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Friction Modifiers for Next Generation Engine Oils

Introduction

Legislation on improving fuel economy and reducing emissions continues to drive innovation throughout the automotive industry, throughout the world. OEMs have adopted numerous technologies to achieve these targets; for example engine downsizing and turbo-charging, hybridisation, improving aerodynamics, light weighting the vehicle, stop-start technology, and a whole host of other technologies.

OEMs and lubricant formulators are also actively working together, seeking new ways to formulate engine oils to minimise parasitic energy losses.

Lubricants can contribute to reducing frictional losses in two ways:

1. reduce the friction associated with churning and pumping of the lubricant (hydrodynamic conditions) by modifying the rheological properties of the oil, achievable by using low viscosity engine oils (which require high quality, low viscosity base oils) and viscosity modifiers
2. reduce friction in the boundary and mixed lubrication regimes through the use of friction modifiers.

Friction Modifiers

Friction modifiers are typically split into two categories; organic and inorganic.

Traditional organic friction modifiers (OFMs) include partial esters and fatty amides such as glycerol mono-oleate and oleyl amide. Following the successful development of a new range of products, Croda can now add polymeric friction modifiers to the range of organic friction modifiers. OFMs typically have a polar head-group which enables the OFM to adsorb onto the metal surface, and a non-polar hydrocarbon backbone which is required to maintain oil solubility and to enable film formation between contacting surfaces.

Inorganic friction modifiers also contain non-organic elements, such as sulphur, phosphorus and molybdenum. Inorganic FMs chemically break down to form products able to chemisorb onto metal surfaces, forming low shear strength films. An example of an inorganic friction modifier that is widely used in Japanese engine oils in particular is molybdenum dithiocarbamate (MoDTC).

Polymeric Friction Modifiers

Over the past 5 years Croda has developed and commercialised a range of organic polymeric friction modifiers (PFMs) that offer exceptional benefits in reducing friction in the boundary and mixed lubrication regimes. Due to their polymeric nature, PFMs effectively have more anchoring points available to adsorb onto the metal surface than conventional organic friction modifiers, which typically have only one or two anchoring points. This alone however isn't the answer to achieving exceptionally low friction; to achieve this requires a unique combination of novel polar head groups with novel oil soluble backbones.

Croda has developed three polymeric friction modifiers, their typical physical properties are shown below:

	Perfad 3000	Perfad 3006	Perfad 3050
Physical Form	Viscous liquid	Viscous liquid	Viscous liquid
Colour	Dark brown	Dark brown	Dark brown
Dynamic viscosity @ 40°C (mPa.s)	10640	6400	114000
Dynamic viscosity @ 60°C (mPa.s)	2730	2000	23300
Dynamic viscosity @ 80°C mPa.s)	990	800	6690
Dynamic viscosity @ 100°C (mPa.s)	440	360	2700
Iodine Value (gl/100g)	25	1.1	6.5
Acid Value (mgKOH/g)	7.5	1.2	4
Density @ 20°C (g/ml)	0.97	0.98	0.97
Flash Point (°C)	270	269	280
Pour Point (°C)	>21	4	>21

Testing Friction Modifier Performance

Historically friction modifier performance has been demonstrated in relatively simple systems; base oil + FM and base oil + zinc dialkyldithiophosphate (ZDDP) + FM. This method has proved very successful in understanding the performance of FMs in combination with such a universally used anti-wear additive. The issue with this type of testing has been that ZDDP is not the only surface active additive in engine oils, one must also evaluate how FMs perform in combination with a range of surface active additives such as detergents and dispersants, viscosity modifiers etc., as well as considering how they perform in different base stocks.

To understand the frictional profiles of commercial engine oils, with and without the addition of polymeric friction modifiers, Croda purchased and tested a wide range of commercial engine oils available in Europe, the United States of America, Japan and other regions of the world. Results from some of these oils will be presented and discussed in this article.

A Mini Traction Machine (MTM) was used to evaluate the frictional properties of the commercially available engine oils. The test profile consisted of determining an initial Stribeck curve (fresh oil, no conditioning of the test ball and disc through rubbing) and a post rubbing Stribeck curve (120 mins rubbing). The profile conditions can be seen in the table below:

Parameter	Value
Temperature	135ºC
Load	36 N (1 Gpa)
Speed	0.005 – 3 m/s
Slide Roll Ratio	0.5
Rubbing Speed	0.05 m/s

A single initial Stribeck curve can be unrepresentative and misleading when testing engine oils and additives. It is essential to understand how the friction of an oil changes over time, i.e. once other surface active additives have been fully thermally and mechanically activated, especially ZDDP. ZDDP anti-wear films are now recognised to comprise of close-packed arrays of solid phosphate glass pads. These robust solid films give excellent wear protection on rubbing surfaces but are themselves relatively high friction surfaces. The main effect of ZDDP on friction is not to increase the boundary friction coefficient at very low speeds, but rather to extend the whole Stribeck curve to the right, so that the contacting surfaces remain in boundary and mixed lubrication regimes over a much wider range of speeds [1-4], this is demonstrated in Figure 1.

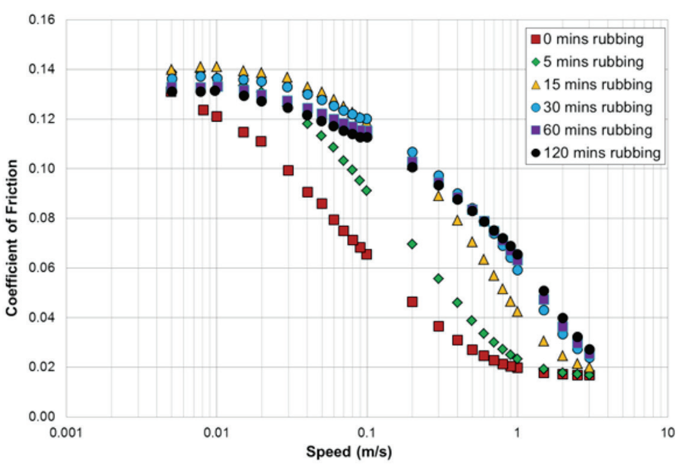

Figure 1: *MTM graph - friction change with increased rubbing time*

The formation of the ZDDP film can be visually observed through optical interferometry techniques. Figure 2 shows the development of a polyphosphate film as a function of rubbing time:

At time 0 mins, there is no observable polyphosphate film.
After 15 minutes we begin to see clearly signs of a polyphosphate film.
As ZDDP chemisorbs onto the surface of the ball the light has to travel further through the additive film, this changes the interference image and we see the film as a dark strip where the ball and disc have been in contact.

The polyphosphate film continues to build as the ball and disc are contacted until a steady state is reached between 60 and 120 minutes rubbing time.

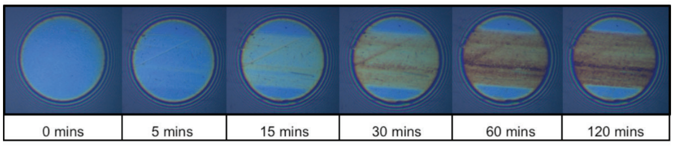

Figure 2: *Interference images with increased rubbing time*

Aside from the first few minutes of an engine's life or under severe wear conditions, the contacting surfaces in an engine should always be protected by a polyphosphate film, hence the need to look at friction both initially and after surface conditioning through rubbing.

Top-Treating Commercially Available Engine Oils with PFMs

Whilst Croda has conducted work in a broad selection of US, Japanese, Chinese, Brazilian and European engine oils, we have selected three commercial engine oils to demonstrate the friction reducing capabilities of Perfad 3000, Perfad 3006 and Perfad 3050. A conventional OFM, glycerol mono-oleate, has been used as a reference organic friction modifier in order to eliminate concentration effects as a variable.

Engine Oil	Viscosity Grade	Specification	Mo Content (ppm)
EU Oil 1	5W-30	ACEA A3/B3, A3/B4, C3	4
EU Oil 2	5W-30	ACEA C3	0
JP Oil 1	5W-20	API SN, ILSAC GF-5	52

Figures 3, 6 and 7 show MTM Stribeck curves for two Mo-free European engine oils and one Japanese engine oil top-treated with 0.5% FM. The dashed lines represent the initial Stribeck curve (no rubbing) and the solid lines represent the final Stribeck curve after 120 minutes rubbing.

EU Oil 1

The frictional properties of EU Oil 1 (Figure 3) are shown in black, the initial friction indicated by a dashed line and the friction after 2 hours rubbing indicated by a solid line. The top-treated oils are also presented similarly but using different colours for each organic friction modifier. With the exception of Perfad 3050, all of the sample oils tested (reference EU oil 1 and EU Oil 1 + friction modifier) showed an increase in friction from no surface conditioning to 120 mins surface conditioning through rubbing. Uniquely, Perfad 3050 provided low friction both initially and after two hours of rubbing.

If we consider the friction profiles of all of the organic friction modifiers, it can be seen that GMO provides a reduction in friction compared to EU Oil 1 of approximately 8% at a speed of 0.005 m/s. Perfad 3000 provides a 13% reduction, Perfad 3006 provides a 40% reduction and Perfad 3050 a 90% reduction. In this particular engine oil and under these conditions, Perfad 3050 has effectively eliminated the boundary regime through the formation of a very low friction film. This suggests that PFMs have the ability to operate under higher load conditions while still maintaining low friction, an area that will be subject to further research.

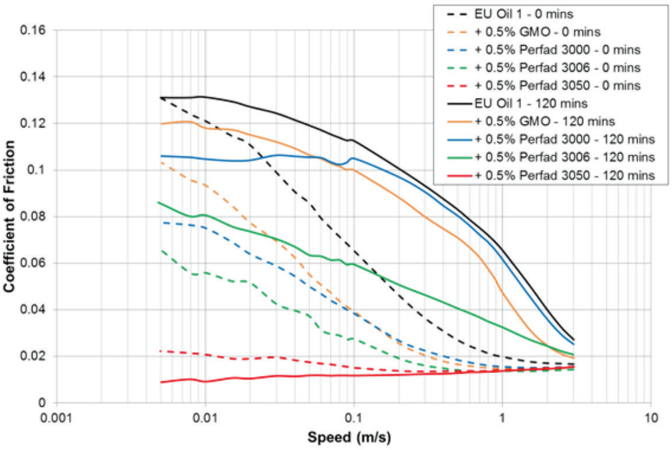

Figure 3: *MTM graph - friction of EU Oil 1 with and without 0.5% FM*

In order to further investigate the activity relationship between PFMs and ZDDP films in EU Oil 1, MTM SLIM images were analysed. Figure 4 shows the interference images of EU Oil 1 with and without GMO, Perfad 3000, Perfad 3006 and Perfad 3050. The first row of images represents the commercial engine oil EU Oil 1. The second row shows that with the addition of 0.5% GMO there is a delay in ZDDP film formation due to GMO adsorbing preferentially onto the metal surfaces. Only after 30 mins rubbing do we begin to observe significant polyphosphate film formation. With the addition of 0.5% Perfad 3006, the development of the ZDDP film is retarded further still but between 30 and 60 minutes we begin to observe a darkening of the image as ZDDP polyphosphate films begin to form beneath the Perfad 3006 FM layer. With the addition of Perfad 3050 the ZDDP film formation is delayed until approximately 120 minutes of rubbing time.

None of the FM top-treated oils appear to have reached a steady state, by which we mean the time when the ZDDP film reaches its full film thickness. Further tests will be conducted to investigate this observation and determine when a steady state is reached with each of the friction modifiers.

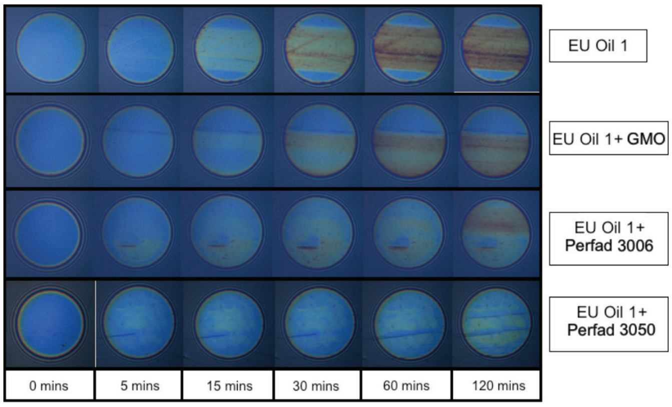

Figure 4: *Interference images of EU Oil 1 + FM with increased rubbing time*

One question that can be justifiably asked is 'once the polyphosphate film has formed, will the PFMs continue to provide low friction?'

The answer to that question appears to be yes. Using a disc which was pre-conditioned with the commercial engine oil EU Oil 1, EU Oil 1 was replaced with EU Oil 1 + 0.5% Perfad 3050. In Figure 5 it can be observed that the coefficient of friction begins to decrease immediately as the polymeric friction modifier begins to adsorb onto the ZDDP film, and it then continues to decrease as the PFM film builds during surface conditioning through rubbing. After 120 mins of rubbing a friction reduction of 75% was observed compared to the friction observed for EU Oil 1 without the addition of organic friction modifier, with a final coefficient of friction of 0.03 at a speed of 0.005m/s.

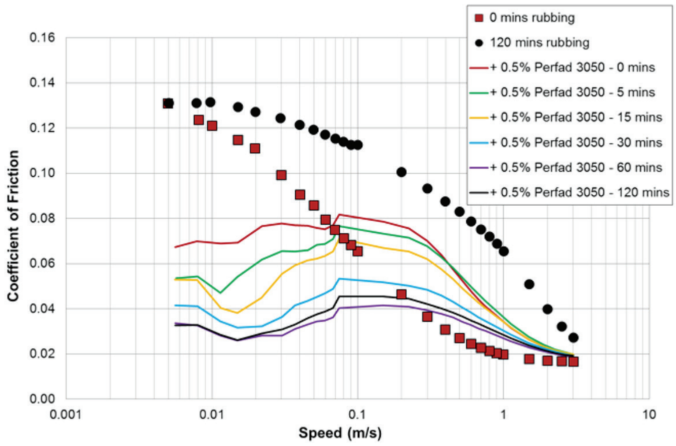

Figure 5: *MTM graph - friction of EU Oil 1 with and without 0.5% FM on ZDDP coated disc*

EU Oil 2

As with EU Oil 1 (Figure 3), the performance of GMO and the PFMs in EU Oil 2 was tested using the same MTM profile (Figure 6). In this formulation we observed different friction reducing performance compared to that observed in EU Oil 1.

GMO provides a reduction in friction compared to EU Oil 2 of approximately 8% at 0.005 m/s, which is similar to the performance of GMO in EU Oil 1. Perfad 3000 provides a 30% reduction, Perfad 3006 provides a 80% reduction and Perfad 3050 gives an 85% reduction, again demonstrating the significant reductions in friction that can be achieved through the use of PFMs under these test conditions.

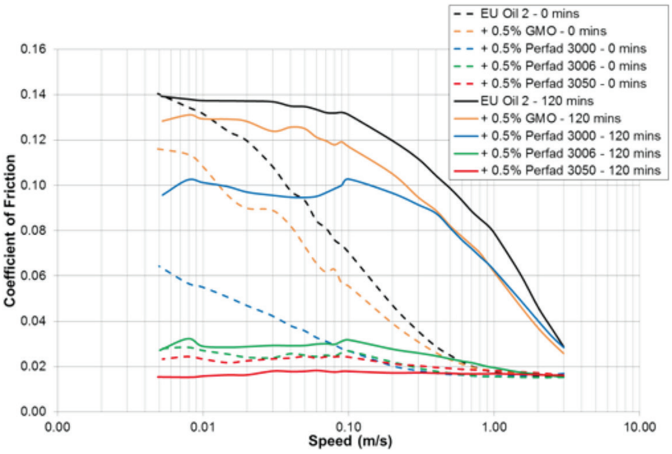

Figure 6: *MTM graph - friction of EU Oil 2 with and without 0.5% FM*

In this formulation, Perfad 3006 is more active and achieved similar levels of friction to Perfad 3050 across the entire speed range.

JP Oil 1

When JP Oil 1 (no additional FM) was tested, there was a significant difference in friction observed between JP Oil 1 and EU Oil 1 and EU Oil 2 after 120 minutes rubbing. The coefficient of friction for both EU Oil 1 and EU Oil 2 at 0.005 m/s was approximately 0.14. In JP Oil 1 the coefficient of friction was determined to be 0.10 at the same speed (Figure 7). This might be an indication that JP Oil 1 already contains a friction modifier that is effective under mixed sliding/rolling conditions.

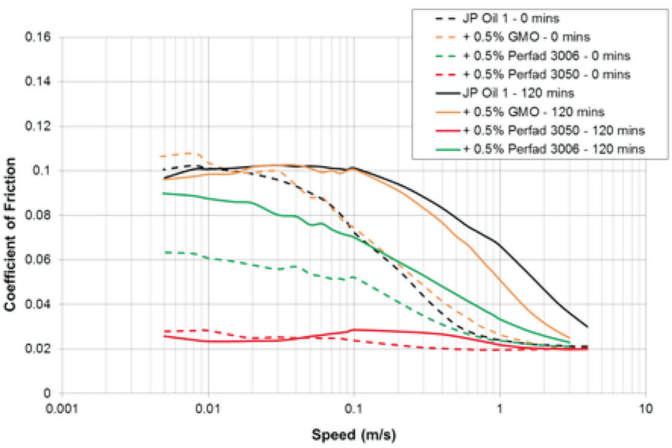

Figure 7: *MTM graph - friction of JP Oil 1 with and without 0.5% FM*

With the addition of 0.5% GMO there was no further reduction in friction when compared with JP Oil 1 across the entire speed range. Perfad 3006 provided a 40% reduction in friction at 0 minutes rubbing but only marginally reduced the boundary friction at 0.005 m/s after 120 minutes. However, if we look to the mixed lubrication regime Perfad 3006 significantly reduces the friction at intermediate speeds, for example by 30% at 0.10 m/s.

Perfad 3050 again provided an exceptional 80% friction reduction at 0.005 m/s and maintained a coefficient of friction of approximately 0.02 across the entire speed range.

Friction Modifier Performance at Lower Temperatures

The results presented so far demonstrate the performance of PFMs at an elevated temperature (135°C). When considering fuel economy and emissions it is also important to understand FM performance at lower temperatures. This is especially the case in Japan and Europe. The New European Drive Cycle (NEDC) comprises a 'Cold Test' to simulate conditions experienced in morning stop-and-go rush hour traffic. Within this test the starting temperature of the oil is 22 ± 2°C and the test is relatively short at 1180 seconds. The testing protocol of the NEDC integrally measures emissions for the presence of CO, CO2, HC, NOx and particulate matters, as well as determining fuel consumption.

To evaluate the performance of FMs at lower temperatures the same MTM profile as described above was used but the temperature of the test was reduced to 60°C (Figure 8). EU Oil 1 was used as the reference engine oil.

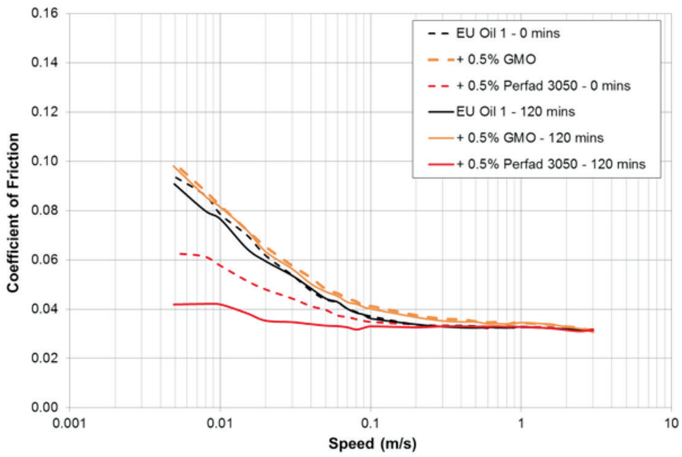

Figure 8: *MTM graph - friction of EU Oil 1 with and without FM at 60°C*

The friction profile of EU Oil 1 initially and after 120 minutes rubbing is effectively the same. If we look at the shape of the two curves it appears that under these conditions the ball – disc contact remains in mixed lubrication even at 0.005 m/s, that is, we have a combination of some asperity to asperity contacts and some separation of asperities by an oil film. The addition of GMO at 0.5% has no consequential effect on frictional performance at this temperature.

What is intriguing is that the addition of Perfad 3050 causes a significant reduction in friction at slower speeds (approximately

55% after 120 minutes rubbing at a speed of 0.005 m/s), indicating the formation of a low friction film is feasible with polymeric friction modifiers even under these lower temperature conditions.

Molybdenum Containing Engine Oils + Polymeric Organic Friction Modifiers

Although not restricted to Japan, the use of MoDTC is a technology that is becoming widely used in that particular region. Some of the newer Japanese engine oils have been analysed and found to contain levels up to 1200 ppm Molybdenum.

MTM tests were conducted using a Japanese engine oil containing 788 ppm Molybdenum to determine its friction profile:

Engine Oil	Viscosity Grade	Specification	Mo Content (ppm)
JP Oil 2	0W-20	API SN, ILSAC GF-5	788

JP Oil 2 was tested using the 135°C MTM profile and tested again after top-treating with Perfad 3050 (Figure 9).

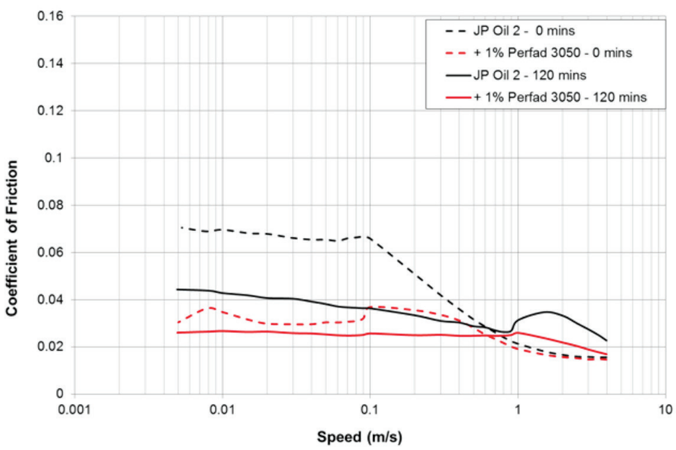

Figure 9: *MTM graph - friction of JP Oil 2 with and without 0.5% FM*

Unlike the engine oils shown in Figures 3, 6 and 7 the friction of JP Oil 2 did not increase with rubbing time, in fact it decreased. This can be explained by considering the mechanism of inorganic FMs like MoDTC. Investigations into MoDTC have shown that under rubbing conditions they can break down to form MoS_2 on metal surfaces. MoS_2 forms a layered lattice structure with low shear strength and low boundary friction properties [5-7].

Figure 9 shows that the coefficient of friction of JP Oil 2 is reduced from 0.07 to 0.04 at 0.005 m/s after 120 minutes of rubbing. With the addition of Perfad 3050 to JP Oil 2 the coefficient of friction without rubbing is reduced to approximately 0.02 at 0.005 m/s, and remains at 0.02 after 2 hours of surface conditioning through rubbing, a 60% reduction compared to the original engine oil. It is interesting to consider whether the low friction result for JP Oil 2 + 0.5% Perfad 3050 after 120 minutes rubbing is due to the PFM (as is observed in Mo-free oils, as previously described), or the MoDTC, or to a synergy which may be occurring between the two.

Controlled Polymeric Friction Modifier and MoDTC Interactions

To begin to assess potential synergistic effects (or indeed antagonistic effects) between PFMs and MoDTC, a number of experiments were conducted using the MTM (135°C) and the High Frequency Reciprocating Rig (HFRR). EU Oil 1 was selected as the reference oil as it contains 0 ppm Mo. EU Oil 1 was then top-treated with either GMO, Perfad 3050, MoDTC, or Perfad 3050 in combination with MoDTC.

Figure 10 shows the 120 minutes rubbing results using the 135°C MTM profile.

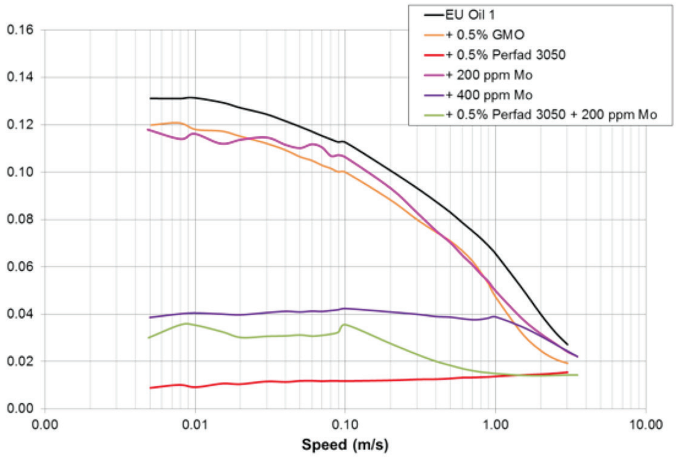

Figure 10: *MTM graph - friction of EU Oil 1 with and without 0.5% FM and Mo (120 mins)*

As shown in Figure 10 the coefficient of friction of EU Oil 1 is approximately 0.13 at 0.005 m/s. With the addition of GMO and 200 ppm Mo the reduction in friction is approximately 8%. 400 ppm Mo reduced the friction by 70%, demonstrating that to gain frictional benefits under these conditions the dose rate of Mo must be over 200 ppm. As previously described, 0.5% Perfad 3050 reduced the friction by 90%.

The most interesting result is perhaps seen when 0.5% Perfad 3050 is combined with 200 ppm Mo, the friction curve for this combination lies between 200 ppm Mo and 0.5% Perfad 3050. However this result is inconclusive as to whether we are observing an improved performance over Molybdenum or antagonism (reduced performance) compared to Perfad 3050 alone.

Molybdenum-containing engine oils generally perform well under reciprocating conditions, such as in the HFRR tests. Using the following conditions, the same oil blends were tested using the HFRR to see if this test could shed any light on the improved performance / antagonism between MoDTC and PFMs.

Parameter	Value
Temperature	135°C
Load	4 N
Frequency	20 Hz
Stroke Length	1 mm
Time	60 mins

The HFRR results are shown in Figure 11.

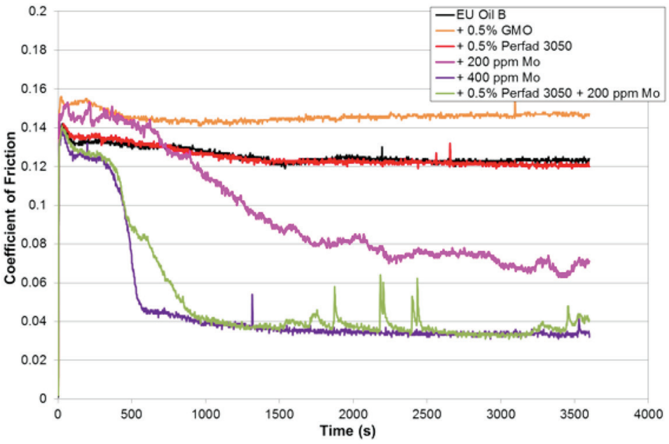

Figure 11: *HFRR graph - friction of EU Oil 1 with and without 0.5% FM and Mo*

After 60 minutes of reciprocating contact the coefficient of friction of EU Oil 1 was measured at 0.12. GMO actually caused an increase in friction compared to EU Oil 1 and whilst Perfad 3050 did not cause an increase in measured friction, neither did it provide a reduction in friction relative to EU Oil 1.

As expected, Molybdenum performed very well in the HFRR tests. EU Oil 1 + 200 ppm Mo reduced the friction of the reference oil by approximately 40% after 60 minutes. EU Oil 1+ 400 ppm Molybdenum reduced the friction by approximately 70%.

The most surprising result however was observed for a combination of 0.5% Perfad 3050 and 200 ppm Mo, achieving a performance level similar to that of EU Oil 1 + 400ppm Molybdenum, indicating that there may indeed be some synergies to be exploited through the use of polymeric friction modifiers and MoDTC. This observation requires much more detailed investigation but is an intriguing result nevertheless.

Summary

In summary, Organic PFMs demonstrate unique frictional characteristics in a wide range of engine oils, from many different geographical regions. Polymeric friction modifiers can provide exceptionally low coefficients of friction in Mo-free and Mo-containing engine oils at high temperatures (135°C) and they are also providing encouraging friction reducing properties at lower temperatures (60°C). Croda's PFMs form low friction films which have the potential to carry higher loads than conventional organic friction modifiers.

Polymeric friction modifiers are unique and provide formulators with a new range of tools to achieve the ever more demanding targets of improved fuel economy and reduced emissions. In offering a range of polymeric friction modifiers, it is Croda's intention to enable formulators to develop high performance engine oils no matter which base oils or additives are used.

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