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2025 | 222

Engine Oil Formulations with Improved Cleanliness for New-Generation Two-Stroke Marine Engines

Lubricants

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ABSTRACT

Engine lubrication is an indispensable part of any Internal Combustion engine. A lubricant not only protects engine hardware from metal-metal friction-related damage, but it also keeps the engine clean from deposits and maintains its ‘good properties’ throughout the service life. The ever-evolving engine hardware & technologies targeting better performance and efficiency, often pushed by environmental regulations possesses the requirement for the development of compatible engine oils to meet specific lubrication demand.

Two-stroke Marine diesel engines, which power most of the transportation ships, require two type of lubricants- cylinder oil & system oil. Marine engines historically have been using residual fuels with high sulfur-content and burning of such fuels produce corrosive acids, SOx and forms heavy deposit. High BN (base number) marine diesel cylinder lubricants (MDCL) are used in such application to effectively neutralize acids and keep the engine components clean.

IMO 2020, which has capped sulfur-content in marine fuels below 0.5%, has triggered discussion on the use of high BN MDCL is with low-sulfur fuels. Especially, the use of high BN (70 BN and higher) MDCL with low Sulphur fuels is considered to be of high risk, mainly arises due to the accumulation of unused oil additives, which may result in excessive deposits formation led to high wear. Considering this, use of a lower BN oil would be a straightforward solution. However, modern two-stroke marine engines are designed to extract higher efficiency, and many of them operate at high BMEP. These engines possess excessive stress on the engine oil- resulting in oil degradation and deposit formation.

To lubricate modern two-stroke marine engines, a lower base number (40 BN) oil with uncompromised detergency level can be envisioned by the lubricant formulators. MAN ES, one of the leading manufacturers of two-stroke marine engines has introduced a superior Category II MDCLs for their new-generation MARK 9 and above engines, is also in line with this approach.

Indian Oil is the largest Oil & Petrochemicals company in India, has been marketing indigenous marine lubricant grades. The present study describes the development of 40 BN MDCL formulations, designed to show excellent cleanliness property equivalent to a commercial 100 BN MDCL. The newly formulated oils were characterized, and their performances and tribological properties were evaluated by a series of laboratory instruments. The detergency tests include- Panel Coker, TEOST and KHT instruments were performed, often by using optmized test conditions to differentiate the candidate blends. Thermo-oxidation property of the oils was also studied by PDSC. The comparative study revealed that the newly formulated 40 BN oils possess equivalent or superior cleanliness property than a commercialized 100 BN MDCL and a MAN ES-approved CAT II 40 BN reference oil. The newly formulated oils show great potential to be used as cylinder oil for new-generation two-stroke marine engines running on low-sulfur fuels.

1 INTRODUCTION

Maritime transport is the backbone of the global economy and supply chain, responsible for more than 80% of world trade by volume and is the cheapest mode of transportation of goods. Large cargo ships are mostly powered by two-stroke crosshead engines largely burning High Sulfur Fuel Oil (HSFO) till recent time emitting harmful SOx gases in the environment. In presence of water SOx forms sulfuric acid which can corrode the engine parts which is a serious concern especially during slow steaming, and the phenomenon is also known as cold corrosion.

The implementation of IMO 2020 (effective from 1st January 2020) targeting to curb SOx emission has capped Sulfur content in marine fuels at 0.5 % m/m maximum from the earlier limit of 3.5 % m/m. This scenario has led the ship operators to select one of the two options- either to go for costlier Very Low Sulfur Fuel Oil (VLFSO, Sulfur content 0.5 % m/m maximum) or installation of scrubber technology (exhaust gas cleaning system) to limit maximum equivalent emission output as VLSFO and continuing burning the HSFO.

To meet IMO 2020 sulfur cap fuel marketers are blending low sulfur paraffinic refinery streams with HSFO. Compatibility between such bunker fuels from different sources and the difference in their combustion characteristics are the concerns that worries the ship operators. HSFO, which contains more aromatic molecules including asphaltenes when blended with paraffinic refinery stream poses serious threat to asphaltene stability. Moreover, the presence of cat fines in the hydrotreated low sulfur fuels may adversely affect engine components through abrasive wear.

Two-stroke crosshead marine engines are lubricated with Marine Diesel Cylinder Lubricants (MDCL) and system oils. The upper part of the engine consists of the combustion chamber where the piston and cylinder are lubricated by MDCL via a total loss lubrication system where the oil gets burnt or disposed of after each combustion cycle. The lower crankcase is lubricated by system oil. MDCLs play critical roles in the operation of a marine engine via reducing friction, preventing corrosion, cleaning, neutralizing acids, providing a gas tight seal, keeping components free from deposits.

While majority of the MDCLs are of SAE 50 viscosity grade, they are available at various base numbers (BN), including- 17, 25, 40, 70, 100 & 140. BN is the measure of alkaline reserved in a lubricating oil and a measure of its acid neutralisation ability. Higher the BN, higher is the acid neutralization ability. Conventionally, BN is the most important parameter for MDCLs used in an engine burning HSFO. Depending upon the fuel sulfur content, MDCL with an adequate BN is used at an optimized feed rate. While the use of too little BN oil may not provide efficient engine protection against corrosion and sludge formation, too high BN oil also may lead to the formation of excessive abrasive deposits on the piston crown top lands and cause cylinder liner wear and scuffing.

The implementation of IMO 2020 has large consequences on MDCL formulations [1]. While ships installed with scrubber technology continue to burn HSFO need not to change MDCL, marine engines that have shifted to VLSFO, the scenario is complicated. Traditionally, high BN MDCL were being used in two-stroke marine main engines burning HSFO where high alkaline reserve was suitable to neutralise large quantities of sulfur-containing acidic combustion byproducts. In Emission Control Areas (ECA), the already existing regulation of maximum 0.1 % m/m of sulfur in marine fuel made the ship operators shift to lower BN (17 - 25) MDCLs.

Modern marine two-stroke engines for ship propulsion are being designed for their high power-to-weight ratio, low fuel consumption, and excellent economy. Lubrication of such engines encounter challenges due to higher cylinder pressures, longer strokes, and lower engine speeds. In addition, slow streaming, which gives a lot of fuel saving and environmental benefit may also increase the risk of cold corrosion.

In the post IMO 2020 scenario, MDCLs need to be formulated to tackle many new challenges. Now, the cylinder lubricant is not required to have very high BN, like in the case with HSFO. However, it must retain its cleanliness ability as modern marine engines may face deposit issues arising due to asphaltene instability and thermal degradation of the oil. In alignment of such requirements, MAN ES - World's major two-stroke marine engine OEM has introduced a new category for MDCLs called- CAT II, to define the lubricant requirement for their new generation two-stroke marine engines [2]. This category of MDCLs requires overall superior performance with special focus on the engine cleanliness [3-4], while listing the conventional MDCLs under CAT I category.

As overbased detergents contribute to both BN and cleanliness of the fully formulated lubricating oil, merely reducing the detergent quantity to formulate a low BN MDCL would compromise with the oil's cleanliness property [5]. Hence a completely new formulation strategy is to be adapted for the development of new generation MDCLs.

The present study describes the development of 40 BN MDCL formulations, designed to show excellent cleanliness properties which is compared to a commercial 100 BN MDCL. The newly formulated oils were evaluated against appropriate industry reference oils by a series of laboratory instruments. For detergency, Panel Coker and Komatsu Hot Tube (KHT) tests were extensively performed, often by using optimized test conditions to differentiate the candidate blends. Thermo-oxidation property of the oils was also studied by the Pressure Differential Scanning Calorimeter (PDSC). One of the candidate blends was also evaluated by CAT-1M-PC bench test resulting in excellent end-of-test piston cleanliness.

2. DEVELOPMENT STRATEGY FOR NEW-GENERATION 40 BN MDCL

MDCLs, like any other engine lubricant are formulated by judicious combination of various additive components with appropriate base stocks, and each component impart on or enhance specific performance characteristics of the finished lubricant suitable to cater specific requirements. Often, a specific well-defined mixture of additive components of different chemical types are used to obtain desired performance. Such additive components are categorised under the terms such as- detergents, dispersants, antioxidants, friction modifiers, extreme pressure, anti-wear, corrosion inhibitor etc. For the subject development, various detergent, dispersant and antioxidants were evaluated and many combinations of the selected additive components were integrated in formulations with other essential components.

2.1 Detergents: Detergents fall under the classification of surfactants, consisting of a polar head and lipophilic tail. Detergents are soaps formed by neutralizing an organic acid with the appropriate alkaline earth metal, such as calcium, magnesium, sodium, or barium, which are included in their hydrophilic head. The organic moieties generally contain sulfonate, phenate, salicylate or carboxylate functional groups. Detergents, particularly those with simpler structures, often contain a reserve metal, typically in the form of metal hydroxides or carbonates, with calcium carbonate being the most common. Detergents that contain this reserve are referred to as overbased.

Overbased detergents contribute to two performance parameters- cleanliness, by preventing deposit formation; and acid neutralization (BN). Optimization of the dosage of overbased detergent is the tool to formulate conventional MDCLs of different BNs. To develop a high BN oil such as 100 BN or 140 BN for HSFO application requires a high dosage of overbased detergent which inherently provides a good cleanliness property. However, this tool alone does not deliver well while developing a 40 BN MDCL with a cleanliness property like higher BN oils, suitable for new generation two-stroke marine engines burning VLSFO.

2.2 Dispersants: Dispersants also help to keep an engine clean, however they are chemically different from detergents. Dispersants are comparatively large molecules containing nitrogen or oxygen containing polar groups which can attach soot particles or other polar contaminants while its hydrocarbon tail or backbone helps it to stay soluble in oil. The main function of dispersants is to keep particles of diesel engine soot finely dispersed or suspended in the oil till the oil's lifetime and prevent formation of sludge, varnish and other deposits on critical surfaces. Some examples of dispersants include: Succinimides, Succinic esters, Alkylphenolamine (Mannich bases), and Polymeric dispersants.

Unlike detergents, the use of dispersant is not extensive in MDCLs as they operate under a total loss system. However, its effective combination with detergents appears to be an effective tool for the formulations of new generation MDCLs where cleanliness is the prime objective and only detergent alone is not sufficient to meet the challenge.

2.3 Antioxidants: Oxidation or thermo-oxidation is the major cause of oil degradation. During operation oxygen containing free radicals and peroxides are generated in a high temperature and high-pressure environment. These free radicals attack the lubricant base oil and other additives in it, propagating through chain reaction mechanisms resulting in the formation of polar and acidic byproducts. The presence of water, wear metals, or other contaminants as found in the combustion chamber and in the oil sump also contribute to the oxidation process. This adversely affects the oils property resulting in- viscosity rise, increase of Total Acid Number (TAN), sludge formation and drastically reduces oil’s life.

Antioxidants (AOs) are radical scavengers, most commonly are *N*-substituted aromatic amines and hindered phenols. They get consumed as they perform their role of preventing oxidation by either scavenging oxygenated free radicals or by terminating chain reaction propagation. AOs are an essential component in nearly all crankcase lubricating oils. However, for a total loss lubrication system such as in the case of two-stroke marine cylinder application, where oil gets consumed in each combustion cycle and fresh lubricant is injected, thereby eliminating the requirement of long oil drain interval. Hence, use of antioxidants in the MDCL's formulation was less significant.

For the development of new generation MDCLs, AOs can play a crucial role by preventing sludge and deposit formation. Like any other engine oil formulation, MDCLs also contain many other additives, the above three additives have the most significant impacts on the overall engine cleanliness.

3. FORMULATION STRATEGY, REFERENCE OILS AND CANDIDATE BLENDS

Indian Oil has been marketing its own additive technology based marine lubricants for more than a decade [6]. The first step of the current development of a new generation 40 BN MDCL involved initial selection of detergent, dispersant, antioxidant additives and their respective combinations. Thorough comparative studies of blends containing different options of specific additive types, while keeping the rest of the additive components fixed was conducted (not included in this paper). In the next step candidate blends of 40 BN MDCL were optimized by using the selected additive components in SAE 50 viscosity grade with API Gr I base stocks. It is important to note that all three types of additives (may) contribute to the BN and hence extracting the desired performance by maintaining the BN at 40 is a great challenge.

The candidate blends were studied for their cleanliness property by using laboratory tests. The target cleanliness was set to be the equivalent of a conventional 100 BN commercial MDCL. The candidate blends were modified in a series of blend optimization steps to obtain the desired cleanliness. Comparative test data is discussed for three candidate oils based on different additive combinations against Reference 1, which is a conventional 100 BN MDCL, Reference 2, a conventional 70 BN MDCL along with Reference 3, a new generation 40 BN MDCL industry reference oil. The three candidate oils were developed based on different detergent chemistries, while candidate 1 contains both phenate and sulfonate detergents, rest of the candidates are phenate-free (Table 1). It is noteworthy to mention that phenates are a source of tetrapropenyl phenol (TPP), which has been classified as a reprotoxin and hence phenate-free MDCLs are important to develop [7].

4. LABORATORY TESTING METHODS AND RESULTS

Selection of the appropriate test methods is crucial for the evaluation of MDCL's cleanliness property owing to their very high detergent-content, unlike any other engine oil. Standard test method like Thermo-oxidation Engine Oil Simulation Test (TEOST, measures oil's susceptibility to deposit formation, ASTM D7097) remains ineffective due to formation of insignificant quantity of deposits where differentiation became inconclusive. Importance was given to the customizability of test methods while selecting the laboratory testing instruments. Subsequently the test conditions were optimized to effectively screen the candidate oils and perform a comparative study against the reference oils.

Table 1. Details of MDCLs studied

Oil	City A	BN (mg KOH/gm)
Reference 1	100 BN MDCL	100
Reference 2	70 BN MDCL	70
Reference 3	New Gen 40 BN MDCL, Industry Reference Oil	40
Candidate 1	New Gen 40 BN MDCL	40
Candidate 2	New Gen 40 BN MDCL (Phenate-free)	40
Candidate 3	New Gen 40 BN MDCL ((Phenate-free))	40

4.1 The Komatsu Hot Tube Test: The Komatsu Hot Tube Test (KHT) is a laboratory test designed to measure the formation of lacquer when a lubricant is subjected to high temperatures. Initially developed to predict the impact of lubricants on diesel engine scuffing, it is widely used today to evaluate lubricants for various applications, including motorcycles, power tools, and recreational marine equipment. The KHT is a straightforward, reliable, and cost-effective test. In this test the sample is passed slowly through a heated glass tube at a specified rate (0.31 ml/hr) for 16 hrs (Table 2). The oil forms a thin layer on the inner wall of the glass tube and undergoes thermal degradation resulting in lacquer formation and coloration. At the end of the test the glass tube is washed with hexane and rated against standard rating tubes in a range of 0 - 10, where 0 being poor and 10 being the best. Higher ratings imply better high temperature detergency of the lubricating oil. This test method has the potential to evaluate MDCLs which are formulated to lubricate the piston and cylinder liner of low RPM marine 2-stroke engines.

Although KHT tests can be performed within a broad range of temperatures, the tests conducted below 310 ºC yielded the highest rating 10 for all candidate blends. Again, tests above 330 ºC for the same oils resulted in complete blackening of the test tubes (hence rated 0). For the purpose of differentiating the candidate oils, KHT tests were done at four different temperatures- 310 ºC, 320 ºC, 325 ºC and 330 ºC to unanimously compare the candidates and the reference oils.

Table 2. KHT test condition.

Variables	Value
Test temperature	310 ºC/ 320 ºC/ 325 ºC/ 330 ºC
Oil injection rate	0.31 ml/hour
Duration	16 hours
Air flow rate	10 ml/min

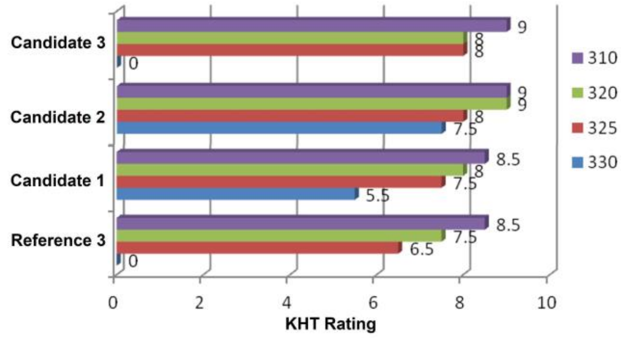

Figure 1. KHT ratings of the Candidate oils & the Reference 3 tested at various temperatures.

Figure 1 shows the comparative KHT ratings of candidate oils with reference 3 at various temperatures. For reference 3, while it produced a high rating of 8.5 at 310 ºC, it yielded a poor rating of 0 at 330 ºC, due to high oil degradation and insufficient detergency. The observation was similar for Candidate 3 as well, although it performed better in the intermediate temperatures. Candidates 1 and 2 showed overall superior ratings than Candidate 3 and the reference oil. Because the candidate blends are only different in their detergent additives, this result established that the appropriate selection of detergent type and their combination plays an important role for the differentiated performance of candidate 1 and 2.

4.2 Panel coker test: This instrument is used to measure the coking tendency of finished oils when exposed to hot surfaces. During the test, the oil sample maintained at an elevated temperature is mechanically splashed onto a hot aluminum test panel. After a specified period, the amount of coke deposited on the panel is measured by weighing it. This test method, being easily customizable by means of oil temperature, aluminium panel temperature and the test duration (even a cycle of splashing and coking could be used), appeared to be an excellent tool to determine cleanliness ability of MDCLs. The test condition for the subject study was also optimized to obtain a significant amount of deposit to differentiate between the reference and the candidate oils. The panel coker tests were performed using conditions mentioned in Table 3.

Table 3. Panel coker test condition.

Variables	Value
Panel temperature	330 ºC
Oil temperature	100 ºC
Duration	12 hours
Oil Splash rate, RPM	1000

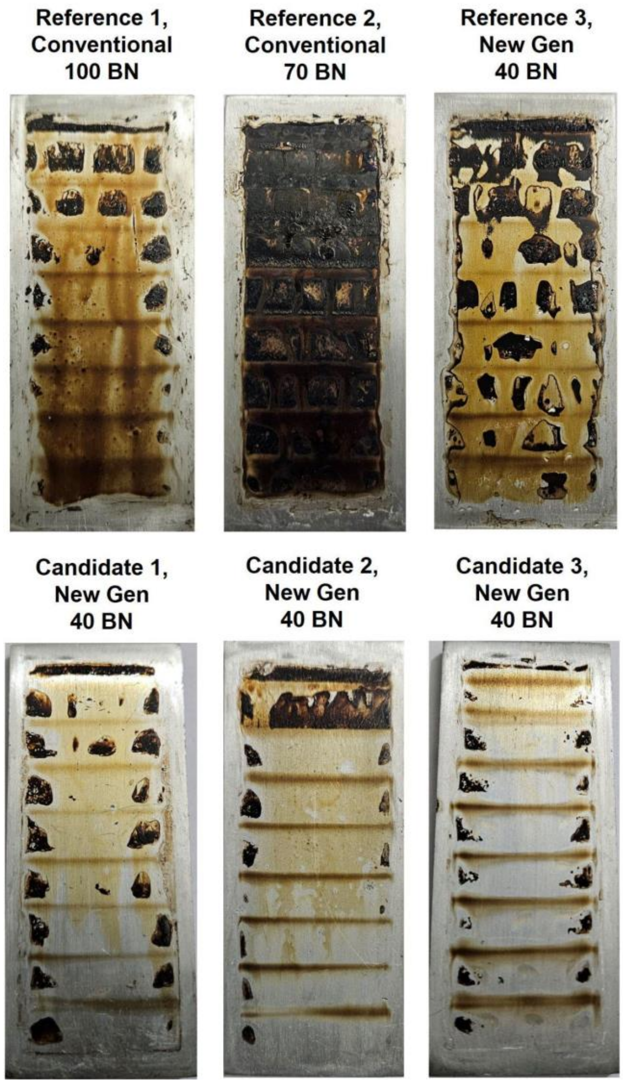

Figure 2. Panel coker end-of-test aluminium panels showing different levels of cleanliness of the new generation 40 BN MDCL candidates against reference oils.

Figure 2 shows the end-of-test images of the aluminium panels of the reference and the candidate oils. The amount of deposit on the conventional MDCLs are clearly different, showing a much better deposit control by the 100 BN oil (Reference 1, 19 mg) compared to the 70 BN oil (Reference 2, 51 mg). However, the deposit formed in case of Reference 3, which is a new generation 40 BN MDCL was much lower than the conventional 70 BN MDCL.

Most interestingly, the candidates 1, 2 and 3 yielded much less deposit on the panel coker test (12 mg, 14 mg and 7 mg respectively, Table 4) than the reference oils, thanks to the selection of superior additive components and their optimized treat rates.

Table 4. Panel coker test results for the reference and the candidate oils.

Sample	Panel Coker Deposit, mg
Reference 1	19
Reference 2	51
Reference 3	24
Candidate 1	12
Candidate 2	14
Candidate 3	7

4.3 Pressure differential scanning calorimetry (PDSC): Pressure differential scanning calorimetry (PDSC) is a technique popularly used to study oxidation induction time (OIT) of a lubricant and interpreted as its oxidation stability or antioxidant performance. This test method requires a very small amount of sample and is comparatively faster than other oil oxidation tests. This test is effective in comparative study of large numbers of samples using ASTM D6186 method.

Table 5. Oxidation induction time (OIT) measured by PDSC at 190 ºC for the reference and the candidate oils.

Sample	PDSC, OIT (min)
Reference 1	73
Reference 2	54
Reference 3	140
Candidate 1	183
Candidate 2	217
Candidate 3	189

A small sample (3 mg) of oil is weighed and placed into a sample pan within a test cell. The cell is heated to a temperature of 190 °C and then pressurized with oxygen at 500 psi. The cell is maintained at this temperature and pressure until an exothermic reaction, signifying the oxidation of the oil, occurs. The time at which oxidation begins is measured, and the extrapolated onset time is reported as the oxidation induction time (OIT) for the lubricating oil at the specified test temperature. OIT measured for the reference and the candidate oils shows much superior oxidation stability of the candidate oils and reference 3. Significantly lower values for reference 1 and 2 imply that the conventional MDCLs are not formulated to withstand oxidation, as this was not a requirement for conventional MDCLs. However, while reference 3 (New gen 40 BN MDCL, industry reference) showed much higher OIT than the conventional MDCLs, the candidate oils yielded further improved OIT owing to the use of superior AOs in their formulations. Interestingly, lowering the dosage of AOs adversely affected KHT and panel coker results of the candidate oils, thereby focusing on the importance of additive treat rate optimization during engine oil formulation development.

4.4. CAT 1M PC (ASTM D6618) engine test results

Based on the laboratory performance tests, a qualitative performance matrix was developed (Table 6) and analysed to select the candidate for engine test against reference 3 (Industry reference). Among the three candidates, 2 performed best in KHT and PDSC analysis, while candidate 3 performed best in the panel coker test.

Table 6. Oil performance test matrix for screening of Candidate oils.

Sample	KHT	Panel Coker	PDSC
Candidate 1	👌	👌👌	👌
Candidate 2	👌👌👌	👌	👌👌👌
Candidate 3	👌👌	👌👌👌	👌👌

Candidate 2 was further evaluated in the CAT 1M PC (ASTM D6618) test to study its detergency property (piston deposit control). This test aims to assess the performance of crankcase lubricants in relation to piston deposits, ring sticking, and the scuffing of pistons, rings, and liners. This test was included in the API categories CF (off road, indirect injection diesel engine, suitable for high sulfur fuel) and CF-2 (severe duty two stroke diesel engine). Although both the specifications are now obsolete, CAT 1M PC is a meaningful test bench to evaluate two-stroke marine engine oils. A Caterpillar 1Y73 single-cylinder, indirect injection diesel test engine is used, designed in a two-valve arrangement with a 5.125-inch bore and a 6.5-inch stroke, resulting in a displacement of 134.1 cubic inches. The engine has a compression ratio of 16.4:1 and utilizes rectangular rings.

The test parts include the piston (1Y3589), ring set (1Y3588), and liner (5H-5657) as per Caterpillar's "3L" quality specifications. The pass/fail criteria include no ring sticking, no piston, ring, or liner scuffing, a weighted total demerit score of ≤ 240, a top groove fill of ≤ 70%, and a loss of side clearance of ≤ 0.0005. The test parameters are mentioned in Table 7.

Table 7. Parameters of CAT 1M PC engine test.

Parameter	value	Parameter	value
RPM	1800	Coolant temp.	88 °C
kW	33	Inlet air temp. at 770 mbar pressure, 125 grains/lb humidity	123 °C
Air fuel ratio	23.5:1	Oil temp.	98 °C
Duration	120 hours		

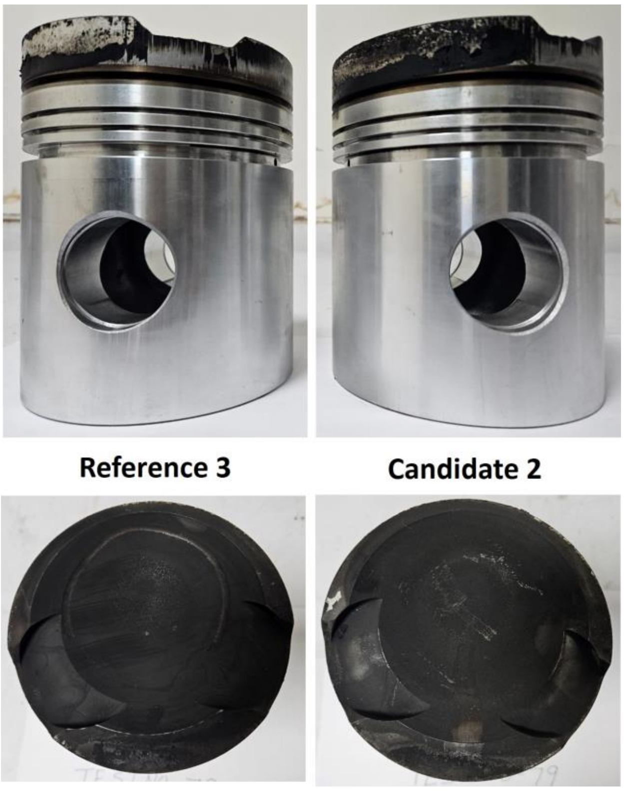

Figure 3. Photographs of pistons (top) and piston heads (bottom) after CAT 1M PC tests of Reference 3 and Candidate 2.

At the end of the test, the four grooves and three lands of the piston are inspected and rated based on the amount (% area) and type (carbon/ lacquer) of deposit. Deposit on the top groove is reported separately as top groove filling (%). The Weighted Total Demerit (WTD) is calculated by adding weighted deposit amounts for all grooves and lands.

The result for Candidate 2 in the CAT 1M PC test showed very low TGF at 5% and WTD at 70 establishing its excellent deposit control property. Moreover, the loss of side clearance was found to be virtually zero. The TGD for Candidate 2 is similar to the Reference 3, while it was found to be slightly inferior in terms of WTD against the reference oil. The results obtained with the CAT 1M PC test undoubtedly boosted the confidence on the subject formulation strategy for a new-generation MDCL.

Table 8. Top Groove Filling (TGD) & Weighted Total Demerit (WTD) values obtained from CAT 1M PC test.

Sample	Top Groove Filling (TGF), %	Limit %	Weighted Total Demerit (WTD)	Limit
Reference 3	5	70	40	240
Candidate 2	7	70	82	240

5. CONCLUSION & WAY FORWARD

Development of marine cylinder lubricants for modern marine two stroke engines are challenging due to the IMO 2020 regulation, quality of fuels and tougher lubrication requirements of new generation engines. To ensure engine's safety, OEMs are also implementing stricter cylinder oil specifications. Very few existing MDCLs can meet lubrication demand of modern marine two stroke engines. Lubricant formulators are working to develop high performing MDCLs in low BN categories.

In this study, three 40 BN cylinder oil formulations were developed in SAE 50 viscosity grade, using different detergent additive technologies. The candidate oils were formulated by effective selection of detergents, dispersants and antioxidant additives and treat rate optimization. Customised test conditions were implemented to screen additive components and finished candidate oils. The comparative study revealed that the newly formulated 40 BN oils possess equivalent or superior cleanliness properties than a commercialized 100 BN MDCL and a MAN ES-approved CAT II 40 BN reference oil in laboratory tests.

One of the candidate oils was tested against a new generation 40BN cylinder lubricant for its engine cleanliness property and found to be performing very well. The newly developed formulations showed potential to cater modern two-stroke marine cylinder lubrication requirements running on low-sulfur fuels. Additional testing is under progress for the selection of the final candidate for the onboard ship trial.

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