Developments in marine lubricant specifications

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The Marine Lubricant Industry is thriving as international trade activities increase and shipbuilding advances continue to develop. Seaborne trading accounts for approximately 30% of global transportation and is still rising. As this market continually develops, biodegradability of marine lubricants is prioritised due to its benefits, including constant viscosity, enhanced safety, and low emission rates. Currently, mineral oils hold the greatest usage rate for marine lubricants because these mineral oils are the most affordable and widely available. Mineral oil is forecasted to surpass 4.5 billion USD in sales by 2024. However, with increasing government demand to reduce nitrogen and sulphur emissions, synthetic and bio-based oils are growing in popularity. Synthetic oil is forecast to show the greatest compound annual growth rate (CAGR) due to its high efficiency under high/low temperature conditions, durability in water, and environmental friendliness. These lubricants are ever-growing but are hindered from smooth growth due to the inherent problems adapting the oil with fuel in order to neutralize combustion acids for safety purposes.

In December 2013, the Environmental Protection Agency (EPA) authorised new regulations with the Vessel General Permit (VGP). The VGP mandates that all large vessels longer than 79 feet operating on US waters will have to adhere to its regulations. According to the new regulations, environmentally acceptable lubricants (EALs) must be able to biodegrade by 60% or more within a 28-day period and must have minimal toxicity and be non-bio accumulative towards the marine ecosystem. Vessels have the potential of leaking oil into the sea through openings in seals, or surfaces, which justifies the implementation of tighter limits on naval regulations. Commercial shipping vessels make roughly 1.7 million visits to ports every year, which could pollute the sea with up to 61 million litres of lubricant oil. Therefore, immediate action is paramount to formulate a grease product that is environmentally safe for the marine ecosystem as a precaution for lubricant spilling.

The EPA recently reduced sulphur level limits from 3.5% to 0.5% on January 1, 2020. New fuels will need to be developed with high variable compositions to comply with these limitations. The greater challenge is to adjust the compositional requirements of lubricants in both two-stroke and four-stroke applications to ensure enough protection of the engine. Plausible points of concern to address include oxidation/aging, viscosity control, wear, and cleanliness. Moreover, there is growing interest in using Group II base stocks that have better antioxidation properties, less sulphur emissions and better fuel economy than Group I base stocks. However, Group II stocks have a lower solvency compared to Group I, which causes the asphaltenes, molecules formed from oxidation and aging, to be harder to stabilise, resulting in unwanted deposits and contamination of the engine. Overall, the current market has lubricants designed explicitly for high sulphur heavy fuel oils (HFO) so new lubricants will need to be developed to conform to future low sulphur oils. The problem lies chiefly in finding the perfect balance between basicity and surfactancy.

Two-stroke and four-stroke engines are readily available in the marine sector. Four-stroke engines are advantageous in their compact size and high-speed ceiling. The lubricants in a four-stroke engine are continually in contact with combustion products which raises the need for a higher base number (BN) to neutralise the acids produced. BN is the measurement of an oil's ability to neutralise acids that are produced in the engine. These acids are produced from low-quality fuel and oil oxidation. On the other hand, a two-stroke engine follows a crosshead engine design and is ostensibly the more popular option because it is cheap, efficient, powerful, reliable and easy to maintain. The formulation of the lubricant oil for two-stroke engines is influenced by a myriad of factors. Combustion acids decrease with low sulphur content which requires there to be less base in the lubricant. Moreover, to avoid agglomeration of asphaltenes, surfactancy needs to be optimized, but lower basicity delivers less surfactancy which is counterintuitive. Optimal high temperature additives may address this issue and aid both facets. However, HFOs are currently dominating the market and low sulphur fuels are yet to be developed, which makes it difficult for new lubricant formulations to develop.

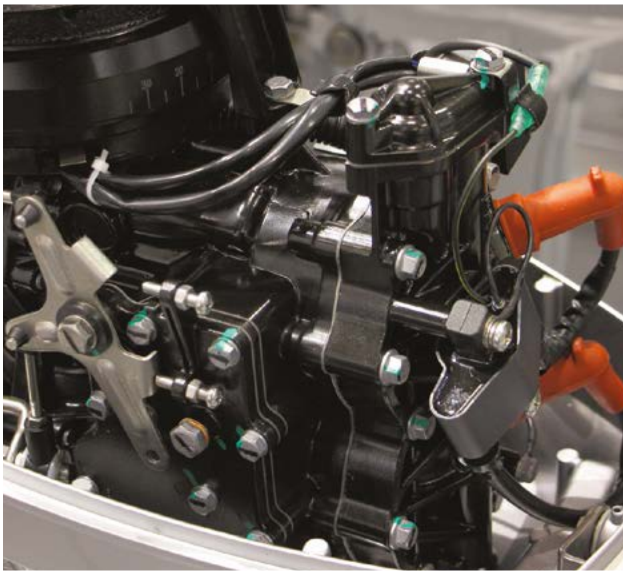

Figure 1: *Two-stroke outboard motor*

With the implementation of a 0.5% sulphur limit, the International Maritime Organization (IMO) forecasts the use of a lower BN cylinder oil in accordance to the new sulphur limit. It is expected that a myriad of different lubricants must be formulated to conform to different types of fuel. Plausible fuel types to use in the future include the following: low sulphur marine fuel with less than 0.5% sulphur content, residual blends with less than 0.5% sulphur content, and high sulphur oils with the use of exhaust scrubbers and high base number. Gaseous fuels such as liquified natural gas, liquified petroleum gas, and biofuels contain very small sulphur percentages, acting as plausible alternatives. The different properties for these fuels may lead to compatibility issues with lubricants which reinforces the necessity to adapt each lubricant to each fuel.

Greases are heavily affected by the choice of the base fluid as their composition is represented mainly by a base fluid. The base fluid is responsible for the grease's ability to lubricate sliding surfaces, solubilise additives and encourage thickener development. The unquestionable importance of the fluid raises the need for industries to make further advancements to optimise it. Thickeners and additives are combined into the base fluid to achieve specific consistencies and properties for performance requirements. The primary base fluids that are considered are synthetic esters, triglycerides, polyalkylene glycols (PAG), and polyalphaolefin (PAO). The biggest challenge of marine lubricants is the susceptibility of the grease to hydrolyze. When greases are exposed to water, the viscosity of the base oil will drop, resulting in a lower load-carrying capacity and increased wear on the equipment due to boundary lubrication. Thus, the hydrolysis of water could cause the acidity level to increase, resulting in corrosion.

In recent developments, synthetic esters have gained more popularity. Many synthetic esters are able to satisfy the VGP criteria for EALs both in terms of biodegradability and toxicity. Synthetic esters are also known for having a high viscosity index, exceptional corrosion preventive properties, and can be adjusted to provide excellent lubrication for specific applications. Common issues with natural esters include poor cold flow behaviour and inadequate oxidative stability. Despite the properties of natural esters, synthetic esters can be specifically designed to excel in those areas. Yet, synthetic esters are still susceptible to hydrolysis and the formation of acid in the presence of water. One company, Dow Chemical Company has recently revealed biodegradable additives that could improve hydrolytic stability for ester-based lubricants. These additives utilise triblock copolymers of polyalkylene glycols to gather and isolate water molecules which prevents water from disrupting the ester composition. Additionally, these additives can minimise the production of deposits and residues as the esters wear out. These triblock copolymers are synthesised from readily available building blocks, which provides an efficient cost performance profile. With the ability to resist breakdown in the presence of water, esters can provide lubrication for marine applications with environmental benefits and display promising equipment protection.

Another primary base fluid, triglycerides, esters formed from glycerol and three fatty acids, are derived from vegetable fat. In earlier developments of EAL greases, triglycerides were a popular base fluid due to its outstanding lubrication performance. However, triglycerides have poor oxidative stability in temperature extremes and tend to break down in the presence of water.

Unlike triglycerides, PAGs excel in lubricity, viscosity indices, oxidative stability, and hydrolytic stability. However, they tend to be incompatible with mineral oils. Therefore, in the case of conversion to an EAL, it will be very costly to wash the lubricated areas or potentially replace the equipment. PAGs also tend to form acids when exposed to water. Similarly, PAO has great hydrolytic stability and long operational life. Group I and Group II mineral oils (MOs), on the other hand, possess the best cost performance index but fail to qualify as an EAL.

In previous years, the lubricant industry has attempted to use additives that contained heavy metals such as lead and antimony with the goal of achieving higher load capabilities at a low cost. However, industries have shifted from the use of such additives while searching for new environmentally friendly additives. As time progresses, information on more environmentally base fluids and additives are being discovered and the industries are working on different combinations of base fluids, thickeners, and additives to improve the quality of the grease.

A study was performed to compare the performance of lithium grease composed of an MO base fluid and lithium complex greases with a PR base fluid. MO lithium grease has an exceptional performance profile for marine lubricants but failed to be environmentally safe according to the VGP. The purpose of the study is to find out whether PR lithium complex grease, an environmentally acceptable lubricant, will match the performance of the MO lithium grease. The results of the study are shown in Table 1.

Tests	Lithium Grease made with MO	Lithium Complex Grease made with PR
Penetration, worked 60, mm/10 ASTM D 217	263	275
Dropping Point, °C ASTM D 2265	187	280
Low Temperature performance, torque at -40°C, N·m ASTM D 4693	7.76	1.87
Weld Point, kgf ASTM D 2596	250	400
EP Performance: LWI, kgf ASTM D 2596	39	65
4-Ball Wear, scar diameter, mm ASTM D 2266	0.47	0.44
Timken EP, OK Load, Lbs. ASTM D 2509	55	55
Water Spray off, % loss ASTM D 4049	42.5	4.0
Water Resistance at 80°C, % loss ASTM D 1264	3.5	4.0
Oil Separation, % loss ASTM D 1742	2.4	0.9
Rust Protection, Rating ASTM D 1743	Pass	Pass
Copper Corrosion, ASTM D 4048	1b	1b
Salt Fog test B 117	2S result after 264 hours.	10 out of 10 after 1,000 hours
Humidity Cabinet ASTM D 1748	Test in Progress	10 out of 10 after 1,500 hours

Table 1: *Results of study comparing performance of lithium grease composed of an MO base fluid and lithium complex greases with a PR base fluid*

Both greases produced good results in the extreme pressure test methods. The two greases obtained a result of 55 lb for the Timken load-carrying capacity test (ASTM D2509) and a result greater than a kilogramme force (KGF) of 250 for the four-ball wear extreme pressure test (ASTM D2596). For the four-ball extreme-pressure properties test (ASTM D2596), the PR lithium complex grease resulted in 65 kgf for the load wear index (LWI) while the MO lithium grease resulted in 39 kgf.

Steel and copper corrosion test (ASTM D4048) requirements were met by both greases. The low temperature torque test (ASTM D4693) showed lower results in the PR lithium complex grease than the MO lithium grease. Results from the four-ball wear preventive test (ASTM D2266), oil separation test (ASTM D1742), and water washout test (ASTM D1264) were similar. The PR lithium complex grease surpassed the MO lithium grease in the water spray-off test (ASTM D4049) with a result of 4% compared to 42.5% in the MO grease.

The PR lithium complex grease is comparable to the MO lithium grease in terms of performance in marine applications. Yet, further thought should be placed on the specific application when deciding the appropriate grease.

Other than lubricant improvements, it is prudent for ship manufacturers and government bodies to improve ship size and create new terminals and straits to expand the capacity of marine carriers since 90% of global trade are from ship transportation. Ultra large container ships (ULCS) are of high demand recently with the increase in trade volumes which drives lubricant demands. With the growth of these formidable carriers, EPA regulations have become stricter not only for sulphur content but also on other facets. Sulphur oxides in the ship's engine and boiler are removed with exhaust gas scrubbers and new technologies such as exhaust gas recirculation is created to reduce nitrogen oxide emissions.

This technology achieves this by lower oxygen concentration and heat absorption in the combustion chamber, subsequently saving fuel. Selective catalytic reduction technique is another method that aids in this department by introducing a reducing agent to the exhaust gas which advocates the separation of nitrogen oxide to nitrogen and water molecules. Other than environmental issues, performance and durability of the ship is salient to optimise. Slow steaming is a technique of operating at lower speeds to minimise fuel consumption and increase durability. These techniques are imperative to smooth marine growth and will continue developing to improve the industry.

Overall, lubricant oils designed for the future must comply with various standards. With time, a new range of fuels will be developed to abide by the novel 0.5% sulphur limit which will connect the gears for the development of lubricant oils. However, time is of the essence as EPA and VGP are becoming increasingly stringent with environmental safety.

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