30	13.80	40
Used Oil (315 h)	91.56	12.74	66
IL1	388.8 [b]	35.4 [b]	–
IL2	429.0 [b]	49.5 [b]	–

Source of information:
[a] Supplier; rest were measured experimentally as mentioned above.
[b] [14].

Table 1 shows the lubricants condition in terms of the kinematic viscosity and elemental concentration of ferrous wear debris measured experimentally by performing ASTM D445 and D4951/D5185, respectively. The main source of this ferrous debris in diesel engine oils is the bore surface of the cylinder liners which experience sliding wear. Mixing of IL and oils was achieved by using an ultrasonic probe (Sonic Systems P100) for 5 min. The visual inspection depicted no phase separation between oil and IL due to slightly different densities even after a month of storage in tightly sealed bottle. Due to the dark (blackish) colour of engine conditioned oils, stability was analysed using Turbiscan Lab Expert (Formulaction) for Used Oil samples containing IL1 and IL2. Stability analysis on each sample was conducted for 11 days and the mixtures were found to be stable.

The simplified non-conformal configuration of piston ring-cylinder liner contact was used instead of conformal mating surfaces. Piston ring specimens were prepared by machining actual unused top compression piston rings (typically used in MAN D2840LE401 engines) into several small segments. Flat specimens were used instead of sections cut from actual cylinder liners (typically used in MAN D2840LE401 engines); however, similar material composition was maintained. The non-conformal configuration was used to achieve the correct alignment of both samples in the test rig. Otherwise if a curved specimen cut from actual liner was used then the curvature of uncompressed piston ring segment will tend to be larger than that of liner specimen. Therefore to avoid this difficult mechanical alignment, flat specimens as representatives of real-liner were used. A piston ring segment with a chromium coating on the running face (segment length 24 mm, coating hardness 990 HV, initial surface roughness R_{rms} of about 0.372 µm) was mounted on a specimen holder to maintain the applied normal load perpendicular to the flat specimen (10 mm × 33 mm) made of grey cast iron (BS1452, hardness of 210–230 HV, initial surface

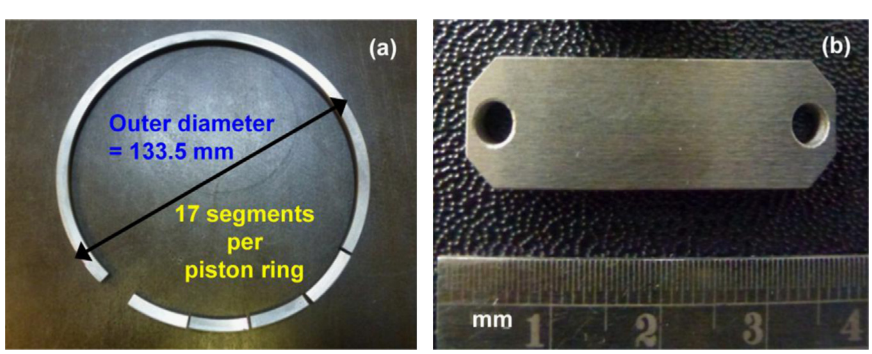

Fig. 1. Test material used in experiments. (a) Actual piston ring segments and (b) Typical cast iron flat sample. Intended for colour reproduction.

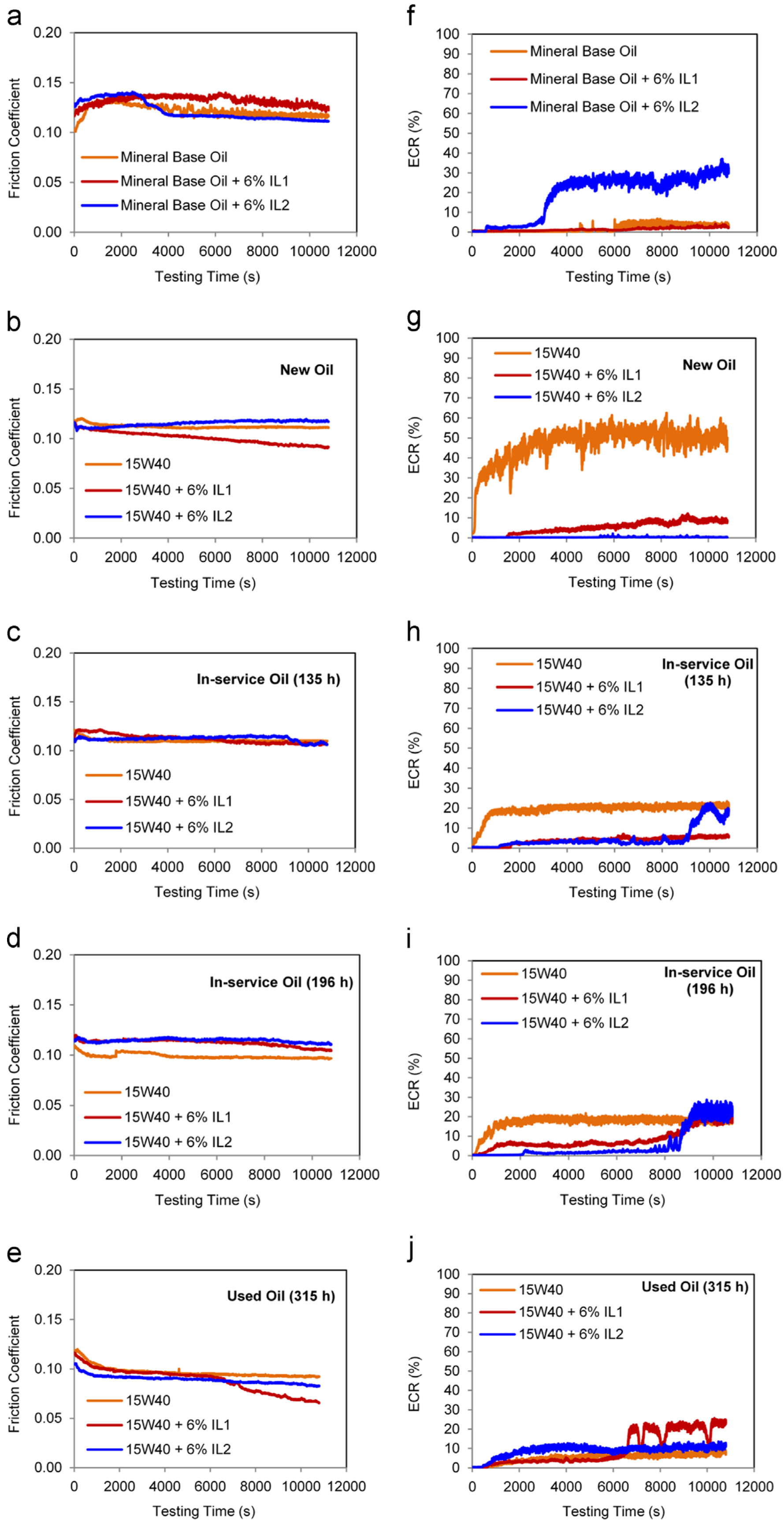

Fig. 2. Mean Friction Coefficient and representative ECR results. Repeatability (relative standard deviation) of friction coefficient results is within 10%. Intended for colour reproduction.

Table 2
Mean friction and standard deviation values for cases shown in Fig. 2.

Lubricants	Friction Coefficient	
	Mean	Std Dev
Mineral Base Oil	0.1218	0.0062
Mineral Base Oil+6% IL1	0.1320	0.0059
Mineral Base Oil+6% IL2	0.1216	0.0217
New Oil	0.1123	0.0056
New Oil+6% IL1	0.1008	0.0067
New Oil+6% IL2	0.1155	0.0060
In-service Oil (135 h)	0.1104	0.0033
In-service Oil (135 h)+6% IL1	0.1122	0.0008
In-service Oil (135 h)+6% IL2	0.1123	0.0031
In-service Oil (196 h)	0.0991	0.0066
In-service Oil (196 h)+6% IL1	0.1124	0.0013
In-service Oil (196 h)+6% IL2	0.1147	0.0031
Used Oil (315 h)	0.0969	0.0012
Used Oil (315 h)+6% IL1	0.0886	0.0051
Used Oil (315 h)+6% IL2	0.0893	0.0056

roughness R_{rms} of about 0.647 μm). Both piston ring and flat specimens were ultrasonically cleaned in acetone for 10 min prior to tribo-testing and are shown in Fig. 1.

Sliding tests were conducted using a High Frequency reciprocating tribometer (Plint TE77). A constant normal load of 50 N was applied which produced the contact pressure of 285 MPa at the ring-on-flat interface at the beginning of each test. The change in contact pressure with increase in contact area at the sliding interface, due to the wear process taking place over the test duration, was assumed to be negligible. Contact pressure calculation was performed using the Hertz theory of non-conformal contacts as mentioned in [20]. In addition, an average reciprocating sliding frequency of 4.4 Hz, stroke length of 5 mm, fully flooded heated oil bath with constant uniform bulk oil temperature of 100 °C was maintained for the test duration of 3 h. ECR results measured the formation of electrically insulating boundary film using the Lunn-Furey Electrical Contact Resistance Circuit [21]. Each test was replicated three times and average value of friction coefficient and wear volume was considered.

The combination of applied load, high temperature and the point contact between the piston ring segment and flat sample resulted in the simulation of a boundary lubrication regime as seen near the top ring reversal region of IC engines, similar to that simulated by other researchers in past [22]. The theoretical confirmation of the lubrication regime was done by calculating oil-film thickness ratio (or λ-ratio) which incorporates the minimum oil film thickness (MOFT) and combined rms roughness of unworn surfaces of piston ring segment and flat sample. MOFT was calculated using the Hamrock and Dowson formula [23] incorporating the aforementioned material and test parameters, such that λ-ratio of approximately 0.01 ensured boundary lubrication regime at the beginning of tribo-testing.

Following the tribo-testing, surface analysis of the worn surface of cast iron flat samples was carried out. 3D White Light Interferometer (ZYGO) was used for wear volume measurements. Wear mechanism study was carried out by SEM (JEOL JSM-6610LV). Chemical analysis was carried by EDX (attachment on SEM), and XPS. An instrument used for XPS was SPECS Phoibos 100 MCD5 system equipped with a hemispherical electron analyser. Monochromatic Mg Kα radiation ($h\nu$ = 1486.7 eV) was used at constant pass energy while survey scan spectra were made typically at pass energy of 90 eV. Individual high resolution spectra were taken at pass energy of 30 eV. All spectra were also calibrated using C 1s peak fixed at 284.6 eV. The spectra were processed by using CasaXPS software.

3. Results and discussion

3.1. Friction and ECR analysis

Friction behaviour of Mineral Base Oil and different fully-formulated engine oils after addition of ILs as additive was found to be similar (Fig. 2a–e).

Table 2 shows the mean friction coefficient and standard deviation values for cases shown in Fig. 2. Interestingly ILs become predominantly effective in reducing the friction response of ring-liner tribo-system when already present lubricant additives are depleted due to engine service and the effect is clearly evident in Used Oil case (Fig. 2e). The net reduction in mean friction coefficient by addition of IL1 and IL2 to the used engine oil was 0.4% and 9.9%, at the beginning of the tribo-test, and, 29.2% and 10.3%, at the end of tribo-test, respectively, in comparison to fully-formulated Used Oil without IL.

The ECR results (Fig. 2f–j) depict interesting boundary film formation phenomenon of different lubricants, although only qualitative comparison can be made using this technique. Fully-formulated New Oil (without IL) exhibited superior boundary film formation capability due to its effective film forming additives (Fig. 2g). The effects of the depletion of film forming additives on ECR results are clearly evident from the in-service and Used Oil cases (without ILs). The addition of ILs to oil increased the metal–metal contact between mating surfaces as reflected by drop in contact resistance in all cases, except with Used Oil. Mixtures of Used Oil and ILs outperformed the boundary film formation capability of neat Used Oil. In the case of a mixture of Used Oil and IL1, frequent reversals in resistance after 6000 s could be attributed to the presence of higher amount of wear debris already present in Used Oil (mainly Fe wear debris, see Table 1). Wear debris can also oxidise during the tribological process and act as insulating layer leading to unstable electrical resistance between the metallic surfaces [24,25].

3.2. Wear analysis

The relative loss of material from cast iron samples in terms of wear volume (Fig. 3) defines the effectiveness of different lubricants and lubricant-IL mixtures. New Oil, which contains a well-designed additive package that provides maximum protection in boundary wear conditions, produced the least wear. Since these additives are absent in Mineral Base Oil the wear is highest here. The trend of increasing wear volume results obtained from tribo-testing was expected since the lubricants had lost their effectiveness as a function of their duty cycles in the actual engine represented by number of hours, i.e. 135, 196 and 315 h. Among all the fully-formulated engine oils, the Used Oil was collected after approx. 315 h in the actual engine prior to tribo-testing produced significantly higher

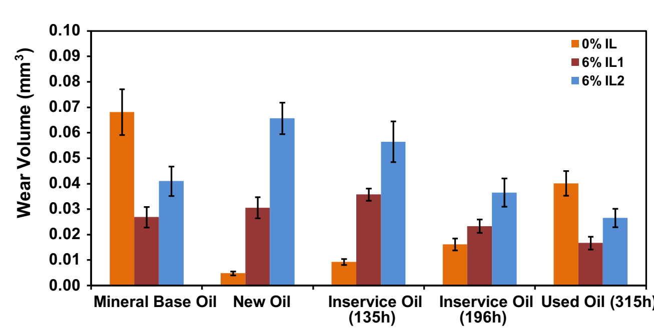

Fig. 3. Wear Volume (mm^3) results of cast iron flat samples after 3 h sliding at 100°C. Repeatability (relative standard deviation) of results is within 15%. Intended for colour reproduction.

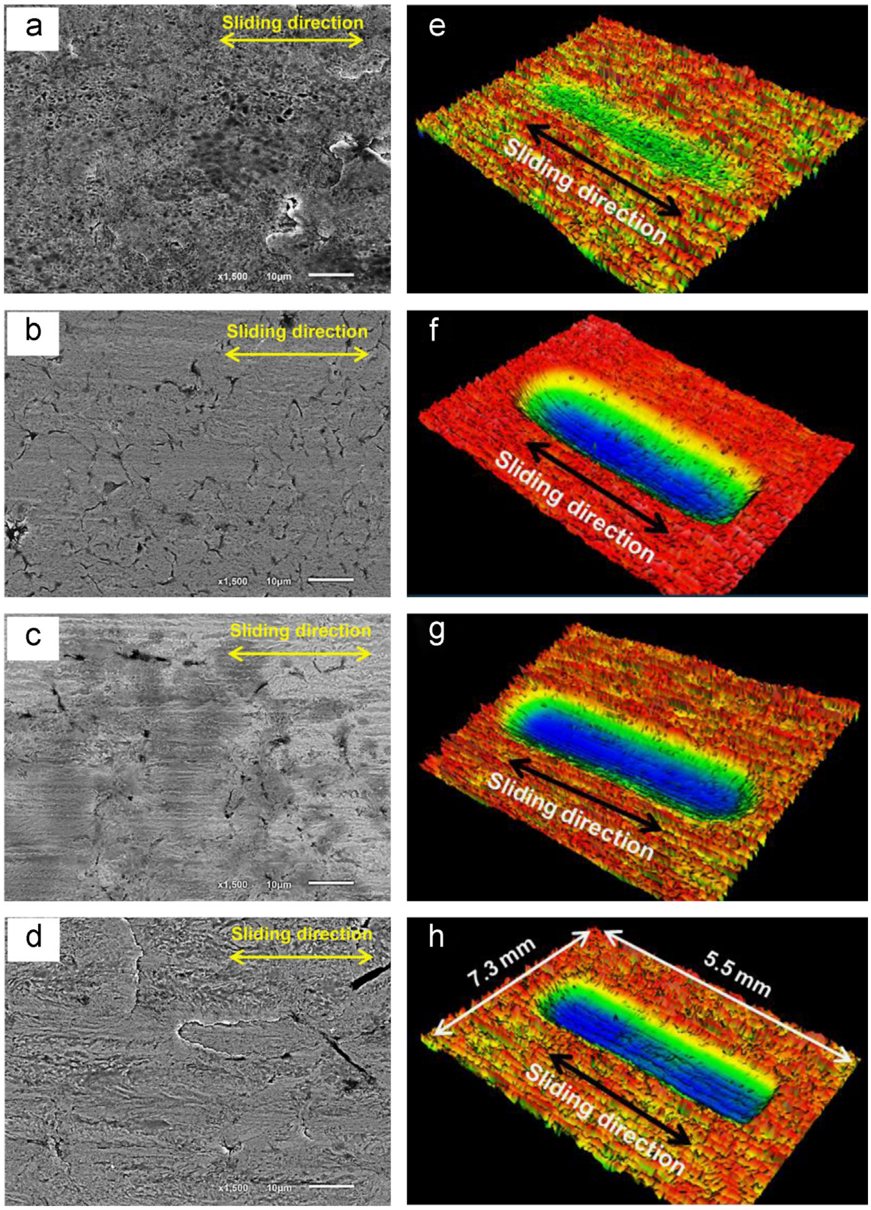

Fig. 4. SEM images (× 1500) and 3D White Light Interferometry images of the cast iron flat samples after 3 h sliding at 100°C lubricated with New Oil (a, e); Used Oil (b, f); Used Oil+6% IL1 (c, g); Used Oil+6% IL2 (d, h). Intended for colour reproduction.

amount of wear but lower than Mineral Base Oil. This can be explained due to the remaining effective additives content in the Used Oil in comparison to Mineral Base Oil, which has none.

The effect of the addition of IL1 and IL2 to the different engine-conditioned oils can be seen in Fig. 3. Wear volume in the case of Used Oil was reduced by 58% and 34% by the addition of IL1 and IL2, respectively. However increments in wear in all other cases of fully-formulated engine oils by addition of both the ILs were also noted. Interestingly, ILs helped reduce wear when added as additive to Mineral Base Oil but the anti-wear performance was not as good as fully-formulated New Oil.

Previous studies [12,16,18] have mentioned that owing to the unique dipolar structure of ILs, its negatively charged moiety tend to get adsorbed on the positively charged metal surface, thus forming a protective film on the surface. The same is also true for ZDDP anti-wear additives typically present in engine lubricants. The aforementioned wear results from current research indicate the antagonistic interaction between the already present additives in fully-formulated engine oils and later added ILs. Such interaction could be attributed to the strong affinity of film forming lubricant additives towards the metal surfaces leading to competitive aggression with ILs, which possess similar tendency. It has been mentioned that tribo-chemical reactions taking place at the surface could also be detrimental when the synergy of chemical (corrosion) and mechanical (e.g., abrasion and adhesion) stresses accelerates material removal [26]. Therefore such phenomenon could have happened by the competitive response of all additives to form boundary film on surface eventually leading to generation of stresses causing higher film removal rate than film formation rate. Hence, it provided more local sites for contact between the mating surfaces which resulted in higher amount material removal from the softer cast iron surface. These findings are also in line with their corresponding ECR curves (Fig. 2).

Due to the similar steady-state friction behaviour of fully-formulated engine oils with and without the addition of ILs, the same was also hypothesised for wear rate response of tribo-system to the newly formulated lubricant-IL mixtures. On the contrary, wear results showed no symmetry with their friction counterpart (Fig. 2). This observation could be justified by the fact that friction and wear are not directly related, as explained by Blau in [27]. The processes that lead to friction and wear may arise from different material and systems properties and often do not reach steady-state at the same time. Therefore, the same friction behaviour of oil with and without ILs does not necessarily mean a similar effect is observed on wear as well. This is because frictional energy input to the system is partitioned differently from one tribo-system to another. This energy may be used to form oxides, grow cracks, plough through the surface, and heat the surface, or shear debris layers [24]. Evidence of this energy dissipation in terms of wear has been observed during the worn surface analyses, discussed in the next section.

3.3. Surface analysis

In all cases, a plastic deformation mechanism is observed under the boundary wear regime. This mechanism led to the smoothing of asperities of the cast iron surface covering the shallow valleys and forming smooth plateaus with a glossy finish. Also higher wear has taken place near the reversal points at either ends of the stroke than that at the middle of stroke where sliding speed is highest (Fig. 4e–h). This is due to reversed tractions experienced by the contacting surfaces near the point of change in direction of reciprocating sliding motion [28]. Scuffing damage was not seen and also not reflected by the mean friction coefficient values (i.e. <0.2). Cast iron surface lubricated with New Oil is covered by a dark lubricant film, Fig. 4(a), unlike the Used Oil case in which material inherited porosities are clearly exposed, Fig. 4(b). In the latter case, mild wear lines were also seen due to debris present at the sliding interface either as free particles within the oil (Ferrous wear debris, see Table 1) leading to 3-body abrasion and/or embossed onto the counterpart piston ring running surface leading to 2-body abrasion. The addition of IL1 (Fig. 4c) and IL2 (Fig. 4d) to the Used Oil resulted in wear reduction evident by fewer mild abrasive wear lines and less exposed porosities. Fig. 4f–h also clearly show the reduction in wear by the addition of ILs to Used Oil. Although the plastic deformation of asperities (peaks) has taken place even after the addition of ILs, the effect of abrasion wear mode is reduced significantly in case of IL1 and less prominently for IL2.

The analysis of chemical composition of surface films formed by lubricant between two sliding surfaces provides much needed information about the interaction of lubricant's anti-wear additives with the rubbed (or sliding) surfaces. XPS provides information about the change in the chemical state of the elements within the first few nanometric layers (i.e. 1–5 nm) whereas the EDX supplements with the information about chemical composition by detecting up to the depth of a few microns. Hence, knowing the chemical composition of the test samples, lubricants and ILs used, tribo-chemical reactions taking place at the sliding interface can be understood.

Table 3 shows the comparison of chemical composition of the surface films formed by neat lubricants and their corresponding Oil–IL blends. Concentration of Ca, P, Zn and S has reduced by addition of ILs to the New Oil, whereas, that of element O has increased. However, reverse in chemical reactivity rather beneficial effect is noted in case of Used Oil after addition of ILs. XPS analyses showed that iron in wear scar region exists in the compound form of different oxides and phosphate. Table 4 indicates the presence of boundary film composed of iron phosphate ($FePO_4$) in case of New Oil, which is known for improving tribological properties [13]. Addition of ILs to New Oil disrupted the phosphorus reactivity with the iron surface and hence is not reflected in the Fe2p3/2 results (Table 4). On the other hand, the addition of ILs to Used Oil increased the intensity of the P2p band, making it comparable to that noted in case of New Oil (see Fig. 5). The position of the P2p peak, in different cases shown in Fig. 5, also suggests the existence of iron (III) phosphates according to the experiments of Otero et al. [29] who assigned P2p peak for $FePO_4$ at 133.7 eV. The low amount of element P causes a high ratio of Fe-oxides/$FePO_4$, thus hardening the detection of $FePO_4$ in the Fe2p3/2 spectra, as found in case of Used Oil with IL2.

Therefore it can be deduced from these observations that addition of ILs to New Oil, reduces the reactivity of ZDDP (antiwear) and Calcium based (detergent) additives with the Fe containing cast iron surface, thence resulting in increased wear. On the contrary, in case of Used Oil, polar ILs reacts freely with Fe surface due to the reduced interference from the depleted ZDDP and Ca additives. Furthermore, synergy between ILs and the remaining additives content in Used Oil can be seen leading to reduction in wear. These observations are also in agreement with the previous wear volume results (Fig. 3). Cr, if any exists, was noted in case of Used Oil without ILs (Table 3), suggesting material transfer (adhesion) from the surface of chromium coated piston ring during the sliding process. Hence, both EDX and XPS results indicate the involvement of ILs into the boundary film formation process during the tribo-testing.

Table 4
XPS results – binding energy shifts for Fe2p3/2 spectra.

Cast iron sample surface lubricated with	Binding energy (eV)	Assigned chemical compounds	Ref[a]
New Oil	710.2	Fe_3O_4	[30]
	712.2	$FePO_4$	[29]
New Oil+6% IL1	710.7	Fe_2O_3	[31–33]
New Oil+6% IL2	710.8	Fe_2O_3	[31–33]
Used Oil (315 h)	710.2	Fe_3O_4	[30]
	711.4	Fe_2O_3	[31–33]
	712.9	$FePO_4$	[29]
Used Oil (315 h)+6% IL1	710.5	Fe_3O_4	[30]
	712.4	$FePO_4$	[29]
Used Oil (315 h)+6% IL2	710.3	Fe_3O_4	[30]
	711.8	Fe_2O_3	[31–33]

[a] Most of these references are extracted from the NIST X-ray photoelectron spectroscopy database, accessible through http://srdata.nist.gov/xps/Default.aspx

Table 3
Elemental concentration inside worn surface obtained by EDX analysis.

Cast iron sample surface lubricated with	Element concentration (in weight%)									
	C	O	Si	S	Zn	P	Ca	Mn	Cr	Fe
New Oil	6.69	5.24	1.99	1.25	1.63	0.92	0.66	0.77	*nd*	80.85
New Oil+6% IL1	6.17	8.92	1.77	0.07	0.47	0.78	0.52	*nd*	*nd*	81.29
New Oil+6% IL2	7.38	7.31	2.10	0.23	*nd*	0.42	*nd*	0.54	*nd*	82.02
Used Oil (315 h)	7.86	8.75	2.24	0.36	*nd*	0.26	*nd*	0.75	0.22	79.55
Used Oil (315 h)+6% IL1	7.56	11.40	2.14	0.28	0.40	0.48	0.45	0.51	*nd*	76.77
Used Oil (315 h)+6% IL2	6.82	12.88	1.80	0.34	0.20	0.58	0.36	*nd*	*nd*	77.01

nd – not detectable.

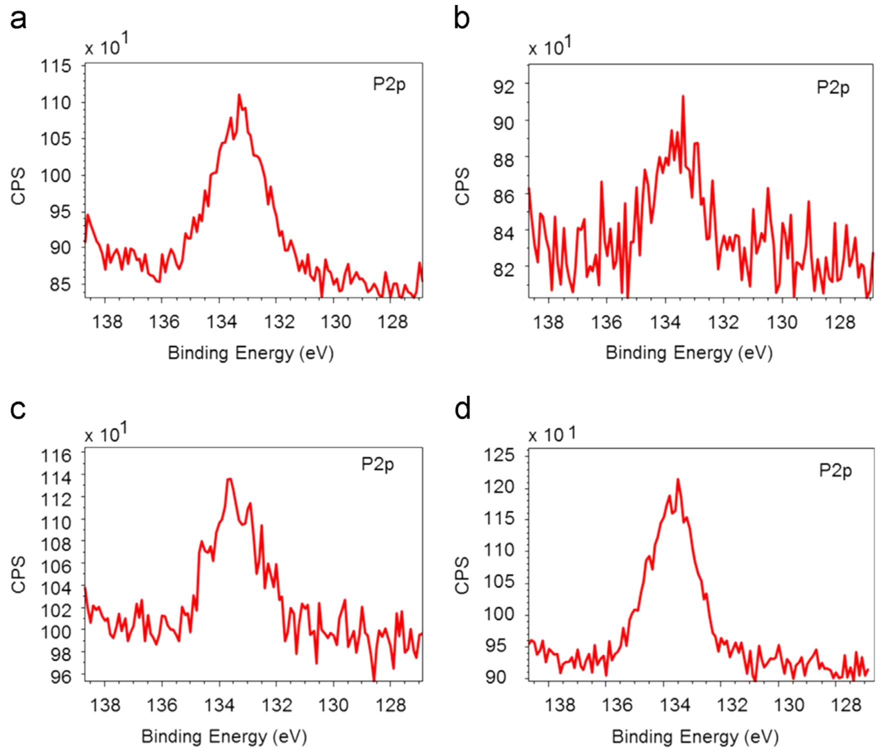

Fig. 5. XPS spectra of P2p of cast iron samples after 3 h sliding at 100°C lubricated with (a) New Oil, (b) Used Oil (315 h), (c) Used Oil (315 h)+6% IL1, and (d) Used Oil (315 h)+6% IL2.

4. Conclusions

- The addition of Phosphonium ILs as additive in the used engine oil (after depletion of the already existing additive package) improved its friction and wear behaviour.
- The addition of Phosphonium ILs to relatively less degraded engine oils e.g. half intended service life (than fully Used Oil) worsens the wear and produces no significant change in friction performance.
- Interference between ILs and existing additives in engine oils was noted.
- ILs effectively contributed to the boundary film formation when already present additives (such as ZDDP) are substantially depleted as seen in the case of used engine oil.
- The extension of the service life of used engine oils can be achieved and has potential of significant savings in terms of fuel economy, engine reliability and by reduced oil consumption and drainage into the environment.
- Further work should focus on lower concentrations of Phosphonium ILs as additives in used engine lubricants to meet limits on overall phosphorus content as per ILSAC GF-5.

Acknowledgements

The authors wish to express their thanks to the BP Technology Centre (UK) for their in-kind support in performing oil analysis experimental work. Also they thank to Santander Bank for funding the research stay of Mayank Anand at the University of Oviedo to conduct surface analysis work (Santander Scholarship Award). Also in-kind support by Repsol S.A. (Spain) in providing the additives-free Mineral Base Oil is acknowledged.

References

[1] S.C. Tung, M.L. McMillan, Automotive tribology overview of current advances and challenges for the future, Tribol. Int. 37 (2004) 517–536.
[2] M.D. Bermúdez, A.E. Jiménez, J. Sanes, F.J. Carrión, Ionic liquids as advanced lubricant fluids, Molecules 14 (2009) 2888–2908.
[3] J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, et al., Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive, Tribol. Int. 71 (2014) 88–97.
[4] I. Otero, E.R. López, M. Reichelt, M. Villanueva, J. Salgado, J. Fernandez, Ionic liquids based on phosphonium cations as neat lubricants or lubricant additives for a steel/steel contact, ACS Appl. Mater. Interfaces 6 (15) (2014) 13115–13128.
[5] V. Totolin, I. Minami, C. Gabler, J. Brenner, N. Dörr, Lubrication mechanism of phosphonium phosphate ionic liquid additive in alkylborane–imidazole complexes, Tribol. Lett. 53 (2014) 421–432.
[6] R. González, A.H. Battez, J. Viesca, A. Higuera-Garrido, A. Fernández-González, Lubrication of DLC coatings with two tris (pentafluoroethyl) trifluorophosphate anion-based ionic liquids, Tribol. Trans. 56 (2013) 887–895.
[7] J. Viesca, A. García, A.H. Battez, R. González, R. Monge, A. Fernández-González, et al., FAP − Anion ionic liquids used in the lubrication of a steel–steel contact, Tribol. Lett. 52 (2013) 431–437.
[8] A.H. Battez, R. González, J.L. Viesca, D. Blanco, E. Asedegbega, A. Osorio, Tribological behaviour of two imidazolium ionic liquids as lubricant additives for steel/steel contacts, Wear 266 (2009) 1224–1228.
[9] D. Blanco, R. González, A. Hernández Battez, J. Viesca, A. Fernández-González, Use of ethyl-dimethyl-2-methoxyethylammonium tris (pentafluoroethyl) trifluorophosphate as base oil additive in the lubrication of TiN PVD coating, Tribol. Int. 44 (2011) 645–650.
[10] A. Hernández Battez, R. González, J. Viesca, A. Fernández-González, M. Hadfield, Lubrication of PVD coatings with ethyl-dimethyl-2-methoxyethylammonium tris (pentafluoroethyl) trifluorophosphate, Tribol. Int. 58 (2013) 71–78.
[11] R. González, A.H. Battez, D. Blanco, J. Viesca, A. Fernández-González, Lubrication of TiN, CrN and DLC PVD coatings with 1-butyl-1-methylpyrrolidinium tris (pentafluoroethyl) trifluorophosphate, Tribol. Lett. 40 (2010) 269–277.
[12] J. Qu, P.J. Blau, S. Dai, H.M. Luo, H.M. Meyer, Ionic liquids as novel lubricants and additives for diesel engine applications, Tribol. Lett. 35 (2009) 181–189.
[13] I. Minami, T. Inada, R. Sasaki, H. Nanao, Tribo-chemistry of phosphonium-derived ionic liquids, Tribol. Lett. 40 (2010) 225–235.
[14] B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, et al., Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives, Wear 289 (2012) 58–64.
[15] J. Qu, D.G. Bansal, B. Yu, J.Y. Howe, H. Luo, S. Dai, et al., Antiwear performance and mechanism of an oil-miscible ionic liquid as a lubricant additive, ACS Appl. Mater. Interfaces 4 (2012) 997–1002.
[16] G. Mordukhovich, J. Qu, J.Y. Howe, S. Bair, B. Yu, H.M. Luo, et al., A low-viscosity ionic liquid demonstrating superior lubricating performance from mixed to boundary lubrication, Wear 301 (2013) 740–746.
[17] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123–150.

[18] X.Q. Liu, F. Zhou, Y.M. Liang, W.M. Liu, Tribological performance of phosphonium based ionic liquids for an aluminum-on-steel system and opinions on lubrication mechanism, Wear 261 (2006) 1174–1179.
[19] S.W. Zhang, L.T. Hu, D. Qiao, D.P. Feng, H.Z. Wang, Vacuum tribological performance of phosphonium-based ionic liquids as lubricants and lubricant additives of multialkylated cyclopentanes, Tribol. Int. 66 (2013) 289–295.
[20] W.C. Young, R.G. Budynas, Roark's Formulas for Stress and Strain, Seventh ed., McGraw-Hill Companies, Inc. (2002) 689–707.
[21] M. Furey, Metallic contact and friction between sliding surfaces, ASLE Trans. 4 (1961) 1–11.
[22] J.J. Truhan, J. Qu, P.J. Blau, The effect of lubricating oil condition on the friction and wear of piston ring and cylinder liner materials in a reciprocating bench test, Wear 259 (2005) 1048–1055.
[23] D. Dowson, Elastohydrodynamic and micro-elastohydrodynamic lubrication, Wear 190 (1995) 125–138.
[24] J.L. Viesca, A.H. Battez, R. González, T. Reddyhoff, A.T. Pérez, H.A. Spikes, Assessing boundary film formation of lubricant additivised with 1-hexyl-3-methylimidazolium tetrafluoroborate using ECR as qualitative indicator, Wear 269 (2010) 112–117.
[25] T. Narayanan, Y.W. Park, K.Y. Lee, Fretting corrosion of lubricated tin plated copper alloy contacts: effect of temperature, Tribol. Int. 41 (2008) 87–102.
[26] J. Qu, M. Chi, H.M. Meyer III, P.J. Blau, S. Dai, H. Luo, Nanostructure and composition of tribo-boundary films formed in ionic liquid lubrication, Tribol. Lett. 43 (2011) 205–211.
[27] P.J. Blau, Friction Science and Technology: From Concepts to Applications, CRC press, 2012.
[28] P. Blau, S.C. Tung, Bench performance test methods for lubricated engine materials, Automotive Lubricants and Testing, ASTM International (2012) 215–230.
[29] I. Otero, E.R. López, M. Reichelt, J. Fernández, Friction and anti-wear properties of two tris (pentafluoroethyl) trifluorophosphate ionic liquids as neat lubricants, Tribol. Int. 70 (2014) 104–111.
[30] B.J. Tan, K.J. Klabunde, P.M. Sherwood, X-ray photoelectron spectroscopy studies of solvated metal atom dispersed catalysts. Monometallic iron and bimetallic iron-cobalt particles on alumina, Chem.Mater. 2 (1990) 186–191.
[31] C. Wagner, W. Riggs, L. Davis, J. Moulder, G. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Prairie, MN, 1979, 1977.
[32] E. Paparazzo, X-ray photo-emission and Auger spectra of damage induced by Ar^{+}-ion etching at SiO_2 surfaces, J. Phys. D. Appl. Phys. 20 (1987) 1091.
[33] H. Seyama, M. Soma, Fe 2p spectra of silicate minerals, J. Electron Spectrosc. Relat. Phenom. 42 (1987) 97–101.