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

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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.

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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

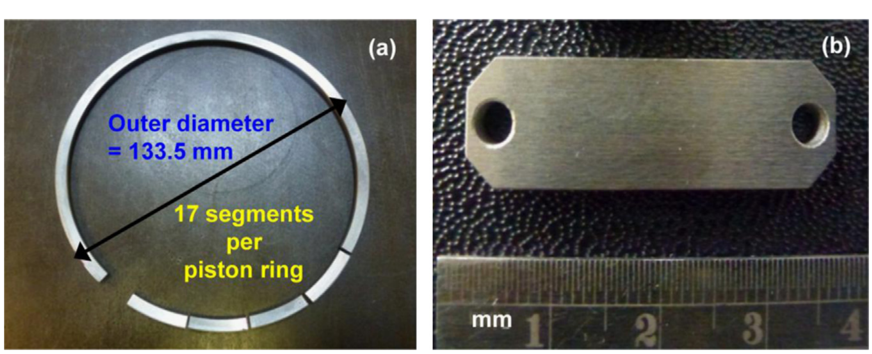

Fig. 1. Test material used in experiments. (a) Actual piston ring segments and (b) Typical cast iron flat sample. Intended for colour reproduction.