Special Issue: MDA2016

Institution of MECHANICAL ENGINEERS

Journal of MATERIALS: DESIGN AND APPLICATIONS

Proc IMechE Part L:
J Materials: Design and Applications
0(0) 1–9

DOI: 10.1177/1464420716663235
pil.sagepub.com
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The depletion of ZDDP additives within marine lubricants and associated cylinder liner wear in RNLI lifeboat engines

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Abstract

Previous work of authors indicated the wear of cylinder liners in marine engines of RNLI lifeboats due to the intense lubricant degradation identified by inductively coupled plasma and Fourier Transform Infrared spectroscopy techniques. In this paper, further analysis carried out to evaluate the effects of lubricant degradation on the actual cylinder liners installed in the Trent Class Lifeboat engines is presented. Surface characterisation of actual cylinder liner's bore surface showed maximum wear near the top dead centre region compared to rest of the piston stroke. Wear in this region of the cylinder liner surface is controlled primarily by the protective film forming anti-wear additives in the lubricant which limit the direct surface contact between the piston rings and cylinder liner. The condition of zinc dialkyldithiophosphates anti-wear additives was analysed using the nuclear magnetic resonance spectroscopy. Tribology analysis was conducted to evaluate the tribological and boundary film forming performance of zinc dialkyldithiophosphates additives by simulating cylinder liner–piston ring contact near the top dead centre. To further understand the wear mechanisms of the cylinder liner, wear debris analysis (Analytical Ferrography) of lubricant samples was performed. Results revealed the depletion of phosphorus containing zinc dialkyldithiophosphates anti-wear additives as a function of the lubricant's duty cycle within the marine engines and its effect on the tribological and boundary film forming performance of lubricants. Wear debris analysis showed the generation of ferrous debris potentially from the cylinder liners as a result of reduced anti-wear protection from the depleted zinc dialkyldithiophosphates additives during the tribological contact with piston rings and piston skirt region. These findings are useful to understand the lubricant degradation mechanisms which affect the functionality of cylinder liners, therefore allowing to plan the engine maintenance strategies.

Keywords

NMR spectroscopy, analytical ferrography, tribology testing, marine lubricants, additives, cylinder liner

Date received: 3 July 2016; accepted: 17 July 2016

Introduction

The RNLI lifeboat fleet incorporates over 350 lifeboats within the UK coastline of various sizes and classes which are needed depending on geographical features and the kind of rescue work. All these lifeboats function in severe and high impact rough sea environments to perform rescue operations. In order to reach the rescue destination quickly, these lifeboats are operated at extreme engine operating conditions which lead to severe degradation of engine lubricants. The details of each class of lifeboats in terms of marine engine description and the type of lubricant used in the respective engines are mentioned in Table 1.

Previous work of authors[1] indicated the wear of cylinder liners in marine engines of RNLI lifeboats due to the intense lubricant degradation identified by ICP and FTIR spectroscopy techniques. In addition, the average service life of lubricant in different lifeboat engines (mentioned in Table 1) was noted to be 300 h with the primary reason for oil change as high concentration of iron debris in lubricants. The main source of iron debris, especially in Trent Class lifeboat engines, was identified as the cylinder liner which has a material composition of approximately 92 wt.% of iron. Also, the concerned engine is comprised of 10 cylinders and each cylinder covers a large surface area where severe wear takes place due to tribological contact with piston rings and piston skirt region. Wear in the TDC region of the cylinder liner is a limiting factor to the lifetime of the engine.

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Table 1. Details of RNLI fleet of lifeboats with engine and lubricant description.

	Marine engines in lifeboats			
Lifeboat fleet	Engine model	Power output	Cylinders	Lubricant oil
Trent Class	MAN D2840LE401	850 hp @2300 r/min	10	SAE 15W40
Tamar Class	Caterpillar C-18	1001 hp @ 2300 r/min	6	SAE 15W40
Severn Class	Caterpillar 3412T	1250 hp @ 2300 r/min	12	SAE 15W40
Mersey Class	Caterpillar 3208T	280 hp @ 2800 r/min	8	SAE 15W40

Such wear phenomena, long since overcome in automobiles, can still cause problems in marine diesel engines.[2]

The anti-wear additives, such as ZDDP, commonly used in the diesel engine lubricants are responsible to form protective boundary film under starved lubrication conditions to prevent direct metal–metal contact. The depletion of such an additive over time with usage leads to loss in optimum functionality, eventually causing tribological and corrosive wear of the main engine components. The condition of ZDDP additive has been analysed in the past using the NMR spectroscopy.[3–7] In addition, the Analytical Ferrography has been used by other researchers[8–10] to identify the wear mode of lubricated components by examining the wear debris present in engine lubricants.

In the current research, lubricant degradation in the Trent Class Lifeboat engines was investigated by performing NMR spectroscopy, Analytical Ferrography and tribological tests. The effect of anti-wear additives depletion on the wear of actual cylinder liners used in Trent Class Lifeboat engines was also studied.

Experimental details

Lubricant samples

The lubricant tested in the experiments is commercially available mineral-based SAE 15 W-40 engine oil typically used in heavy duty marine diesel engines. The lubricant already contains ZDDP anti-wear additives as part of its additive package and no additional additives had been added to lubricant in this study. The lubricant samples of 1 L were collected directly from the engine sump of capacity 30 L of marine diesel engines installed in the Trent Class RNLI lifeboats. These oil samples were collected at various service intervals of 135, 196, 270, 280, 300, and 315 h respectively. Table 2 shows the viscosity of each lubricant sample measured experimentally by performing ASTM D445. Furthermore, these oil samples were collected from the engine oil sump after running the engine for at least half an hour. This was done to allow for heating and thorough mixing of the oil by circulation within the engine prior to its sampling so that a uniform mixture of oil could be collected as representative of the whole engine sump oil.

Methodology of NMR and Analytical Ferrography analysis

Three engine-conditioned lubricant samples collected after the service intervals of 135, 196 and 315 h were analysed to evaluate the condition of ZDDP additives using the NMR spectroscopy. The results were benchmarked against the fresh lubricant sample, i.e. 0 h. Around 3 mL of each lubricant sample (without solvent) along with benzene for field locking was added to a 10 mm diameter tube. P-31 spectra were then recorded for each sample using an AVANCE III HD NMR Spectrometer. Each lubricant sample was tested for 8 h and the obtained results are discussed in the next NMR analysis section. The details about the NMR spectroscopy can be referred in Wooton.[3]

Another three engine-conditioned lubricant samples collected after the service intervals of 270, 280 and 300 h were analysed using Analytical Ferrography. This technique was employed to identify the wear mode of lubricated engine components by examining the particles present in lubricants due to wear or as foreign contamination. A ferrogram was prepared which is a special glass microscope slide and has mainly magnetic particles (such as ferrous debris) deposited on its surface. The prepared ferrogram was then examined under the optical microscope to distinguish particle size, concentration, composition, morphology and the surface condition of the ferrous and non-ferrous wear particles. Results of the wear debris analysis are discussed in the Analytical Ferrography Analysis section. The details about the Analytical Ferrography technique can be referred in literature.[13]

Methodology of tribological analysis

Tribology tests were performed to evaluate the effect of depletion of the ZDDP additives within RNLI lifeboat engines on the lubricant performance such as friction, wear and boundary film formation. Therefore, to study this effect, an engine-aged lubricant sample (300 h) near the end of its service life was benchmarked against the fresh engine lubricant (0 h).

Table 2. Viscosity of the lubricants at different service intervals.

	0 h[a]	135 h[a]	196 h[a]	270 h	280 h	300 h	315 h[a]
Viscosity at 40 °C (cS)	106.1	100.3	102.3	–	–	101.5	91.5
Viscosity at 100 °C (cS)	14.3	13.7	13.8	13.6	12.7	14.1	12.7

[a]Source: Anand et al.[11,12]

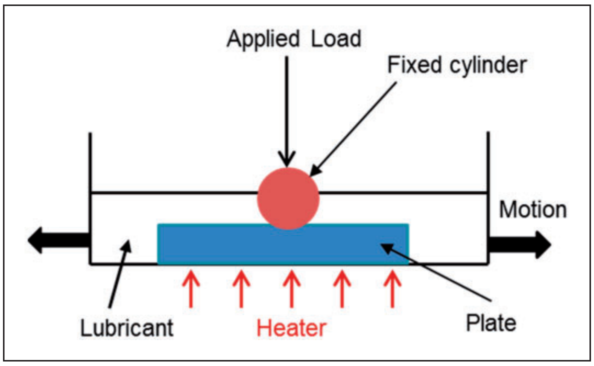

Figure 1. Schematic of cylinder-on-plate test configuration employed in this study.

Table 3. Tribology test conditions.

Test parameter	Value	Unit
Contact pressure	208	MPa
Applied load	50	N
Sliding frequency	38.33	Hz
Stroke length	5	mm
Oil temperature	100	°C
Test duration	10	h

A reciprocating cylinder-on-plate test configuration, as shown in Figure 1, was used on Plint TE77 tribometer to simulate the line contact between piston ring and cylinder liner. The cylinder was a hard ground steel (Grade 100Cr6) made dowel pin of diameter 6 mm and length 10 mm, whereas the plate sample was a grey cast iron (Grade BS 1452) made flat coupon of L 33 × W 10 × T 3 mm. The test conditions, as shown in Table 3, were used to simulate the boundary lubrication regime as experienced by the TDC region of cylinder liner near the top compression ring reversal point.

Coefficient of Friction (COF) and Electrical Contact Resistance (ECR) results were recorded at every 10-s interval for complete duration of each test. ECR results provide the information about the formation of electrically insulating boundary film using the Lunn–Furey Electrical Contact Resistance Circuit.[14] Post-test surface analysis of wear scar region on test samples was conducted using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and white light interferometry (WLI). SEM-EDX equipment used for analysis was Zeiss Supra 35 VP and the intensity of incident electron beam used was 20 KeV. Results of the tribology analysis are discussed in the Tribological analysis section.

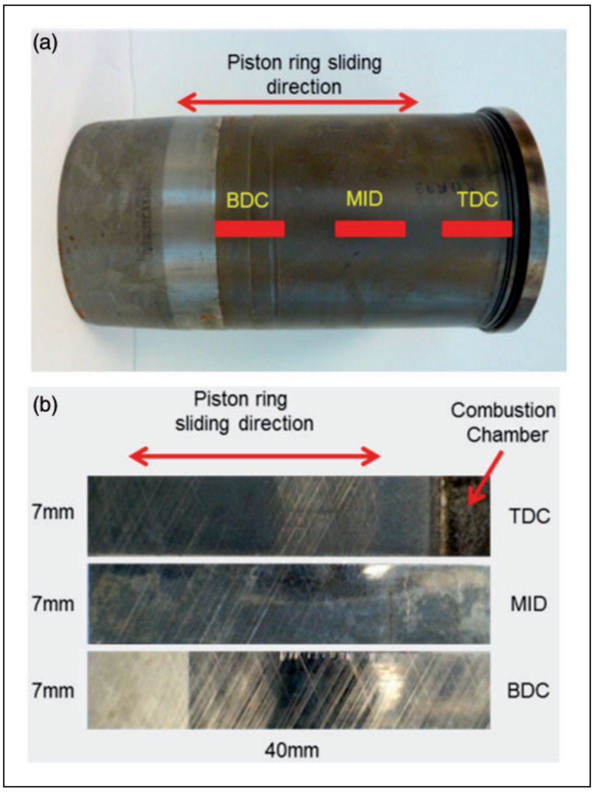

Figure 2. Actual cylinder liner used for wear analysis of bore surface is shown in (a), and its cut sections are shown in (b).

Methodology of wear analysis of actual cylinder liner

A typical chromium phosphorous alloyed grey cast iron-made cylinder liner was obtained from a four-stroke heavy duty diesel (MAN D2840LE401) that was undergoing a full overhaul. Figure 2(a) shows the actual cylinder liner which was installed in the marine engine of a Trent Class Lifeboat of the RNLI. Three sections each of L 40 × W 7 mm were cut at TDC, mid-stroke (MID) and BDC locations using a band saw cutting machine. Figure 2 (b) shows the bore surfaces of the three sections cut from the cylinder liner. These sections were cleaned in an ultrasonic bath using acetone for 10 min to remove wear debris from the samples been generated during the cutting process. Cylinder liner samples were subjected to surface characterisation using

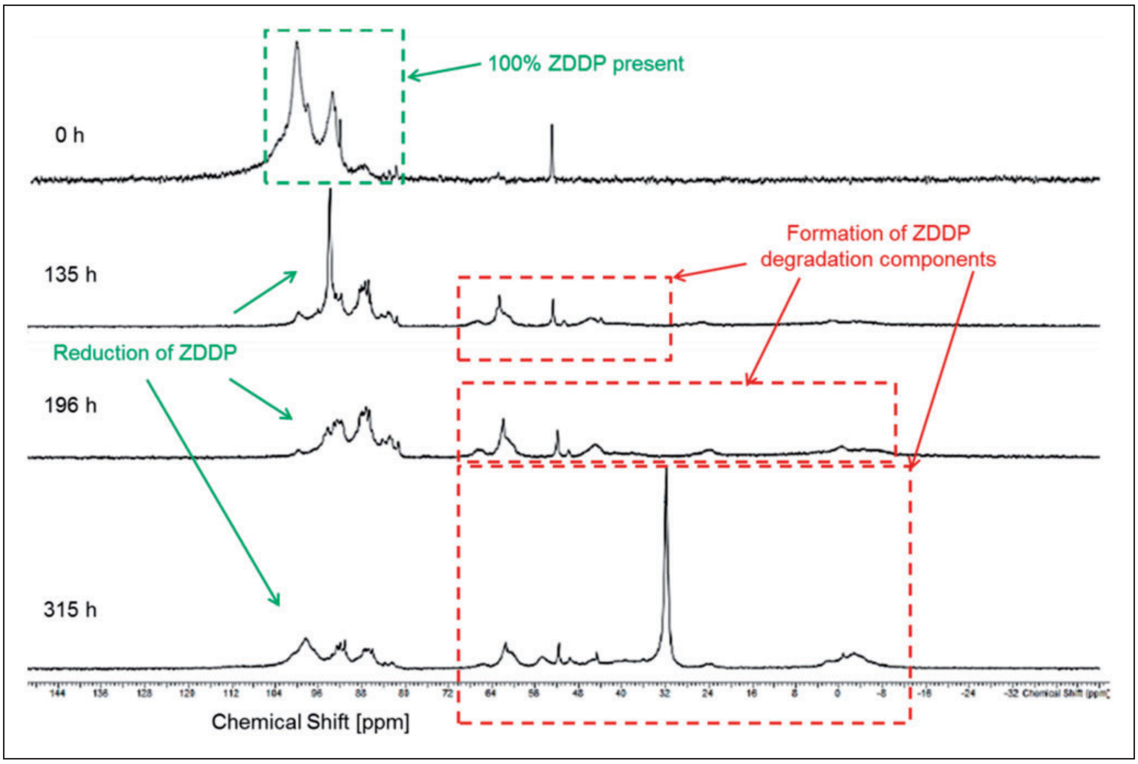

Figure 3. 31-P NMR spectra for fresh and engine-conditioned lubricant samples.

WLI spectroscopy. Measurements of the wear scar profiles in the direction of the piston ring (or piston) sliding motion were made at lower magnification using the stitch application of software Metropro version 8.3.3. The results of the wear analysis of actual cylinder liner are discussed in the Wear analysis of cylinder liner section.

Results and discussion

NMR analysis

Figure 3 shows the 31-P NMR spectra of four lubricant samples including 0 h, 135 h, 196 h and 315 h. Each lubricant sample contained ZDDP anti-wear additive. The fresh oil (0 h) contains the highest concentration of ZDDP additive in its most effective form which can provide maximum protection against the wear of engine components. The used oil (315 h) contains the least concentration of effective ZDDP additive due to lubricant degradation within the marine engine over several duty cycles in its 315 h service life. The other two oil samples, 135 h and 196 h, contain intermediate level of ZDDP additive.

Results show that the spectrum peak noted between 80 and 100 ppm (as shown along the horizontal axis in Figure 3) for fresh oil (0 h) relates to the presence of effective ZDDP in its new form. However, lubricant usage within the lifeboat engine leads to breakdown of ZDDP molecules and hence its chemistry changes. This is clearly reflective from the reduction in the peak height and formation of new peaks on the right-hand side of x-axis in case of engine-conditioned lubricants. The presence of multiple peaks along the x-axis of the 31-P NMR spectrum indicates that phosphorus is present in several different chemical environments.[3] Comparison of the NMR spectra shows the trend of depletion of ZDDP additive as a function of lubricant duty cycle in engine. Under normal engine running conditions, ZDDP in engine oil decomposes due to oxidation. This process converts P–S compounds into P–O compounds such that a shift in the chemical state is noted on the x-axis of the spectra.[3]

Analytical Ferrography analysis

Analytical Ferrography was performed on three engine-conditioned lubricant samples each of which was near the end of its service life. Figure 4(b) to (d) shows the micrograph of wear debris from the samples 270 h, 280 h and 300 h, respectively, whereas, Figure 4(a) shows the micrograph of fresh lubricant (0 h).

The microscopic analysis revealed that a vast amount of ferrous rubbing wear particles, mostly smaller than 5 μm in diameter, were present in the oil samples. In addition, a variety of different types of ferrous wear particles, including severe sliding, abrasive wear, fatigue chunks and flakes with maximum diameters of 15, 10, 15 and 20 μm, respectively, were also present. Heat treatment at the temperature range of 330 °C showed a 60/40 ratio in medium/low alloy steel composition in lubricant sample shown in Figure 4(c).

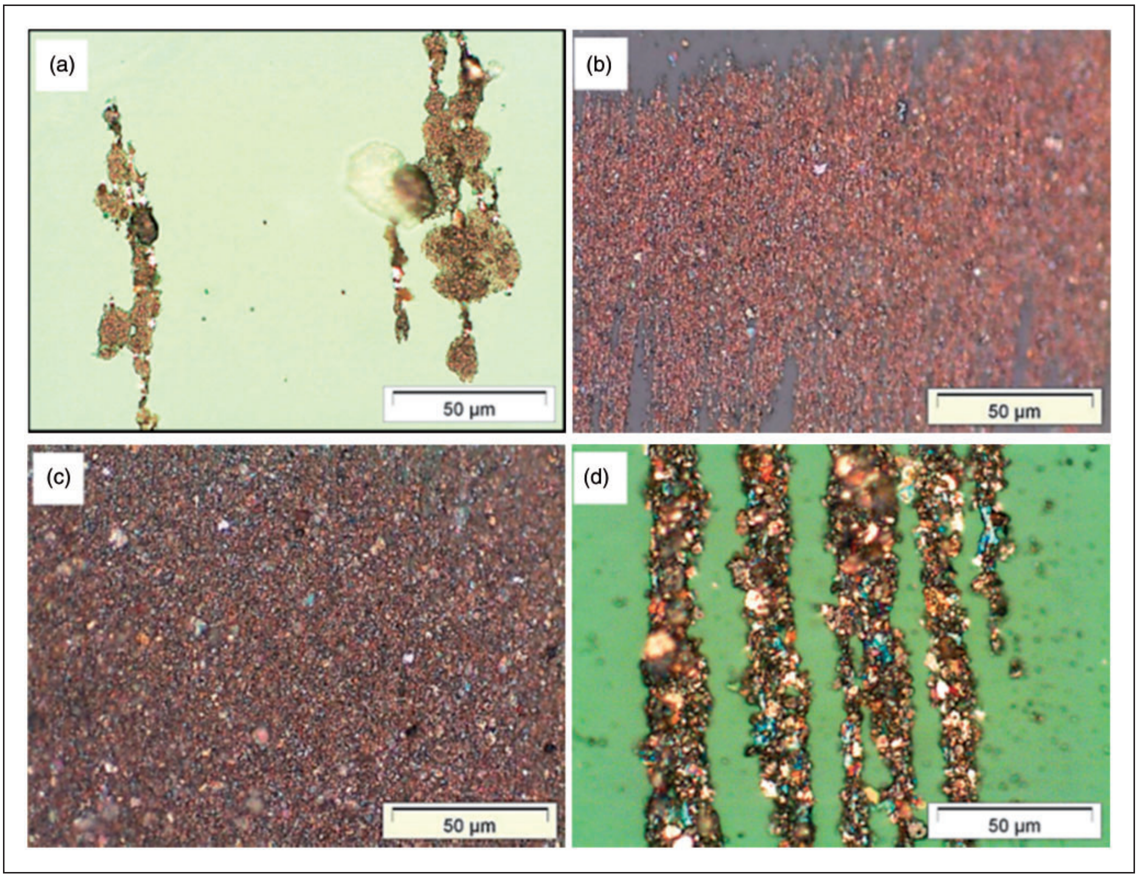

Figure 4. Analytical Ferrography micrographs of engine-conditioned lubricant samples.

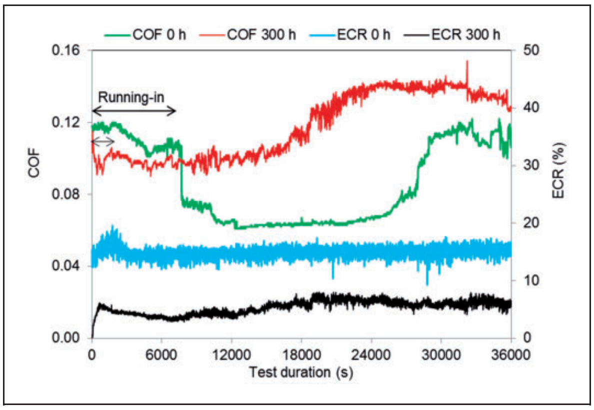

Figure 5. COF and ECR curves for fresh (0 h) and engine-aged (300 h) lubricants.

A high level of dark ferrous oxides (rust) was noticed along with traces of oxidised non-ferrous rubbing wear. Also contamination particles including predominantly fine crystalline and carbonaceous material were also observed.

Tribological analysis

Figure 5 shows the friction coefficient (COF) and ECR results against the test duration. Fresh lubricant (0 h) showed longer running-in period ($\sim$ 7700 s) after which COF stabilised until 24,000 s and then rises again. Engine-conditioned lubricant (300 h) showed much shorter running-in period possibly due to the presence of wear debris generated as a result of its engine service prior to tribotest. The debris resulted in high wear rate at very initial stages and then the wear rate stabilised; however, the friction is erratic due to presence of wear debris. The increase in COF for both lubricants after a certain period of stabilised stage, 24,000 s and 15,000 s in case of fresh and engine-conditioned oil, respectively, was also noted. ECR curves show a similar behaviour to their friction counterparts. The curves indicate that a much thicker boundary film was formed by the fresh lubricant (0 h) than by the engine-conditioned lubricant (300 h).

Figure 6(a) and (b) shows the presence of embedded metal debris on the worn area on the plate test samples for fresh and engine-conditioned lubricants. The number of embedded debris was less in case of fresh lubricant and also worn surface was covered in a uniformly spread dark lubricant layer which suggest formation of boundary film by lubricant additives. The worn surface of plate sample from the engine-conditioned lubricant has relatively large number of metal debris embossed on its worn surface. The part of debris was generated during the tribotest and some were already present in the lubricant prior to the tribotest. These wear debris resulted in the plastic deformation of both the cylinder and plate sliding surfaces, as shown in Figure 7. Figure 7(c) and (f)

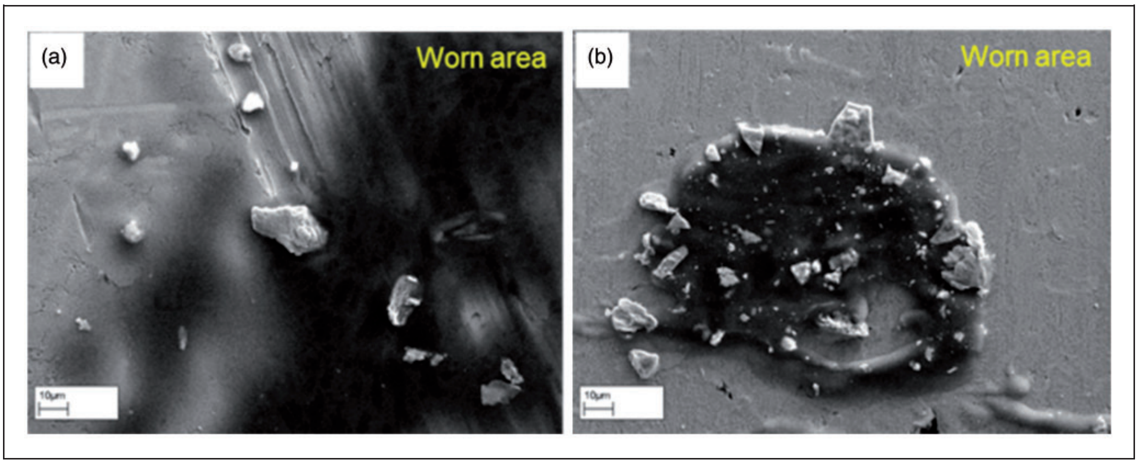

Figure 6. SEM images (at 2000×) of plate samples after test (a) with fresh lubricant 0 h and (b) with engine-conditioned lubricant 300 h.

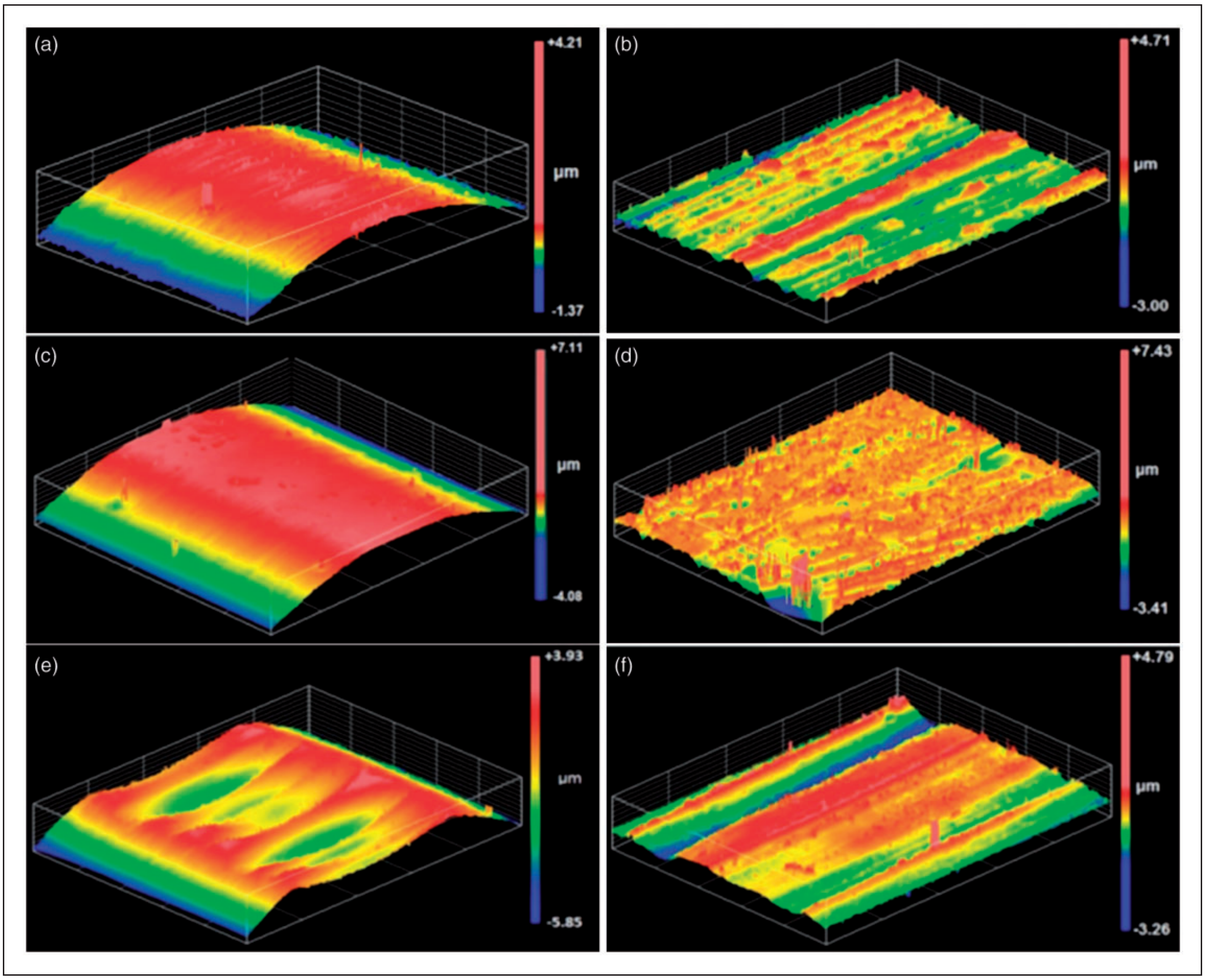

Figure 7. 3D WLI images of cylinder and plate (a and d) before test, (b and e) after test with fresh lubricant 0 h, and (c and f) after test with engine-conditioned lubricant 300 h, respectively. Scale on the right side shows surface roughness distribution.

shows much deeper and wider ploughing grooves mainly on the cylinder and also some on the plate due to 2-body and/or 3-body abrasion wear mechanisms caused by wear debris in engine-condition oil. Such a phenomenon was almost negligible in case of fresh oil, refer to Figure 7(b) and (e), potentially due to the presence of boundary film.

The above observations were further confirmed by EDX analysis of the surface of the worn regions both in fresh and engine-conditioned lubricant cases.

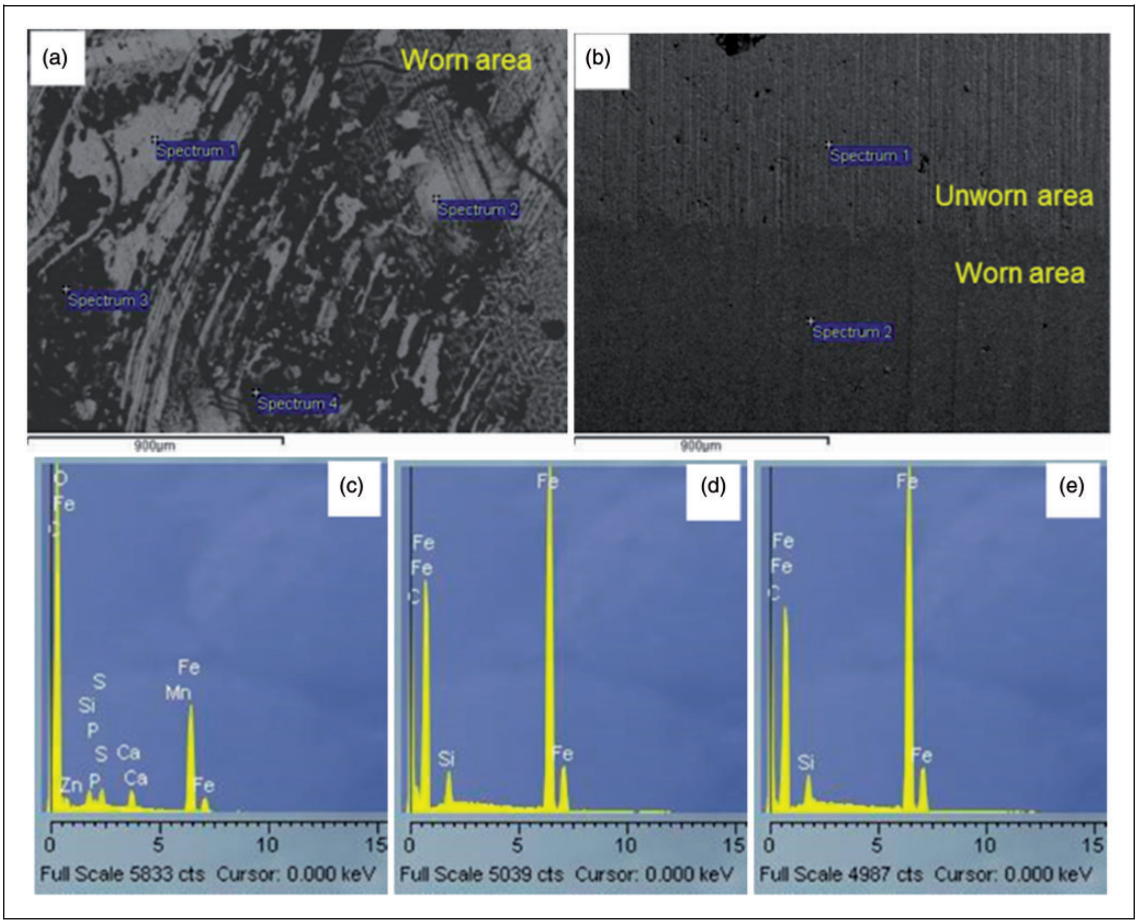

Figure 8. EDX analysis (at 200×) of plate sample with (a) fresh oil (0 h) and (b) engine-conditioned oil (300 h). Spectrum at point 3 in (a) is shown in (c), whereas spectrum at points 1 and 2 in (b) is shown in (d) and (e), respectively.

Figure 8(a) shows the worn area tested with fresh oil (0 h) along with the EDX spectrum taken at point 3 as shown in Figure 8(c). Clearly the spectrum shows the presence of elements such as Zn, P, S and Ca which are commonly known to be part of ZDDP antiwear additive and calcium-based detergent additive.[15] On other hand, Figure 8(e) shows the spectrum of worn area (see Figure 8(b)) tested with engine-conditioned oil (300 h). Clearly in this case, the above elements of additive package are missing. In addition, the later spectrum is similar to the one shown in Figure 8(d), which is taken at unworn area (see Figure 8(b)). Therefore, these observations suggest that due to depleted content of additives in engine-conditioned oil (300 h), an effective boundary film could not be formed for the complete test duration and hence the wear was highest in this case, unlike fresh oil (0 h).

Wear analysis of cylinder liner

The abbreviations used in Figure 9, i.e. first RR, second RR and ORR refer to first compression ring reversal, second compression ring reversal and oil ring reversal points, respectively. Figure 9 shows the higher amount of wear at the first RR region on the thrust side of the cylinder liner surface at TDC. The wear depths of the surface profile noted at TDC are 3.03 µm at the first RR and 2.01 µm at the second RR which is clearly higher than the depth of the respective surface profiles in MID and BDC locations.

These findings could be attributed to the fact that the combustion gas pressure is at its maximum in the TDC region for every alternate cycle (power stroke) in a four-stroke engine. The combustion gas pressure acting behind the piston rings pushes them radially towards the liner surface. This contact pressure at ring–liner interface is a few orders higher that the pre-loaded elastic nature of piston rings which provides them with a tight fit to the liner surface ensuring minimal gas leakage into the crankcase. High wear also takes place in this region due to the reversed tractions experienced by the contacting surfaces near the point of change in direction of the reciprocating sliding motion.[16] In the case of RNLI lifeboats' operations, the marine engines are run at their highest load, and hence the cylinder pressure is high which leads to the intense loading of piston rings against liner surface.

In addition, the extremely high combustion temperature and low piston sliding speed limits the availability of lubricant in this region. Here, the momentary cessation of lubricant entrainment in

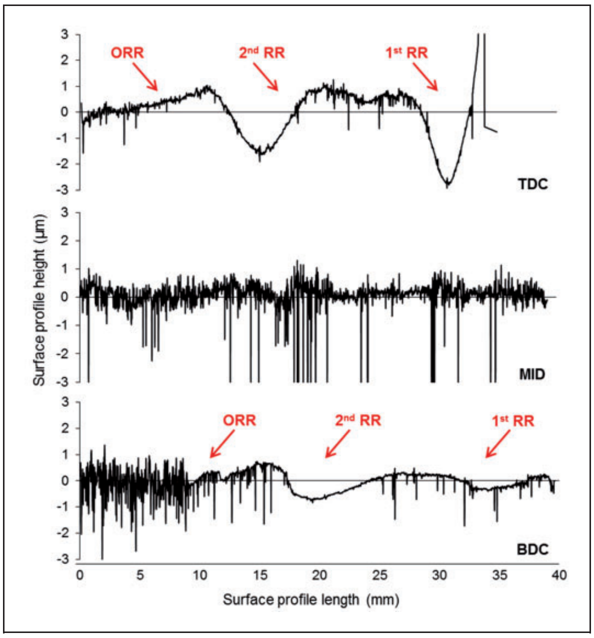

Figure 9. Surface profile of three sections cut from an actual cylinder at TDC, MID and BDC locations of stroke.

ring–liner contact results in asperities interaction since the lubricant is retained in the contact zone either due to squeeze film action or entrapment in the rough contiguous surfaces.[17,18] The boundary lubrication regime exists under such tribological conditions and the protective film forming anti-wear additives present in engine lubricants are responsible for keeping the asperities interaction to a minimum, and hence, controlling the wear rate. Due to the extreme marine engine operating environment, the lubricant degradation results in the depletion of anti-wear additives, therefore leading to accelerated wear of cylinder liners.

Conclusions

An investigation was carried out to understand the mechanisms of the lubricant degradation within the marine engines of RNLI lifeboats, and its effect on the wear of cylinder liners. A variety of oil analysis of engine-conditioned lubricants and wear analysis of an actual cylinder liner were performed. As a result, NMR analysis revealed the depletion of phosphorus containing ZDDP antiwear additives as a function of duty cycles of lubricants within the marine engines. Analytical ferrography showed the generation of small ferrous debris of size range 5–20 μm in the lubricants. Tribological analysis demonstrated the effect of depletion of the ZDDP additives on the tribological and boundary film forming performance of lubricants. Wear analysis of actual cylinder liner showed the extent of wear near the TDC region which leads to impair functionality. These findings are useful to understand the lubricant degradation mechanisms and plan the lubricant change as part of engine maintenance strategies.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

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