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THE USE OF LUBRICITY ADDITIVES TO MAINTAIN FUEL QUALITY IN LOW SULPHUR DIESEL FUEL

Abstract

The introduction of lubricity protection as part of the EN 590 diesel specification in Europe has led to the wide-spread use of lubricity additives as a cost effective means to achieve the required level of performance. At the moment there are a number of different lubricity additive chemistries available to refiners and some discussion as to the merits of the different products. During the initial introduction of lubricity additives for low sulphur diesel fuel certain chemistries were found to have negative interactions that led to field issues. These products were mainly acid based and found to interact with basic components present both in the fuel and in the lubricant. These issues led to a move to neutral lubricity additives being favoured in preference to products based on acidic chemistry. However, even some of the neutral chemistries were found to have negative harm effects.

In this paper we will discuss how the development of no harm testing of refinery additives has led to the safe use of both neutral and acidic lubricity additives. The well-established DGMK test protocol allows refiners to select the most cost effective lubricity additive based upon extensive no harm testing in preference to selection being based upon generic chemistry.

Key words: lubricity, additives, chemistry, testing

Sažetak

Uvođenje mazivosti kao zaštitne značajke u specifikaciju za dizelska goriva EN 590 u Europi je dovelo do rasprostranjenog korištenja aditiva za mazivost, kao jeftinog načina za postizanje potrebne razine učinka. U ovom trenutku rafinerijama je dostupan veći broj različitih kemijskih rješenja za te aditive, uz rasprave o boljim svojstvima različitih proizvoda. Na početku uvođenja aditiva za mazivost u nisko-sumporno dizelsko gorivo za određene je kemijske spojeve utvrđeno da imaju negativne interakcije što je dovelo do problema u uporabi. Ti su proizvodi uglavnom bili kisele osnove pa je utvrđeno da reagiraju s baznim (lužnatim) komponentama prisutnim i u gorivu i u mazivu.

Ovi problemi su ukazali da aditivi neutralnih svojstava imaju prednosti nad onima kisele osnove. Međutim, čak i neki od takvih aditiva imaju negativne učinke.

U radu će se raspravljati o razvoju neštetnog testiranja rafinerijskih aditiva koje je dovelo do sigurnog korištenja i neutralnih i kiselih aditiva za mazivost. Uhodani postupak DGMK testiranja omogućuje rafinerijama odabir najučinkovitijeg aditiva za mazivost temeljem opsežnog neštetnog testiranja kojem daje prednost u odnosu na odabir temeljen na generičkoj kemiji.

Ključne riječi: mazivost, aditivi, kemija, ispitivanje

Background

During the last few decades we have seen tremendous advances in the design of diesel engine technology as vehicle manufacturers strive to meet the more demanding government vehicle emissions regulations. This has also required oil companies to make available fuels which will allow new vehicle hardware to continue operating to the latest design specifications. The biggest impact of these changes relates to the sulphur content of the fuels and this is captured schematically in the Fig. 1.

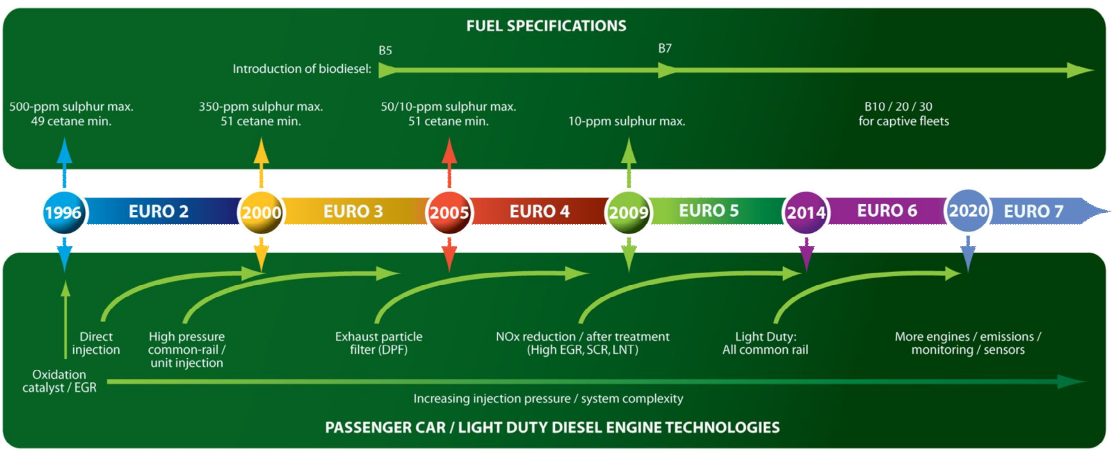

Figure 1: Vehicle emissions regulations development during last two decades

The refinery processes required to produce these low sulphur diesel fuels results in a fuel having a viscosity lower than conventional fuels and with a lower level of polar and polycyclic aromatic compounds. This results in low sulphur diesel fuel having poorer natural lubricity characteristics with the potential to cause vehicle mechanical problems. The introduction of environmentally friendly city diesel in Sweden in 1991 led to an outbreak of vehicle field problems. Upon investigation it was found that the removal of sulphur, aromatics and other polar compounds had resulted in fuels having poor inherent lubricity characteristics.

Failures are manifested as pump mechanical issues which brought many vehicles to a standstill. These failures were associated with passenger cars operating with Bosch rotary pumps after only 3000 to 10000 km. At the same time complaints were also seen in California where low sulphur and low aromatic fuels had been introduced. The industry recognised that there was likely to be an additive solution to this problem due to the fact that lubricity additives had been used to improve lubricity and give pump protection in jet fuel for a number of decades. Tests were conducted with an approved jet fuel lubricity additive using diesel fuel and the BOCLE lubricity test. Extensive performance and no harm testing were conducted and the additive was approved by the Swedish EPA for use as a diesel fuel lubricity additive. Before the additive solution could be implemented it had been necessary to develop a reliable test that could recreate the diesel pump failures as seen in the field and to use this test to evaluate the additive solution. Bosch developed a pump test that could be used to evaluate the propensity of a fuel to create wear in a diesel rotary distribution pump. Many of the field problems were seen in the Bosch VP44 pump used in the Opel Vectra and in direct injection engines. The pump test involved evaluating a fuel under controlled conditions for a period of either 500 or 1000 hours. Critical parts of the pump were weighed and visually rated prior to testing and then re-checked after completion of the test. The visual rating involved comparing specific pump parts with a set of parts from new, used and worn pumps. The pump was then rated for wear using a scale from 0 to 10 where 0 represented a new pump condition and 10 heavily worn. Acceptable performance was agreed to be at a level greater than 3.5 with a repeatability of 0.5 [1]. The industry recognised that the pump test was a useful tool for evaluating the lubricity characteristics of a diesel fuel but could not be used as a quality control test.

Figure 2: Standard test for diesel fuel lubricity - High Frequency Reciprocating Rig (HFRR) *(Source: PCS instruments)*

Consequently a working group was established with the objective of developing a convenient and reproducible test that could measure the lubricity characteristics of a fuel. This test is based upon a rig test in which the only lubrication between two metal surfaces is the fuel. The diameter of the wear scar is assessed at the end of the test. This test is controlled as CEC-F-06-A-96 and is known as the High Frequency Reciprocating Rig (HFRR) test (Fig. 2).

Potential additive solutions

Now that a reliable wear test had been established and accepted by the industry it was possible to evaluate a number of known chemistry as a potential solution to poor wear from low sulphur diesel fuel. A number of lubricity additives were already known to the industry due to the application in jet fuel and in low sulphur diesel fuel that had been marketed in Scandinavia since 1991 in 50 ppm (class 2) and 10 ppm (class 1) sulphur diesel fuel.

Most commercial lubricity additives were produced from long chain carboxylic acids. If the acidic head group is left and not further reacted the product is classed as acidic. When the carboxylic acid contains two head groups and two tails they are classed as dimer acids or one head group and one tail they are mono-acidic products. If the head group is reacted with an alkanol amine then the chemistry would be an amide and alternatively reaction with polyhydric alcohols, amongst others, would produce an ester. Both Esters and amides are classed as neutral lubricity additives. An example of lubricity additive chemistry is shown in Fig. 3.

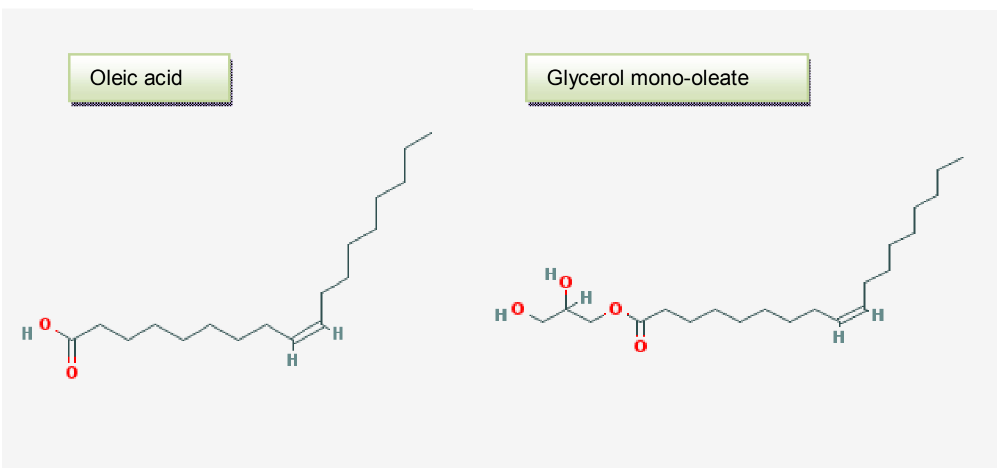

Figure 3: Examples of long chain carboxylic acid and their ester used as commercial lubricity additives
(*Source: Chemical Register*)

Lubricity additives used in jet fuel were mostly based upon dimer acids whilst the lubricity additives used in low sulphur diesel fuel at that time were mostly ester type chemistry.

A number of oil companies decided to use the jet fuel dimer acids for the low sulphur diesel fuels being marketed in Scandinavia due to the attractive treat-costs. A number of vehicle trials were conducted and the dimer acids were seen to give satisfactory protection against pump wear. ‘’No harm’’ fleet tests were conducted and dimer acids were found to be fit for purpose. One major global oil company decided to use the dimer acids for lubricity protection in Scandinavia and went to full commercial use. However, after a short period of time a number of field problems were reported when fuels were treated with dimer acid. Investigations were conducted by the industry in order to understand the cause of the field problems. In the meantime dimer acids were removed from the low sulphur diesel fuel application pending the results of the investigation.

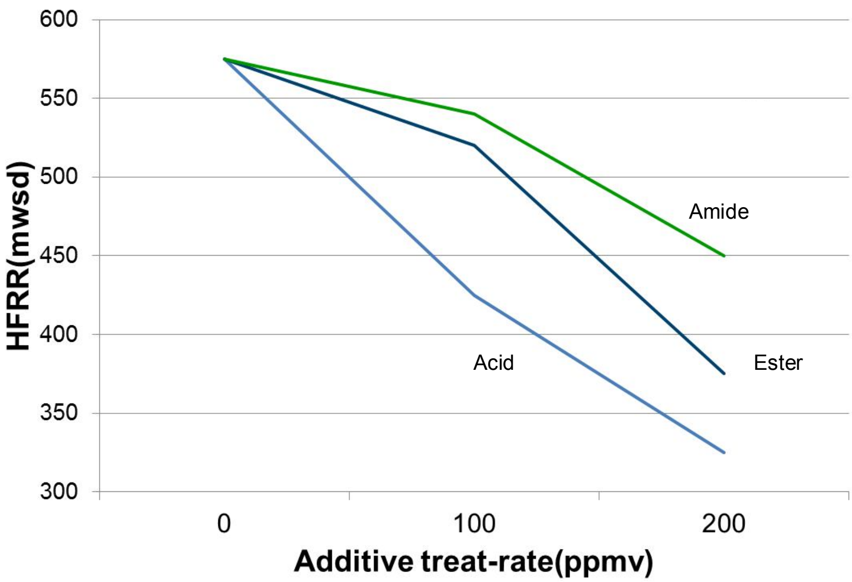

Figure 4: Difference between acidic and neutral lubricity additives (ester and amide) based on long chain carboxylic acid

The investigation started with analysis of blocked filters and pumps which had stopped operating due to deposits on the cam plates and shafts that led to pump failure. The analysis of pumps and filters clearly showed the formation of insoluble carboxylate salts coming from acid-base reactions. Further studies showed that the dimer acids, under certain conditions, were coming in contact with over based calcium sulphonates used in crankcase lubricants.

The mechanism of this interaction is shown below:

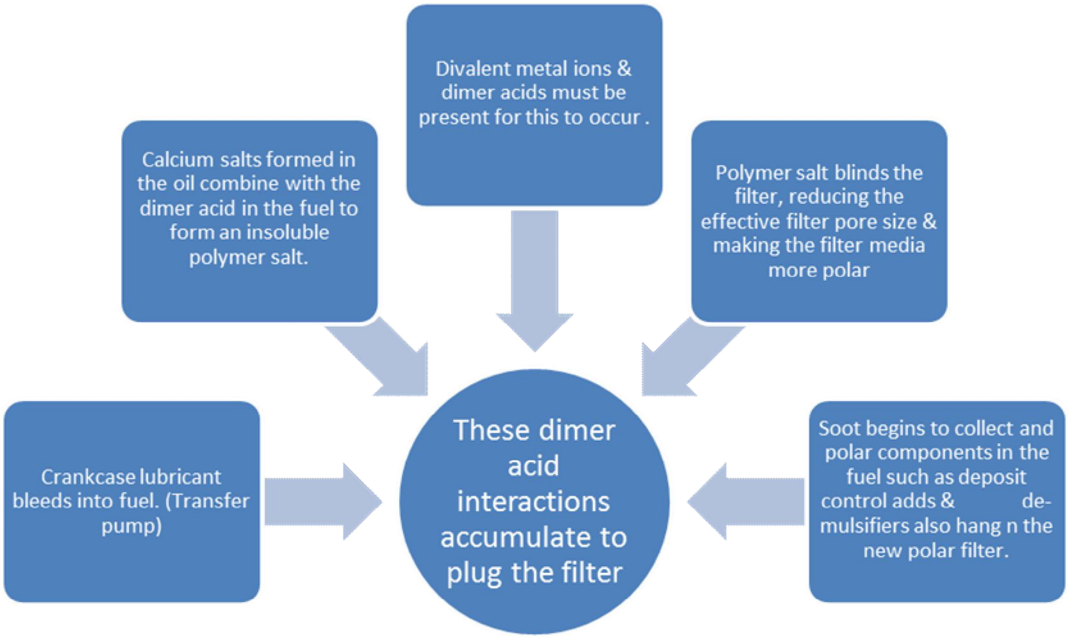

Figure 5: Origins of the filter blockage and pumps stopping

The investigation concluded that fuel additives can interact with lubricants in some injection pumps and injectors in tight orifices and annular spaces. It was also found that some truckers bleed or dispose of used engine oil by tipping into vehicle fuel tanks, believing that this will reduce fuel consumption and maintenance costs and is also a convenient way to dispose of used oil.

Since dimer acids were implicated with field issues the conclusions of the investigation led to the withdrawal of dimer acids as lubricity additives in low sulphur diesel fuels and more focus on neutral chemistries.

The question of Neutral or Acidic lubricity additives

The investigation led to the conclusion that the use of dimer acids in low sulphur fuel had the potential for acid-base reactions which could have an impact on vehicle operation mostly in the form of filter blockage and consequent fuel starvation. In order to safeguard against a reoccurrence of this issue a number of laboratories and rig tests were developed to evaluate existing and new lubricity additive chemistries. Some of these tests are discussed in an SAE papers written by Neste oil [2].

These tests were, by definition, severe in order to reproduce the issues in a timely manner. It was also convenient to use a dimer acid lubricity additive as a benchmark in order to validate the no harm test. Most of the tests focused on acid-base reactions and the impact on filters.

At the same time there was recognition that all acidic lubricity additives were not the same in terms of acid-base reactions and mono-acidic lubricity additives were found to be as cost effective as dimer acids without the same potential for field problems. Mono-acidic additives were compared to the bad reference (dimer acids) in these tests and gave very similar performance to neutral chemistries.

A number of the key tests are discussed below.

Aral engine oil compatibility test:

This is a severe test in which 10 g of neat lubricity additive is mixed with 10 grams of a high TBN lubricant. This mixture is stored for 3 days at 90 °C and then visually inspected for any signs of reaction and precipitate formation. The mixture is then blended into 500 ml of diesel fuel and filtered through a 0.8 millipore cellulose filter. A pass is classed as being able to filter the 500 ml in less than 180 seconds.

Typical performance for different chemistries is shown in Fig. 6.

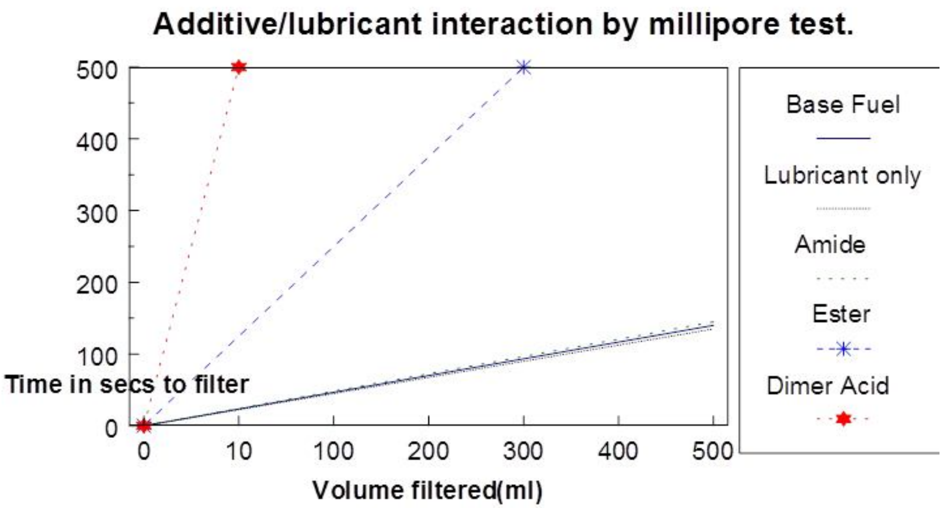

Figure 6: Interaction between additive and lubricant by Millipore test

The dimer acid fails very quickly due to an acid-base reaction leading to insoluble precipitates that block the Millipore filter. The mono-acidic lubricity additive easily passed since 500 ml of treated fuel was filtered in 63 seconds, the same as the amide and lubricant alone. This particular ester product also fails this test but this is partly due to borderline solubility in this fuel due to the high treat-rates (20000 ppm) used in this test.

Shell / ESSO / Infineum lubricant interaction test

This test has been designed to evaluate the lubricity additives at more realistic treat-rates (double recommended). The additive is mixed with the lubricant oil in a bottle and 2000 ml of fuel is added and the mixture is shaken for 2 minutes to mix. This mixture is then stored for 48 hours at 70 °C, allowed to cool to room temperature. The mixture is filtered through a 3 micron filter at a rate of 20 ml/min. The pressure drop across the filter is measured every 100 ml filtered.

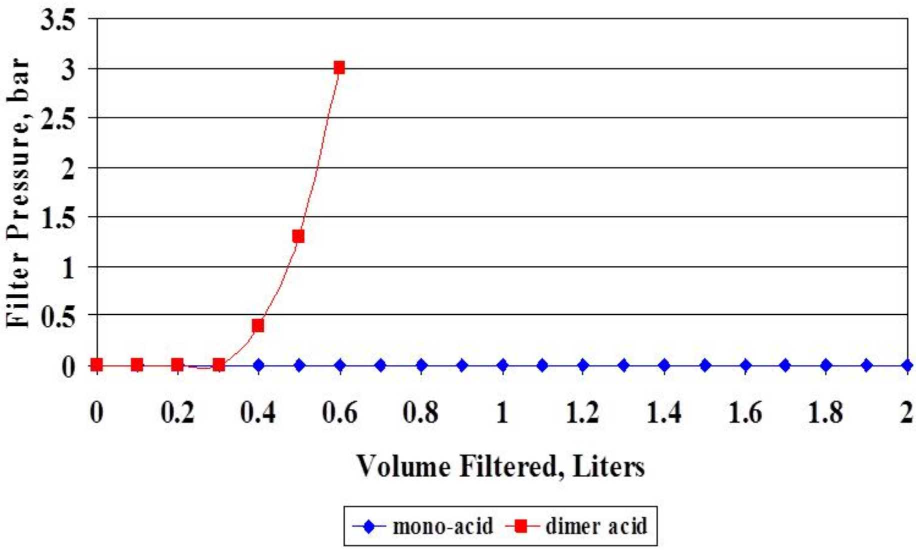

Figure 7: Interaction between additive and lubricant by Shell/ESSO/Infineum test

These tests gave a clear indication that monoacid lubricity additives do not react with the basic products found in high TBN lubricants. However, the next step was to move from laboratory tests, which simulate real world conditions, to actual vehicle tests. Afton Chemical developed a vehicle test based upon a heavy duty Caterpillar truck which was known to be prone to filter blockage. This test was run for 5000 miles on the road and the vacuum across the filter was continuously monitored. The evaluation of a dimer acid showed filter blockage after only 500 miles but the mono-acid lubricity additive gave no vacuum increase after 5000 miles of operation as shown in Fig. 8. The filters were examined after the test and there was clear evidence of deposit build up on the filter operated with the dimer acid, the filter from the mono acidic test was perfectly clean as seen in Fig. 9. Analysis of the deposits on the failing filter showed clear evidence of carboxylate salts resulting from dimer acid-base reactions.

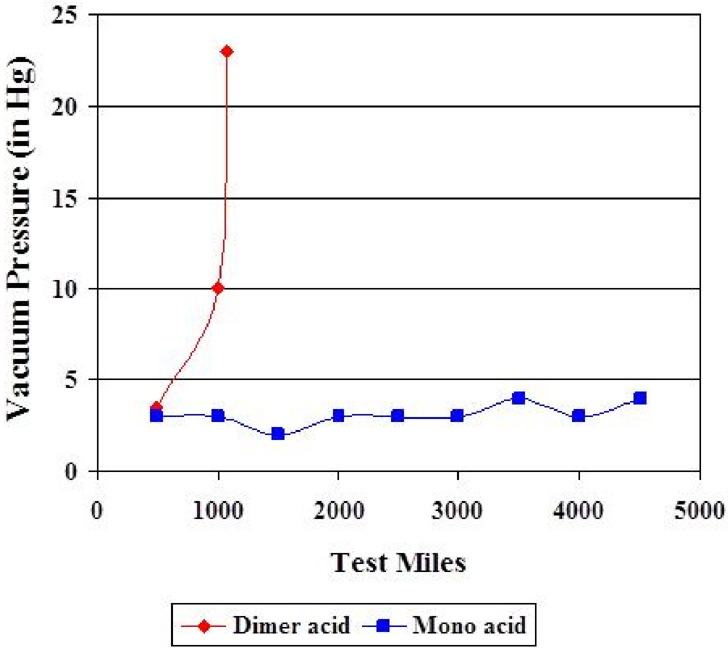

Figure 8: Evaluation of lubricity additive by a heavy duti Caterpillar truck test
(Source: Afton Chemical Ltd)

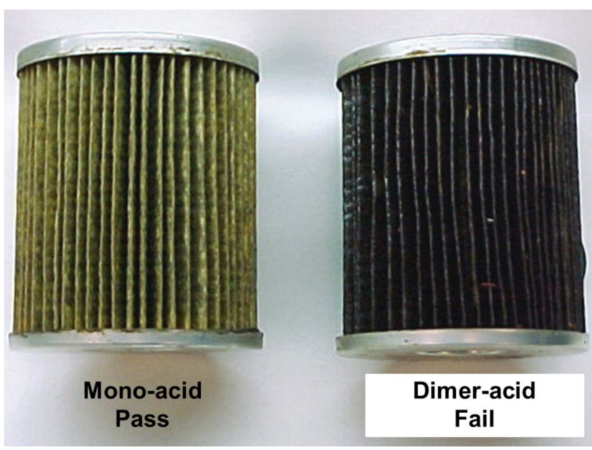

Figure 9: Deposit of lubricity additive on the filters after a heavy duti Caterpillar truck test *(Source: Afton Chemical Ltd)*

The testing conducted at that time together with a better understanding of the mechanism of failure, see Fig. 11 led to a wide acceptance of mono-acidic lubricity additives. The mono-acid lubricity additives were not only seen to be more cost effective than neutral chemistries, but also were proven to not cause field problems. The micelles formed by the dimer acids are oligomeric / polymeric in nature in contrast to the micelles formed by the monoacidic lubricity additives.

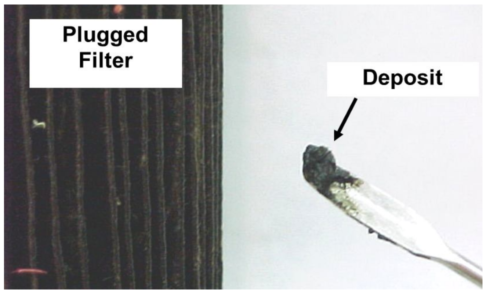

Figure 10: Appearance of deposit and plugged filter *(Source: Afton Chemical Ltd)*

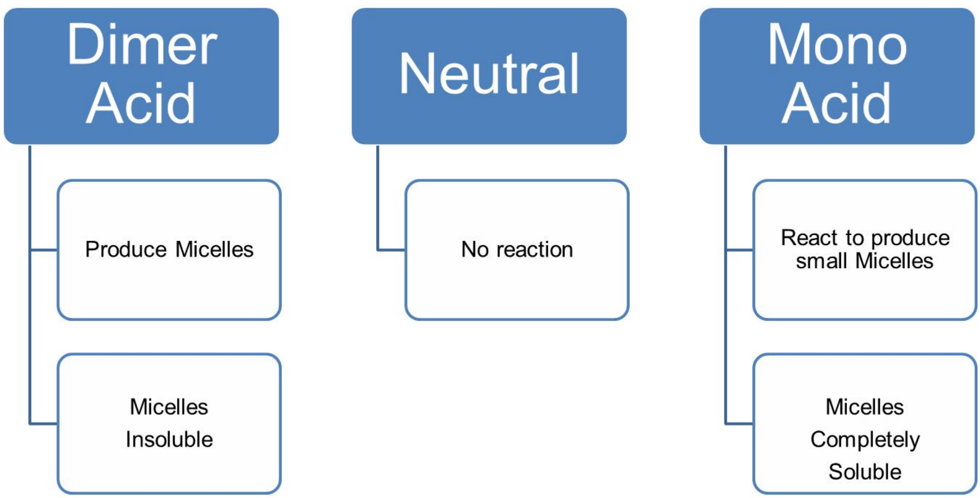

Figure 11: Difference in micelles formation inclination in dimer acid, neutral and mono-acidic lubricity additives *(Source: Afton Chemical Ltd)*

Since the beginning of the new millennium the use on mono-acidic lubricity additives is well established globally and this is partly due to the rigorous approval test procedures that have been established by the DGMK organisation in Germany. This organisation is responsible for approving all additives to be used in German refineries and this protocol has been adopted by many oil and additive companies worldwide.

At the present moment lubricity additives for diesel fuel produced in Germany has to meet the requirements of DGMK research report 531-1 [3]. Once approved, additives are listed on the DGMK approval list. Mono-acidic lubricity additives have been evaluated against the existing test regime specified by the report 531-1 and a summary of the tests and the results is shown in Table 1.

Table 1: Test protocols and results for mono-acidic lubricity additives

Test protocol	Description of test	Pass criteria	Monoacid evaluation
1A Engine oil compatibility	The reference engine oil is heated to 40 °C and then mixed with an equal amount of the additive to be tested. When at room temperature the diesel fuel is mixed with additive/oil mixture and stored at 90 °C for 3 days. The fuel is assessed visually and the filtered according to the SEDAB test.	Mixture should be clear with no indication of chemical reaction and no significant increase in filtration time	Clear & bright Filtration time of base fuel 55 s Filtration time with additive 66 s
1-B Emulsion behaviour	Modified ASTM D1094 test with repeated fuel water contact. Additive tested at 3 times recommended treat-rate	No worse than base fuel	No worse than base fuel at 450 ppm
1-C Storage stability	The neat additive is stored for 28 days at different temperatures	No phase separation or gel by visual inspection	No phase separation
1-D Compatibility with WASA and MDFI	15 g of WASA and 10 g of the additive are mixed in a glass vessel. The mixtures and the individual components (MDFI, WASA and the lubricity additive) are then stored under exclusion of light for 14 days at 20 ± 2 °C. This is then examined visually over time to check for separation After fourteen days storage the mixtures are dissolved at a dosing rate of 250 mg/kg (corresponding to 150 mg/kg WASA and 100 mg/kg lubricity additive) with an additional 300 mg/kg MDFI in diesel fuel containing no additive. Checks are then made to ensure no negative impact on cold flow properties and lubricity performance. Filterability is also checked by SEDAB	Should not impact HFRR performance Should not increase filtration time Should not adversely impact cold flow properties of the treated fuel	No impact on HFRR Base = 63 s + additive = 57 s No impact on cold flow properties No negative interaction with WASA and MDFI
1-E Compatibility with performance additives	Two fuels are tested one treated with performance additive and no lubricity and the same fuel treated with both. The two fuels are then tested for lubricity performance and filtration using SEDAB procedure.	The combination of additives should not negative impact performance	No negative impact
1-F Influence on oxidative stability	500 ml of diesel fuel, containing 5 % RME, is filled into two sealable glass vessels. One sample remains untreated whilst the other sample is treated with the lubricity additive. Both samples are left standing for two weeks at room temperature and then evaluated for oxidative stability by using the Rancimat test.	The difference in results of the two fuels should be less than the repeatability of the test method	Difference of 0.34 hours which is less than repeatability of Rancimat test

These test results mean that mono-acidic lubricity chemistry is capable of meeting the stringent requirements of the DGMK organisation as specified as part of DGMK project 531. There are a number of commercial mono-acidic lubricity additives on the DGMK approved list for use in German refineries.

The storage and handling of lubricity additives

Another important consideration not necessarily addressed by the DGMK test protocol is the handling conditions of the different lubricity additive chemistries. When using a lubricity additive it is important to ensure that the additive remains homogeneous during storage and injection. Some mono-acidic additives have a relatively high cloud point, meaning that precipitation can happen at normal winter ambient temperatures. In this case dilution or heated storage may be required.

Another important consideration is the solubility of the lubricity additive in diesel fuel when exposed to low temperatures. Some lubricity additives are known to have only limited solubility in fuel after prolonged storage at low ambient temperatures.

Conclusion

It is a recognised fact that low sulphur diesel fuel has poor natural lubricity characteristics which can be addressed by the use of lubricity additives. The incorporation of an HFRR requirement in the European EN590 specification means that lubricity additives are regularly used by refineries throughout the European region and in countries exporting to Europe. Initial lubricity additive use in the early 90's led to a number of field problems related to negative interactions between dimer acid lubricity additives and crankcase lubricants but following a thorough investigation the root cause of this issue has been well understood and is exclusively an issue associated with dimer acids.

A number of relevant no harm tests were developed that have led to clear evidence that field issues, when using low sulphur diesel treated with dimer acids, do not occur through the use of mono-acidic lubricity chemistry. The introduction of the DGMK project 531 and the use of proven no harm tests together with extensive refinery use of mono-acidic lubricity additives has led to mono-acid chemistries being accepted as a cost effective and safe option to neutral lubricity additives.

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