Octamar™ LI-5 and LI-5 Plus

Understanding Lubricity & other Benefits to Marine Distillate Fuel

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Introduction

The purpose of this document is to give an explanation about lubricity, and other issues Innospec’s Octamar™ LI-5 range of fuel treatment products address associated with the use of marine distillate fuels. These issues can be quite complex and should be fully understood by all. The document will outline the background, the history, the implications, the specifications, the test methods and the Innospec solution!

Through experience of lubricity additive use in automotive application, Innospec has good understanding in relation to the subject of lubricity dating back to the early 1990’s, where the introduction of low sulphur diesel fuel had catastrophic effects on vehicle fuel injection equipment. The phenomenon of abnormal and high pump wear rates caused by the loss of lubricity in low sulphur diesel fuels are not only well documented, but have been studied extensively in Europe and North America [1, 2, 3, 4].

Fuel lubricity is little understood by the marine industry in general. The reason for this lack of understanding is that lubricity has never been a fuel characteristic which need be considered, until now.

Before explaining more about lubricity it is important to understand what is driving this subject to become a concern.

In recent years, international and regional legislation on emissions from shipping has driven the maximum permissible Sulphur content of marine fuel down. In the near future these limits will become even more stringent. More specifically this applies in both emission control areas (ECA’s) and globally. Fig. 1 illustrates current ECA designated areas.

The legislation(s) in question are Marpol Annex VI, CARB and EU directive 2005/33/EC.

- **Marpol Annex VI, Regulation 14** states the following:
  - The sulphur limit applicable in Emission Control Areas (ECA’s) beginning on 1st July 2010 would be 1.00 % (10,000 ppm), reduced from the current 1.50 % (15,000 ppm);
  - The global sulphur cap would be reduced to 3.50% (35,000 ppm), from the current 4.50 % (45,000 ppm), effective from 1st January 2012;
  - The sulphur limit applicable in ECA’s effective from 1st January 2015 would be 0.10 % (1,000 ppm);
  - The global sulphur cap would be reduced to 0.50 % (5,000 ppm) effective from 1st January 2020, subject to a feasibility review to be completed no later than 2018. Should the 2018 review reach a negative conclusion, the effective date would default to 1st January 2025.

- **CARB** (California Air Resource Board) dictates that within 24 nautical miles of the Californian Coast the following applies:
  - From 1st January 2007 the maximum permissible sulphur content of Marine Diesel Oil is 0.5% (5,000ppm) and Marine Gas oil 1.5 % (15,000ppm);
  - From 1st January 2010 the maximum sulphur content of MGO and MDO has been reduced to 0.1% (1,000ppm)

- **EU Directive 2005/33/EC** states the following:
  - From January 1st 2010, under the Directive, the maximum allowable sulphur content of fuel oil used by ships ‘at berth’ in EU ports, other than those in the outermost regions, will be 0.10% (1,000ppm) by mass. Exception: Certain named ships, and ships which are timetabled to be at berth for less than two hours, will be exempt from the requirements.
It should be noted that ECA areas are set to expand, with the Mediterranean Sea and Coastal USA expected to follow in the coming years.

For the time being the use of heavy fuel oil is acceptable providing the Sulphur content is at the level required for the particular region where the vessel is sailing. Ultimately though, except where abatement technology such as exhaust gas scrubbers have been employed, these limits could force a gradual industry change to distillate fuels, from the traditional use of heavy fuel oil. In any case, there are many implications of using low sulphur fuels that any vessel operator must consider. One such implication is the effect sulphur removal has on the lubricating properties of the fuel.

It is also important to note that the International Standards Organisation is in the process of introducing a new version of ISO 8217 – Specification for Marine Fuel. In this proposed version of the standard, due for release in July 2010, distillate fuels with a sulphur content of less than 500ppm (0.05%) must be subjected to the lubricity testing to ensure sufficient protection. Also, the proposed standard places a stability limit on all distillate fuel grades.
What is Lubricity and what are the Implications of Poor Lubricity to Marine Engines?

The definition of Lubricity is “The intrinsic ability of a fluid to prevent wear on contacting metal surfaces”.

It is a common misconception that lubricity properties can be improved simply by increasing viscosity. There are two distinct regimes of lubrication to consider when discussing fuel pump lubrication – Hydrodynamic lubrication and Boundary Lubrication [5].

Hydrodynamic lubrication relates to the oil film created between the moving components. This area of lubrication is directly dependent on the viscosity of the fuel and is one of the reasons the OEM’s are recommending a minimum viscosity of 2cSt when operating on distillate fuel. If the viscosity is too low the oil film can become insufficient and seizure can occur. The other reason for this is that with a viscosity of less than 2cSt, excessive fuel leakage occurs past the fuel pump plunger and in the nozzle needle valve. This can lead to problems when starting engines and when operating at both high and low loads. Such problems on a marine vessel have serious safety implications.

Lubricity however relates to the boundary lubrication, and to a huge extent the fuel injection equipment relies on the characteristics of the fuel for lubrication. Where boundary lubrication really plays a part is within fuel pumps where the clearance between the plunger and body is extremely small and can decrease further when the components reach operational temperature. Boundary lubrication dictates that to a certain extent the substance penetrates the surface of the moving components creating a mono molecular layer. This reduces the friction between the contacting metal surfaces and prevents excessive wear. Therefore boundary lubrication is just as, if not more important than hydro dynamic lubrication in the case of fuel pumps.

With insufficient boundary lubrication within fuel injection equipment excessive and accelerated wear can be expected and premature failures thereafter. The areas most affected by this are fuel pumps without external lubrication sources. Typically this applies to individual cylinder reciprocating fuel pumps or common rail pumps. Failures such as this would be extremely costly, not only in financial terms, but also in terms of safety and lost time.

What Causes Poor Lubricity in Fuel?

Another common misconception is that the sulphur in the fuel provides the lubricity characteristics. This is not strictly correct and the sulphur content itself is not the main cause of poor lubricity. In fact it is the processing used in a refinery for removing sulphur, commonly termed hydro-processing which impacts fuel lubricity. Hydro-processing’s primary function is to reduce fuel sulphur content, and is an essential refinery process in order to produce the low sulphur content fuels the specifications demand. However, the processing not only removes the sulphur, it also removes the naturally occurring polar components which give a fuel inherent lubricity [6]. Therefore sulphur content is not necessarily a direct correlation with respect to fuel lubricity although there is a strong likelihood that a low sulphur fuel or one of its blend components has been hydro-processed. Equally fuels of a higher sulphur content, i.e. >500ppm can potentially exhibit poor lubricity depending on the crude oil source and the processing which the fuel has undergone.

History of Lubricity from Automotive Fuels

Lubricity was little understood or appreciated until the early 1990’s when low sulphur diesels (<500ppm) appeared in the market for automotive use. Very quickly thereafter vehicles using such fuels experienced problems, with excessive wear and failure of the rotary fuel injection pumps. Across all manufacturers it is estimated up to 65 million pumps were affected by this. Failures occurred quickly and it was reported that fuel pump failure was occurring after only 5,000 – 10,000 kilometres, which at an average speed of 50km/hr equates to 100 – 200 hours of operation. In terms of a marine engine this is a very short operating period and translating this experience directly to a marine engine, illustrates that the supply of one bunker of poor lubricity fuel could potentially result in the failure of fuel injection equipment.

The experience in automotive application led the industry to investigate diesel lubricity in detail and provide means for fuels to be assessed for lubricity behaviour. This necessitated the need for a rapid laboratory bench test which could discriminate between fuels of good and poor lubricity.
How to Test for Lubricity and How the Test was Developed

The standard way to measure lubricity of a fuel is the HFRR (High Frequency Reciprocating Rig) test as per IP450 / ASTM D6079 / CEC F-06-A-96. In the HFRR test a sample of the fluid under test is placed in a test reservoir which is maintained at the specified test temperature. A fixed steel ball is held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball is oscillated at a fixed frequency and stroke length while the interface with the plate is fully immersed in the fluid reservoir. The metallurgies of the ball and plate, temperature, load frequency and stroke length are specified. The ambient conditions are used to correct the size of the wear scar generated on the test ball to a standard set of ambient conditions. The corrected wear scar diameter (WSD) is a measure of the fluid lubricity [7].

The HFRR test has been adopted in many fuel specifications as the standard method to evaluate lubricity. During its development correlation with the more time consuming diesel pump rig test, conducted using a Bosch pump known to have experienced problems in the field was established [8].

This test consists of a Bosch pump driven by an electric motor at varying specific speeds. Forty litres of fuel is continuously cycled through the pump for 100 hours, at which time the fuel is replaced with a further 40 litres of fresh fuel. This test is repeated with the same components 10 times, making a total of 1000 hours testing using 400 litres of fuel. Upon dismantling of the rig the critical wear components are rated between 1 and 10, using a visual rating system developed by Bosch. An overall rating below 3.5 was deemed a pass and demonstrated lifetime performance (100%). A rating of 4 – 6 indicated a reduced lifetime (20%) and a rating of 7 – 10 was a fatal breakdown (1%).

Figure 3 illustrates the condition of components relative to the pump wear rating and HFRR. Figure 4 shows the results of the above described tests and the clear correlation between the two methods.
What are the Relevant Limits for Lubricity?

For the automotive industry, the correlation chart in figure 4 demonstrates the correlation between a pump wear rating limit of 3.5 and a typical HFRR limit of 460μm included in many automotive fuel specifications. It is important to note that in terms of test precision, the repeatability of this test is +/- 60μm.

- European specification for automotive diesel fuel EN590 specifies the maximum at 460μm
- The American ASTM standard states a maximum of 520μm
- Fuel injection manufacturers recommend a maximum of 400μm
- The proposed version of ISO 8217 (Specification for Marine Fuels) states a maximum of 520μm

As stated earlier, the International Standards Organisation is in the process of amending ISO 8217. The proposed standard contains the requirement for lubricity testing of distillate fuels which contain less than 500ppm sulphur (0.05%). This standard is due to be formally released on 1st July 2010. The ISO committee has clearly recognised that lubricity is a characteristic which must be considered when dealing with low sulphur marine distillate fuels. However there is still debate around the proposal in this standard. The ISO has adopted the ASTM limit of 520μm but it is possible that this limit may be unsatisfactory in order to protect fuel systems. It can be argued that the conditions inside a marine engine fuel pump are much more severe than those within an automotive engine, and therefore perhaps the proposed limit should be lower. In addition the proposal states that only fuels with less than 500ppm require testing, which is clearly suggesting that fuels above this level are safe, and that lubricity and sulphur content correlate. This is not the case and to reinforce this point Innospec has tested fuels with sulphur contents above 500ppm which have failed the proposed limit of 520μm (see figure 6).
Implications for Fuel Testing Labs

It is interesting to note that the addition of the requirement for HFRR lubricity testing, and the other additional test requirements of the proposed ISO 8217, will require additional investment by marine fuel testing laboratories. This in turn could result in the price and time required for ISO 8217 fuel testing to increase dramatically.

Effect of Octamar™ Lubricity Improvers

Octamar™ lubricity improvers act to restore the natural lubricity of middle distillate fuels with low intrinsic lubricity, or in fuels that have been affected by sulphur removal processes at the refinery. This works by addressing the boundary lubrication regime, re-forming the mono-molecular layer which is absorbed on the surface of the components.

![Working Mechanism of Octamar™ Lubricity Improver](image)

Figure 5 – Working Mechanism of Octamar™ Lubricity Improver

Figure 6 illustrates the HFRR response of various sulphur content marine distillate fuels, at increasing dosage rates of Octamar™ lubricity improver. In all cases, ranging from 500ppm to 10ppm the HFRR response is excellent, dramatically reducing the WSD. Bearing in mind that the proposed ISO 8217 indicates that the lubricity limit is not required for fuels with above 500ppm (0.05%) it is important to note that this diagram clearly indicates that fuels with 500ppm sulphur (0.05%) can measure above this limit.

![Sulphur Content Vs HFRR Wear Scar Vs Octamar™ Lubricity Improver Treat Rate](image)

Fig. 6 – Sulphur Content Vs HFRR Wear Scar Vs Octamar™ Lubricity Improver Treat Rate
Octamar™ Lubricity Improver Product Range

Innospec has been supplying lubricity improvers to automotive fuel globally for almost 20 years and has unparalleled knowledge on the subject of lubricity. This proven technology has now been redeveloped to be suitable for low sulphur marine fuel and has been integrated into the Innospec Octamar™ product range. The two available products are Octamar™ LI-5 and Octamar™ LI-5 plus.

Octamar™ LI-5 is a lubricity improver with the secondary benefit of corrosion resistance. Its properties are:

- **Appearance**: Yellow liquid
- **Density**: 910 kg/m³ at 15°C
- **Viscosity**: 16 cSt at 40°C
- **Pour point**: -12°C
- **Flash point**: > 100°C
- **Dosage Rate**: 1:10,000

Octamar™ LI-5 Plus is a combined product to address all the potential issues associated with the use of low sulphur marine distillate fuels. It offers improved fuel lubricity, improved fuel stability, protection against fuel injector fouling, protection against fuel filter plugging and protection against corrosion. Its properties are:

- **Appearance**: Clear Amber Liquid
- **Density**: 925 kg/m³ at 15°C
- **Viscosity**: 25 cSt at 40°C
- **Pour point**: < -51°C
- **Flash point**: > 61°C
- **Dosage Rate**: 1:4,000

Additional Issues Addressed by Octamar™ LI-5 Plus - Stability & Degradation

Transport fuels are by nature a complex mixture of hydrocarbons. These complex mixtures are susceptible to degradation through:

- Auto-oxidation of hydrocarbons – gum formation
- Acid-base reactions – Salt / Sediment formation
- Esterification reactions – Sediment formation
- UV (sunlight) initiated reactions

Similar to residual fuels advanced refining processes used to manufacture distillate fuels can lead to fuels which are of limited stability. External factors such as temperature, light and oxygen can all impact the stability of a fuel. These factors can have severe consequences with respect to long term storage of such fuels, and can lead to sediments or gums forming which can negatively affect a ships fuel handling system, such as fuel filters.
IP388 is used to measure the thermal stability of middle distillate fuels by aging and oxidising the sample, and measuring the total insolubles. Use of Octamar™ LI-5 Plus is very effective at improving middle distillate fuel stability when measured by IP388.

![Fig. 7 – Illustration of typical effect of Octamar™ LI-5 Plus performance in IP388 test]

![Fig. 8 – Visual Illustration of performance of Octamar LI-5 Plus on stability]
Additional Issues Addressed by Octamar™ LI-5 Plus -
Deposit Formation & Fuel Injector Cleanliness

Octamar™ LI-5 plus contains a powerful detergent which prevents formation of, and removes existing, deposits caused by fuel decomposition. This results in optimal fuel spray pattern, improved fuel atomisation leading to a number of benefits including:

- Better fuel economy
- Reduced emissions
- Improved engine durability

![Fig. 9 – Difference in Injection spray that occurs when deposits form on injector nozzles holes](image1)

![Fig. 10 – Comparison in condition where Innospec detergent has been used](image2)
Additional Issues Addressed by Octamar™ LI-5 Plus - Corrosion

Octamar™ LI-5 Plus also offers corrosion resistance, which will prevent corrosion of metals when water is present in fuel tanks. Corrosion resistance is measured using the ASTM D665A procedure. This involves immersing a steel probe in fuel/water @ 60°C for 24 hours. The steel probe is then inspected and rated in terms of level of corrosion.

Fig. 11 – Comparison of typical performance of treated fuel against basefuel in ASTM D665A test

<table>
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<tr>
<th></th>
<th>% Corrosion</th>
<th>NACE Rating</th>
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<tr>
<td>Basefuel</td>
<td>100</td>
<td>E (Fail)</td>
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<tr>
<td>Basefuel + Octamar™ LI-5 Plus</td>
<td>0</td>
<td>A (Pass)</td>
</tr>
</tbody>
</table>
References


[7] IP450 Test Method - Assessment of Lubricity using the High Frequency Reciprocating Rig (HFRR)

[8] CEC TDG-F-032 Test Method – Assessment of Lubricity using Diesel Fuel Pump Rig
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