From fresh cylinder lubricant to drain oil – an evaluation of its performance profile *

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Drain oils in 2-stroke marine engines are receiving a lot of attention as they are expected to become a major contributor to optimise cylinder unit operation or define their predictive maintenance. Given the complexity of drain oil analysis and adequate interpretation, the objective of this study is to simulate and understand the transformation of Marine Cylinder Lubricant from “fresh oil” to “drain oil” during the engine running. It is also to establish a performance profile along the liner wall of the lubricant in use, in terms of thermal stability, neutralisation capacity and protection from abrasive and corrosive wear.

Two different mechanistic approaches are proposed to describe the transformation process, combining neutralisation with oxidation reactions. Validation of the test conditions is done through comparative testing of proven formulations of MCL, and simulation of drain oils sampled in the field.

The study finally proposes a preferred mechanism. This will allow to further optimise formulations of Marine Cylinder Lubricants to the actual and future engine demands.

1 Introduction

The market demand for more power per cylinder and the advent of the electronic engine have led to an increase in engine efficiency and flexibility. This gives rise to a very wide range of potential operating conditions, increasing the demands on the Marine Cylinder Lubricant (MCL) with respect to service temperature and pressure.

At the same time, the drive to optimise operating costs by cutting lubricant feed rates is pushing the built-in safety margin level of the lubricants even further. Finally, recent IMO regulations on the sulphur content of bunker fuel will lead to ships burning bunker fuel of varying sulphur contents and of extremely variable quality. These changes require an in-depth understanding of the interactions between engine operating conditions, type of bunker fuel and the mechanisms by which the cylinder lubricant protects the engine.

The conventional route to generate this in-depth understanding is the monitoring of engines in service and specifically sample and analyse on- or off-line drain oils. This route is progressed as the number of drain oil samples and the experience accumulate.

A complementary, more rapid and flexible route was designed so as to simulate in the laboratory the drain oils, that would have an equivalent constitution and macro-properties to that of drain oil sampled in service. Once the degradation mechanisms would be understood, the underlying objective was to be able to monitor the transformation of MCL along its flow down the liner wall and its degradation into drain oil and to establish a performance profile of the lubricant in use, in terms of thermal stability, neutralisation capacity, and protection from abrasive and corrosive wear.

2 The function of a cylinder lubricant

As with most engine oils, marine cylinder lubricants (MCL) used in 2-stroke marine engines have many functions. First among them is the neutralisation of acids. Sulphur in the fuel reacts with oxygen on combustion to form SO₂ gas. Although most of these gases go into the exhaust, some of them come into contact with water vapour, also formed on combustion or introduced with the inlet air, giving products that can produce sulphuric acid (H₂SO₄). This sulphuric acid vapour condenses and becomes liquid and very corrosive if it drops below a temperature referred to as the dew point. To avoid corrosive wear, this acid must be neutralised. This is the role of the basic or over-based detergent additives contained in the oil.

The neutralisation capacity of a lubricant, expressed as Base Number (BN in mgKOH/g oil) can vary considerably depending on the over-based additives content.
The quantity of acid that can be generated will depend on various parameters, including the engine design and operating window. It varies also with the liner wall temperature as well as with the sulphur content in fuel, the consumption of fuel and the rating of the engine. A minimum value of the BN is necessary: if the BN decreases below this value, the protection against corrosive wear will be not sufficient, and wear of liners and rings will occur. Yet, if the BN is too high or the lubricant feed rate (LOFR) is too high, there is an excess of CaCO₃. This excess can contribute to a higher quantity of deposit (precursors), thereby leading to the risk of wear. There is therefore a balance between the BN reserve required to combat corrosive wear and the lubricant feed rate necessary to avoid abrasive or adhesive wear.

3 In service performance of cylinder lubricant

Adequate formulation of cylinder lubricant requires a proper balance between detergency, thermal stability, resistance to oxidation and resistance to wear. The accepted BN level for MCL is BN70 for today’s bunker fuel qualities and engine operating conditions. But, in addition to having the right BN level, it is necessary to have the correct BN efficiency - the speed at which neutralising species can diffuse in the oil film and contact harmful acidic molecules before these can attack the surface. This BN efficiency has been extensively studied in previous works 1,2,3, in which TOTAL introduced the NAMO (Neutralisation Ability of Marine Oils) testing procedure that allows measurement of the speed at which CaCO₃ reacts with the acid species formed during combustion.

Given continued pressure to cut cylinder lubricant feed rates, a number of service trials are being monitored to gather significant sets of relevant data and their initial results were presented in an earlier paper ⁵. With all these service trials, extensive sampling of the drain oil was carried out with off-line analysis, where extra attention was given to the measured values of BN and Fe content. The data and preliminary conclusions presented in the earlier paper ⁵ highlighted the many issues linked with the analysis of drain oil. As the service trials continue, more drain oil analysis data are collected and the following comments can be made.

3.1 Ingress of system oil in the scavenging air trunk

Contamination of the MCL by the system oil can be important, with measured rates as high as 70%. This introduces a major flaw in the overall mass balance and requires re-calculation of the analysis of the drain oil especially in terms of the BN level.

3.2 Drain oil inter-cylinder contamination

We have strong indications that drain oil inter-cylinder contamination can occur depending on the specific engine design. This phenomenon can take place within the scavenging air trunk in which drain oil droplets fall down from the bottom part of the liner and can be entrained as a mist due to the high air flow present in this engine area. Depending on specific engine design, mixing of the mist originating from adjacent cylinder units is feasible and results in what is called drain oil inter-cylinder contamination. When occurring this can impact the relevance of the drain oil analysis as a monitoring tool of the specific cylinder unit. We experienced in several cases that the drain oil Fe constant is constant across the engine cylinders, independently of the actual operation of each of the cylinders.

3.3 Drain oil flow

Flow of drain oil can vary considerably depending on the cleanliness of the draining pipe. This can influence drain oil analysis, depending on the volume collected. It is therefore advisable to calculate contaminants such as Fe in absolute units such as g/day rather than in ppmw.

4 Simulation of drain oil in the laboratory

Given the previous debate, analysis of actual drain oil and its interpretation require utmost attention to be able to properly monitor the cylinder operation and condition. It is however the only tracer of such in situ performance. A better understanding of the mechanisms by which fresh MCL is degraded into drain oil is required to subsequently define ways in which the lubricant formulation can be optimised with the cylinder operation. These mechanisms will in turn generate the knowledge of the performance profile of the lubricant in use in terms of thermal stability, detergency, neutralisation capacity and wear protection.

The knowledge of this performance profile requires large amounts of drain oils, preferably having a known history and covering a wide range of physico-chemical characteristics. Such samples would require the availability of dedicated engines operating under pre-defined and most probably extreme operating conditions. The unavailability of such a facility motivated the move to use laboratory-made
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A prerequisite is to ascertain the equivalence of such oils with actual drain oils collected in service. As no laboratory test is yet able to simulate the full array of operating conditions present in an operating cylinder unit, our scope was limited in simulating the lubricant part of drain oils, excluding wear elements such as Fe and elements or species originating from the combustion of fuel.

Given the previous restrictions, a basic hypothesis was made that degradation of fresh MCL to drain oil involves the following main reactions:

- Oxidation and thermal degradation of the hydrocarbons. This reaction can be monitored through the evolution of the lubricant colour and viscosity.
- Neutralisation reaction between the overbased detergents and the mineral acids produced during the fuel combustion. This reaction consumes CaCO₃ and produces calcium sulphate.

4.1 Ageing of the lubricant through oxidation

Numerous ageing or oxidation procedures are known, such as standardised bulk oxidation tests (IP48, ICOT, etc) or other tests (Panel Coker (PCT), Elf Cokefaction Bench test (ECBT)). All these testing procedures have been utilised for many years and are recognised to properly simulate the ageing of a lubricant in an engine when considering high temperature and high pressure conditions.

In this work, a specific testing procedure using the ECBT was applied. This equipment was originally developed in the 1960's to be representative of the environment to which engine lubricants, especially marine cylinder lubricants, are submitted in engine cylinder units. In this test, 400ml of lubricant under test is vigorously mixed and splashed by a rotating brush onto the underside of an Aluminium beaker heated at 613K (340°C). The splashed lubricant slowly drips down the heated plate back into the bulk. Varnishes and deposits can be formed on the heated surface depending on the thermal stability and detergency of the lubricant. The properties of the bulk of the lubricant also slowly degrade, simulating what normally occurs in a crankcase.

4.2 Neutralisation of acidic species by the overbased detergents

Laboratory simulation of this reaction is usually performed by reaction of the lubricant with concentrated sulphuric acid, to a pre-defined resulting BN level. As the reaction proceeds, water and CO₂ are produced and CaCO₃ is transformed into CaSO₄. Though the general chemical reaction is fully accepted as that occurring into a cylinder unit, reaction of CaCO₃ into CaSO₄ can lead to various intermediate or final products, for example different crystallographic forms of CaSO₄ can be produced. The actual status of CaCO₃ or CaSO₄ in the cylinder liner can influence macroscopic performance aspects such as liner wear, thus a mandatory step was to ensure that equivalent forms of CaSO₄ and CaCO₃ are present in drain oil sampled in service and synthetic drain oil manufactured in the laboratory.

As can be seen in Table 1, a series of drain oil samples generated in service from 2-stroke engines lubricated with TALUSIA HR70 of TOTAL Lubmarine were analysed using electronic Transmission Electron Microscopy (TEM) coupled with X-ray microanalysis Diffraction (XRD). These measurements were carried out at the LTDS (Laboratoire de Tribologie et Dynamique des Systèmes) at the Ecole Centrale de Lyon (France), under the direction of Prof. JM Martin. After centrifuge and dialysis, all of these samples
exhibit CaSO₄ that is produced during the neutralisation of acidic species by the over-based detergents. Several forms of CaSO₄ are present in the various samples with the most common being the anhydrous γ-CaSO₄. Quantitative measurement of particle size was also performed indicative of an average size of γ-CaSO₄ of between 20 and 50 nm, independent of the origin of the sample.

Table 1: Microscopic comparison of service and lab-simulated drain oils *(published with kind permission of Prof JM Martin of LTPS, Ecole Centrale de Lyon, France)*

<table>
<thead>
<tr>
<th>Sample origin</th>
<th>BN of drain oil</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Forms present</td>
</tr>
<tr>
<td>service</td>
<td>5 - 65</td>
<td>*</td>
</tr>
<tr>
<td>laboratory</td>
<td>5 - 60</td>
<td>*</td>
</tr>
</tbody>
</table>

The conclusion is that neutralisation carried out in the laboratory is adequate to simulate phenomenon occurring during cylinder operation.

5 Performance profile of drain oil

Several mechanistic approaches can be taken when predicting the transformation path followed by MCL when degrading along the cylinder liner:

- Severe thermal degradation and oxidation in the top part of the liner occurs during and immediately after the fuel combustion. This is followed by progressive neutralisation of the acidic species that migrate into the oil film.
- Complete combustion of part of the MCL in the combustion space accompanied by gaseification of the products. The remaining part of the lubricant rapidly neutralises the formed mineral acids before draining down the liner and progressively degrades through oxidation.

It is expected that either of the 2 previous mechanistic approaches is preferably occurring and its identification will allow to simulate the performance profile of partially degraded MCL at various locations along the liner wall.

5.1 Experimental approach

Samples of TALUSIA HR70 were submitted to the ageing procedures depicted in Fig. 2.
load is applied by a pneumatic jack and the wear measured on-line by a gap sensor. Several preliminary tests were necessary to define the final operating conditions characterized by a final load of 5000 N applied for 60 minutes.

Other tribometer arrangements were used in the study, such as the Tokyo University of Marine Science and Technology (TUMSAT) 3 pin-on-disc machine. This machine belongs to the laboratory of Prof. Shima and has been adapted to the specific conditions of this study.

This apparatus provides a continuous motion in oil bath between a rotating disc specimen (Tarkalloy) and three stationary pin specimens (Uballoy).

A range of temperatures above 523K (250°C) is required to fully fit to actual engines condition, and in order to minimize base oil viscosity effects.

Moreover, the localized pressure between actual engines’ ring and liner is estimated to be between 30 and 80 MPa. The loads used for this wear test will be chosen to correspond to this pressure range, as a 100 MPa contact pressure is possible. The maximum allowable speed of the machine is 1 m/s.

The wear evaluation is achieved by the measurement of the wear scar diameter on the disc and the measurement of the pins dimension before and after test completion.

5.2 Results and discussion

5.2.1 Pre-neutralised MCL

Various MCL formulations were neutralised with increasing acid content equivalent to the following BN losses: -10 points, -30 points, -50 points and -65 points. The corresponding BN are 60, 40, 20 and 5 mgKOH/g. With a given BN decrease (Fig. 3), viscosity is usually slightly decreasing - except for one formulation - and these data were utilized as reference material in the later stages.

Fig. 3: Viscosity variation after pre-neutralisation

Thermal stability measured in the ECBT-varnish procedures reported in Fig. 4. Applied temperature ranges differ with sample and expected performance level. Neutralisation deteriorates thermal stability as measured in this test.

Fig. 4: Thermal stability of pre-neutralised MCL

TALUSIA HR70 was submitted, after pre-neutralisation to 3 p-o-d tests and the results are exhibited in Fig. 5. The merit rating is generated by image analysis of the underside of the heated beaker: values can be between 0 (dark surface and poor performance) and 100 (clean surface and excellent performance). Under these conditions, wear resistance remains until the most severe neutralisation is applied.

Fig. 5: 3 p-o-d wear measured for pre-neutralised MCL

5.2.2 Pre-oxidised MCL

Various formulations of MCL were submitted to the ECBT at 613K (340°C) ageing procedure. As the test duration is a controlling parameter, its effect on the lubricant viscosity and BN is depicted in Fig. 6.

Fig. 6: Viscosity at 40°C
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5.3 Simulation of drain oil

From the above previous sections, both the pre-neutralised and pre-oxidised MCL exhibit deteriorated thermal stability as usually measured with drain oil samples taken from service. Their protection against abrasive wear is maintained until almost all BN reserve is depleted. Detergency reserve is differentiated as pre-neutralised lubricants tend to have an improved detergency level whereas pre-oxidised samples do not exhibit a significant change in detergency when compared with the fresh lubricant.

Several drain oil samples obtained from actual engines lubricated with TALUSIA HR70 were selected to act as reference products. Such samples have BN ranging from 20 down to 5 mgKOH/g and viscosities ranging from 350 to 500 mm²/s.

Two different mechanistic approaches were considered to describe the transformation process, combining neutralisation with oxidation reactions, as depicted in Fig. 2.

5.3.1 Pre-neutralisation followed by oxidative degradation

A TALUSIA HR70 formulation was pre-neutralized to a given BN level, followed by oxidation in the ECBT ageing procedure till a viscosity of around 400 mm²/s. Given that the oxidation procedure generates a BN loss of approximately 20 points, the intermediate BN level was fixed at 40 mgKOH/g.

The thermal stability of the lab-simulated drain oil is not as degraded as that obtained with the service drain oil. Together with the detergency that is similar to that of the fresh lubricant whereas that of the service drain oil is much improved, this mechanism does not appear to properly reflect the performance profile typical of service drain oil.

5.3.2 Pre-oxidation followed by neutralisation

A TALUSIA HR70 formulation was pre-oxidised in the ECBT ageing procedure, followed by neutralisation to a level of 20 and 5 mgKOH/g. When performing neutralisation on a pre-oxidised lubricant, the resulting viscosity increase was much larger than anticipated. In order to meet final viscosity target a much weaker oxidation procedure is necessary.

After relaxation of the pre-oxidation step, adequate final combinations of viscosity and BN were obtained, that properly simulate that of service drain oil.

All measured performance levels of lab-simulated drain oils is in line with those on service drain oils, with a degraded thermal stability, improved detergency/fuel compatibility.
From fresh cylinder lubricant to drain oil - an evaluation of its performance profile and little effect on wear.

From the above, a mechanism in which a weak pre-oxidation is followed by neutralization can simulate actual degradation of fresh MCL into drain oil.

6 Conclusions and perspectives

Building onto the past knowledge gained with the monitoring of drain oils sampled from several engines, service sampling was continued with special attention given to the measured values of BN and Fe. The data reported in the present work confirm that several key factors have to be taken into account:

- Correction of the measured BN to compensate for the System Cliff present in the scavenging air trunk.
- Reporting of Fe in mg/day rather than ppmw to compensate for the strong variations in drain oil flow.
- Extra attention be given to indications we have for drain oil inter-cylinder contamination.

The subsequent laboratory study was successful to simulate drain oil by controlled degradation procedures so that the mechanism for transformation of MCL into drain oil is better understood.

- A laboratory method has been developed that simulates partial neutralisation of a cylinder lubricant by sulphuric acid. The resulting pre-neutralised lubricants have a similar microscopic profile to actual drain oils sampled in service. Such pre-neutralised lubricants have a maintained resistance to wear, when compared with the fresh lubricant.
- Another ageing method was developed to simulate oxidation occurring in the cylinder unit. Thermal stability of such aged lubricants is strongly deteriorated but resistance to wear is maintained.

The association of the two previous degradation reactions was studied in order to simulate the degradation mechanism of fresh MCL into drain oil sampled in service. The better candidate mechanism is a pre-oxidation followed by neutralisation. Further work is in progress to fully validate this preferred mechanism.

A proper simulation of the transformation of fresh MCL into drain oil will then be used to assess which formulation tools can be applied to optimize cylinder operation, also in the context of the intelligent lubrication concept.

References


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