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ORIGINAL PAPER

Friction Modifier Additives, Synergies and Antagonisms

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Abstract

There is growing interest in reducing friction in lubricated machine components to thereby increase the energy efficiency of machines. One important way to minimise friction is to employ friction modifier additives to reduce friction in thin film boundary lubrication conditions. There are currently three main types of friction modifier additive, organic friction modifiers, oil soluble organomolybdenum friction modifiers and functionalised polymers. In common practice, a single such additive is generally employed in a formulated lubricant, but it is of interest to explore whether combinations of two friction modifier additives may prove beneficial. In this study, the performance of eight commercial friction modifier additives spanning all three main types was first measured in three quite different friction tests. The aim was to identify the contact conditions under which each additive was most effective. Additive solutions in both a base oil and a formulated engine oil were investigated. In general, functionalised polymers were most beneficial in sliding–rolling contacts, while oil soluble organomolybdenum friction modifiers worked best in severe, reciprocating sliding conditions. However, all friction modifier additive response was strongly affected by the other additives present in formulated engine oils. The friction performance of combinations of friction modifier additives was then explored. When two different friction modifiers additives were combined in solution, several possible outcomes were observed. The most common was for one of the additives to predominate, to give friction that was characteristic of that additive alone, while in some cases friction lay between the values produced by either additive on its own. In a few cases the additives behaved antagonistically so that the combination gave higher friction than either additive by itself. In a few cases true synergy was observed, where a combination of two additives produced lower friction in a given test that either individual component at the same overall concentration. Another, and possibly more important synergy could also occur, however, when a pair of FMs worked more effectively than either individual additive over the range of test conditions present in different friction tests. This study suggests that optimal combinations of FMs may provide a means of reducing boundary friction and thus increasing the efficiency of machines, especially if the latter contain a range of lubricated machine components that operate with different types of tribological contacts.

Keywords Friction modifier additive · Synergy · Antagonism · Organic friction modifier · OFM · MoDTC, molybdenum friction modifier · Functionalised polymer additive · Boundary friction · HFRR · MTM

1 Introduction

Concern for the global environment has led to growing interest in increasing the energy efficiency of all types of machines. This in turn has led to the need to reduce friction in most lubricated machine components. One very important way to minimise friction has been to use lower viscosity lubricants so as to reduce hydrodynamic friction losses, but a second, complementary approach has been to employ friction modifier additives to reduce boundary friction.

There are several types of such friction modifiers, with the most important being organic friction modifiers, oil soluble organomolybdenum friction modifiers and functionalised polymers [1]. As outlined below, research has shown that these work in quite different ways. Because of this they may act most effectively in different contact conditions and thus behave in a complementary fashion; such behaviour is often called synergism. However, since they all involve interaction with rubbing surfaces it is also possible that they may interfere with one another, so-called antagonism. Such possibilities are

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important since it means that friction modifier combinations may be more or less effective than individual ones at reducing boundary friction. The aim of this paper is to explore whether, indeed, different friction modifier additive may be synergistic or antagonistic. However, since different friction modifiers are likely to be most effective under different rubbing conditions, it is not sufficient to explore possible synergies and antagonisms in just one type of lubricated contact. A secondary aim of this paper is thus to compare friction modifier behaviour, and the behaviour of combinations of friction modifiers, in a variety of contact conditions.

2 Background

2.1 Friction Modifier (FM) Additives

Currently there are three types of friction modifier additive in common use, organic friction modifiers, oil soluble organomolybdenum additives and additives based on functionalised polymers [1].

Organic friction modifiers (OFMs) have an amphiphilic molecular structure with a polar head group that adsorbs on polar metal or ceramic surfaces and a long, straight hydrocarbon tail that aligns outward into the lubricating oil to form a hydrocarbon surface having low shear strength against a similar, opposing surface. This is shown schematically in Fig. 1a [1]. It is generally presumed that in order to most effectively reduce friction, OFMs must form quite dense monolayers so as to enable lateral van-der Waal attraction between adjacent, vertically oriented, hydrocarbon chains [2–4]. However, some recent work has suggested that even loosely packed films may significantly reduce friction [5, 6]. OFM films form extremely rapidly, limited only by the rate of diffusion of their molecules from lubricant to surface and subsequent organisation [7]. A number of studies have shown that they have a temperature limit, with friction reduction being lost above a critical temperature [8]. For physisorption, this represents a desorption temperature, while, if a chemical adsorption has occurred, as in fatty acid absorption on some metals, it corresponds to the melting point of the soap [9]. There is also some evidence based on AFM studies of OFMs having a critical pressure limit at which the close-packed molecular film collapses [10].

Organomolybdenum additives (MoFMs) react to form nanocrystals of MoS_2 at the extreme conditions present as asperity contacts when rough surfaces slide together and, because MoS_2 has a layer-lattice structure, these nanocrystals provides a low shear strength surface and thus very low boundary friction [1]. Figure 1b shows a 400 nm × 400 nm lateral force image of a MoFM tribofilm; the dark regions represent the low friction nanocrystals [11]. Some MoFMs such as the molybdenum dithiocarbamates (MoDTCs) and molybdenum dithiophosphates (MoDTPs) already contain an atomic grouping in which at least two sulphur atoms are bonded to a molybdenum atom, which probably provides the basis of the final MoS_2 reaction product. However, some MoFMs contain no sulphur and are only effective when used in conjunction with sulphur-containing additives such as an extreme pressure additives or some detergents. An important feature of MoFMs is that they only form MoS_2 at quite severe contact stresses, which in practice means that they only form when asperity–asperity contact takes place [12, 13]. This has the advantage that MoS_2 is formed only where it is needed to reduce boundary friction, on the load-supporting high spots of surfaces [11]. However, it means that with smooth surfaces, MoFMs only reduce friction at quite high loads, when any micro-EHD films that might otherwise separate asperities break down. Another feature of MoFMs is that if the supply of MoFM is halted, friction reduction is lost very rapidly, implying that the MoS_2 film is lost or transformed to a higher shear strength material such as an oxide unless continually replenished [14].

The first polymer friction modifiers (PFMs) were developed adventitiously as viscosity modifiers with a supplementary dispersant capability due to the inclusion of polar aminic groups; their ability to adsorb on rubbing surfaces and thus reduce friction was only recognised in the 1990s [15]. Recently, polymeric additives have been developed specifically to act as friction modifiers [16]. PFMs are generally based on a block polymer structure, with a block containing a high proportion of polar monomers, attached to a longer block of primarily non-polar monomers. The polar segment then bonds to polar metal or ceramic surface while the non-polar block reaches into the adjacent oil to form a

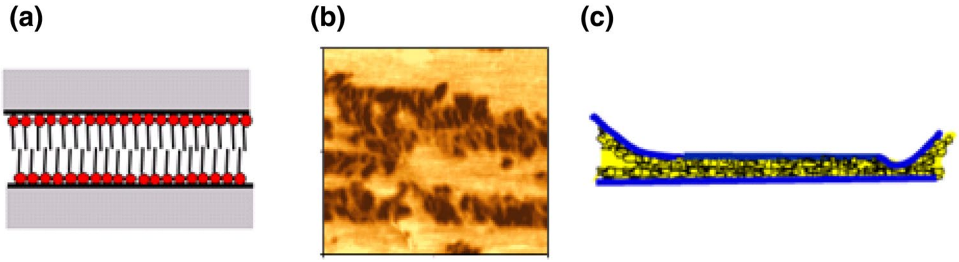


Fig. 1 Schematic diagram of three main types of friction modifier film

thin fluid layer of enhanced viscosity [17]. This layer then acts in a quasi-hydrodynamic fashion to maintain separation of the rubbing surfaces as shown in Fig. 1c. Most PFMs are relatively ineffective in low speed conditions since they are not strong enough to maintain separation of surfaces against high pressures. However, because they create a highly viscous layer they promote fluid entrainment and thus formation of a hydrodynamic or elastohydrodynamic film at lower rubbing speeds that would otherwise be the case [18].

2.2 Synergy and Antagonism

A key problem in formulating lubricants is that lubricant additives can often perform quite differently when in combination than they do when tested individually in a base oil [19]. If a combination of two additives provides better performance than the individual additives alone (e.g. gives less wear or slower oxidation), the additives are loosely said to be synergistic; if they give poorer performance, they are said to be antagonistic. More precisely, synergism is defined as occurring when a combination of two additives gives better performance than both of the individual additives alone when the latter are used at a concentration which is the sum of the concentrations of the two additives employed in the combination. Antagonism is less formally defined but is generally considered to occur when the performance of an additive in combination with a second additive is worse than its performance when used alone at the same concentration.

A review of additive interactions was given in [20]. This suggests that there are four main underlying mechanisms by which synergism/antagonism can arise. One is direct additive interaction in the liquid phase that may be physical or chemical, and may be beneficial or harmful. A well-known antagonism is the negative impact that aminic dispersants can have on the antiwear performance of ZDDP which is believed to arise in part from the additives forming a complex in solution to reduce the chemical activity or adsorption of the ZDDP molecules. The second mechanism is interaction at rubbing surfaces such as co-adsorption, competing adsorption or interaction of one additive with the tribofilm formed by another. For example it has been found many rust inhibitors are antagonistic to the action of extreme pressure additives since they block surface sites. It has also been shown that the friction modifier MoDTC forms MoS_2 more easily on rough ZDDP tribofilms than on smooth steel and that the ZDDP film may protect the MoS_2 from removal, thus increasing the durability of this additive.

The above two types of synergy/antagonism involve direct molecular interaction of pairs of additives, between themselves or their reaction products. There are also two more subtle mechanisms that do not involve such direct interaction [20]. In one, additives of the same class can each contribute a different beneficial effect whose sum is greater than its parts. For example a combination of peroxide-decomposing and radical-inhibiting antioxidants is well known to be generally much more effective than either separately since they attack different stages of the hydrocarbon oxidation cycle. Finally there is graded response in which a combination of different additives of the same class extend the overall performance because each component is active under slightly different conditions, thus providing superior performance over a range of operating conditions. Mixtures of different ashless phosphorus-based antiwear additives may achieve this, by being active over a wider temperature range than either structure alone. This effect is probably also the reason that impure additives often work better than carefully purified ones.

There is very little published work on the performance of combinations of friction modifiers and whether such combinations exhibit synergistic or antagonistic response. One patent suggests that combinations of aminic/amidic surfactant with ester/alcohols ones are synergistic when tested in a ball on cylinder tribometer [21]. Here both of the additives are OFMs. In 2007 Muller et al. explored the friction behaviour of combinations of PFMs with MoDTC and MoDTP in both reciprocating and rolling–sliding contact [22]. For both MoFMs they found that the combinations gave lower boundary friction that the individual additives. In rolling–sliding contact the PFMs appeared to promote low friction film formation by the MoFMs. The authors also found that an amine-based OFM suppressed the effectiveness of PFMs.

A recent study measured the friction behaviour of combinations of MoDTC with several fatty amine-based OFMs [23]. Some OFMS were found to greatly reduce the concentration of the MoFM needed to be effective. In some cases the MoDTC improved the performance of the fatty amines and in other not; differences were ascribed to whether the OFMs inhibited the formation of MoS_2.

From the above it should be evident that the various types of friction modifier may be synergistic or antagonistic but that information in this area is quite sparse. The current study aims to extend this knowledge by examining combinations of the three main types of commercial FM.

3 Test Materials

Eight commercial friction modifier additives were studied as listed in Table 1. The two MoDTCs were from different suppliers. These additives were blended into two fluids:

(i) GTL4 base oil with dynamic viscosity $\eta_{40C} = 14.8$ cP, $\eta_{100C} = 3.1$cP
(ii) Fully formulated engine oil with dynamic viscosity $\eta_{40C} = 42.6$ cP, $\eta_{100C} = 7.4$ cP.

Table 1 Friction modifier additives studied

FM type	Abbreviation: description
OFMs	Amide: oleylamide
	GMO: glyceryl monooleate
MoFMs	Moly 1: molycarbamate trimer
	Moly 2: molybdenum dialkyldithiocarbamate (MoDTC)
	Moly 3: molybdenum dialkyldithiocarbamate (MoDTC)
PFMs	Poly: low MWt polymer FM
	VM 1: functionalised PMA viscosity modifier
	VM 2: functionalised OCP viscosity modifier

Table 2 FM solutions in GTL4 studied (a corresponding set in formulated engine oil was also studied)

Base fluid	FM1	FM2
GTL4	Amide, 1.5% wt	–
GTL4	GMO, 1.5% wt	–
GTL4	Moly 1, 500 ppm Mo	–
GTL4	Moly 2, 500 ppm Mo	–
GTL4	Moly 3, 500 ppm Mo	–
GTL4	VM 1, 1.5% wt	–
GTL4	VM 2, 1.5% wt	–
GTL4	Poly, 1.5% wt	–
GTL4	Amide, 0.75 wt %	GMO, 0.75 wt %
GTL4	Moly 2, 250 ppm Mo	GMO, 0.75% wt
GTL4	Moly 2, 250 ppm Mo	Amide, 0.75% wt
GTL4	Moly 2, 250 ppm Mo	VM 1, 0.75% wt
GTL4	Moly 2, 250 ppm Mo	Poly, 0.75% wt
GTL4	GMO, 0.75% wt	Poly, 0.75% wt

The formulated oil was an FM-free, 5W30 Heavy-Duty Diesel engine oil designed for fuel economy.

Each FM was blended individually in the two oils at 1.5% wt for the OFMs and the PFMs and 500 ppm Mo for the MoFMs. In order to identify synergies, six blends also contained two of the FMs at half these concentrations. Table 2 lists the FM blends in GTL4 and a similar set were prepared in the formulated engine oil. It should be noted that this study does not study formal antagonism; this would have required measurement of the performance of blends in which one of the FMs had the same concentration as in its individual solution, while the concentration of the other was undefined. In this study, the term *apparent antagonism* is therefore used to describe a combination that gave higher friction than a solution of either individual component tested at double its concentration in the blend.

4 Test Methods

Three different friction tests were carried out on each fluid, a reciprocating HFRR test, a unidirectional, slow speed sliding ball-on-disc friction test and a rolling–sliding MTM Stribeck curve test. All tests used hardened AISI 52100 steel test specimens and these were cleaned in an ultrasonic bath in acetone followed by Analar toluene before testing.

4.1 HFRR Test

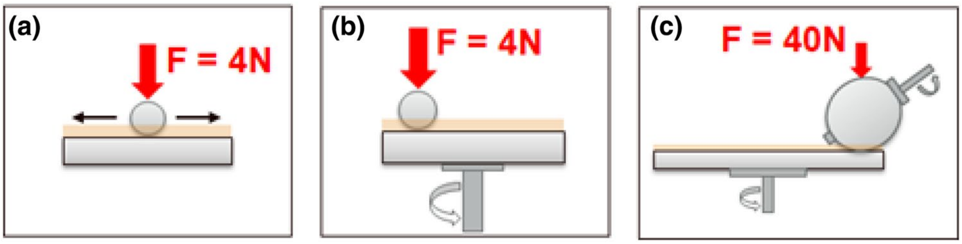
A high-frequency reciprocating rig (HFRR, PCS Instruments) was used to measure the friction properties of the test oils over a 2 h test. In this, a 6-mm-diameter steel ball is loaded against the flat surface of a sinusoidally reciprocating steel disc, as shown schematically in Fig. 2a. Test conditions were stroke frequency = 50 Hz, stroke length = 1 mm, load = 4 N, temperature 100 °C. The AISI 52100 balls had hardness 880 Hv and root-mean-square roughness 5 nm, while the disc counter-surface hardness and roughness were 790 Hv and 5.5 nm, respectively. The nominal maximum Hertz pressure was 1.04 GPa. This test rig measures friction every second throughout a test and in this study mean friction coefficient values were calculated by averaging over a test, excluding measurements during the first 10 min.

Under the test conditions used the mean sliding speed was 0.1 m/s, corresponding to a theoretical elastohydrodynamic (EHD) film thickness based on the Dowson and Chittenden equation [24] of 2.5 nm for GTL4 and 4.5 nm for the formulated oil.

4.2 Pin-on-Disc Test

A CETR UMT-2 tribometer was employed to measure friction at unidirectional, very low sliding speed. A ball-on-disc configuration was used, with a 6-mm-diameter HFRR ball loaded against the flat surface of a rotating steel disc,

Fig. 2 Schematic diagrams of the three friction test set-ups



as shown schematically in Fig. 2b. The disc hardness and roughness were 810 Hv and 8.5 nm, respectively. In a test, the sliding speed was gradually decreased in stages from 5 mm/s to 0.3 µm/s and friction measured at each speed stage. The applied load was 4 N and the test temperature 86 °C.

At the maximum sliding speed of 0.005 m/s, the theoretical EHD film thickness is 0.25 nm for GTL4 and 0.45 nm for the formulated oil, so that the whole test operated in full boundary lubrication conditions.

4.3 MTM Test

In the MTM (MTM, PCS Instruments), a 19-mm-diameter steel ball is loaded and rotated against the flat surface of a rotating steel disc immersed in lubricant, as shown in Fig. 2c. Ball and disc are driven by separate motors so that any combination of sliding and entrainment speed can be obtained, and in this work this facility was used to obtain Stribeck curves in which friction was measured over a range of entrainment (mean rolling) speed while maintaining a fixed ratio of sliding to rolling. The resulting curves show how friction coefficient varies with increasing entrainment speed and thus EHD film thickness. In this study, two Stribeck curves were obtained for each fluid, one at the start of a test and one after 2 h slow speed rubbing. The conditions for each Stribeck curve were entrainment speed over the range 3–0.005 m/s, slide-to-roll ratio (ratio of sliding to entrainment speed) = 0.5, load = 40 N, temperature 100 °C). Between the first and second Stribeck curves, ball and disc were rubbed in slow entrainment speed conditions (entrainment speed = 20 mm/s, slide-to-roll ratio = 0.5, load = 40 N, temperature = 100 °C). The nominal maximum Hertz pressure was 1.03 GPa. The AISI 52100 balls had hardness 850 Hv and root-mean-square roughness 5.5 nm, while the disc counter-surface hardness and roughness were 835 Hv and 11 nm, respectively.

The entrainment speed range of 3 m/s to 0.005 m/s corresponds to a theoretical EHD film thickness range from 36 to 0.5 nm for GTL4 and 65 nm to 0.8 nm for the formulated oil. Thus, the Stribeck curves span the range of conditions from full EHD lubrication to nearly full boundary lubrication.

5 Results: Single Additive Blends

5.1 FMs in GTL4

Figure 3 compares the mean friction coefficients measured in the HFRR for the individual FM solutions in the base oil GTL4. Moly 1 was not soluble at the concentration used, though it should be noted that this molythiocarbamate trimer is generally used at lower concentrations in lubricant formulation than the conventional MoDTCs. The two most effective FMs under these conditions are Moly 2 and Poly. Three of the FMs are quite ineffective, Moly 3 and the two functionalised VMs. This difference between the MoDTCS is quite striking for two nominally similar additives. The two OFMs both reduce friction, the Amide more than the GMO. Figure 4 shows HFRR friction traces for each additive and indicates that friction reduction for GMO, Amide and Moly 2 is very rapid. Examination of friction in the first few seconds indicated that friction actually dropped to a stable value within one second (50 cycles) for the OFMs and the MoFM but took about 20 s for Poly.

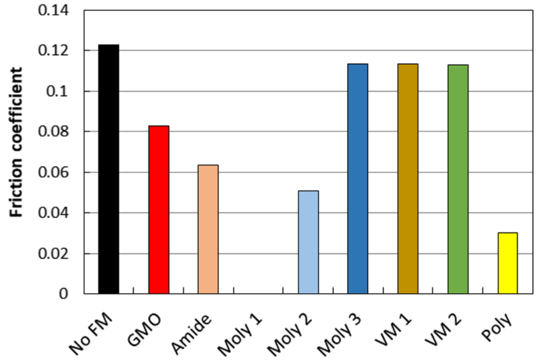


Fig. 3 HFRR mean friction values for individual FM solutions in GTL4 (Moly 1 was not soluble at the concentration and temperature used)

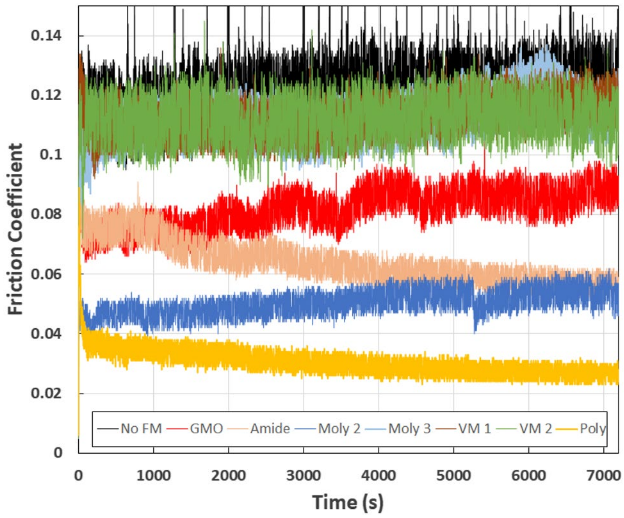


Fig. 4 HFRR friction traces for individual FM solutions in GTL4. Moly 2, VM 1, VM 2 and no FM have friction coefficients between 0.10 and 0.14 and overlay one another

Figure 5 shows friction coefficient versus sliding speed in the CETR tests. It is noteworthy that the FM-free GTL4 has much higher friction in this test than in the HFRR. This is because the very low sliding speed means there are no

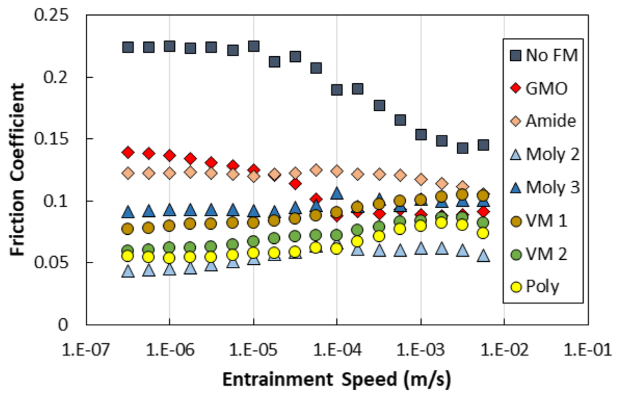


Fig. 5 Slow speed unidirectional sliding CETR friction tests for individual FM solutions in GTL4

micro-EHD effects; the contact is in full boundary lubrication conditions where, in the absence of a protective additive film, asperity adhesion occurs. At the highest speed, the friction falls closer to the HFRR level as some asperities become separated by a very thin fluid film. In these unidirectional, very low speed conditions Poly and VM2 are very effective at reducing boundary friction, but become less so as the speed increases, possibly because the adsorbed films start to be lost as shear in the contact increases. As in the HFRR, Moly 2 is very effective and Moly 3 much less so. The two OFMs are not very effective at reducing friction especially at very slow sliding speed, and this may reflect an inability to withstand high, quasi-static load.

Figure 6 shows MTM friction coefficient versus entrainment speed curves at the start and end of a test for the individual FM solutions in GTL4. At the beginning of the test the three PFMs are highly effective, Poly and the OCP-based functionalised VM more so than the PMA-based one. This ability of functionalised polymers to reduce low speed friction in rolling–sliding conditions has been noted previously on several occasions [15, 17, 25]. Moly 2 is quite ineffective, presumably because asperity stresses are not severe enough to stimulate its reaction to MoS_2. Moly 3 shows lower friction at low speeds but it is not clear if this represents MoS_2 formation; it may be due to polar impurities in the additive acting as a weak OFM. Amide is quite effective at reducing friction but the GMO much less so. A similar ordering of the Amide and GMO has been noted previously in the MTM [26].

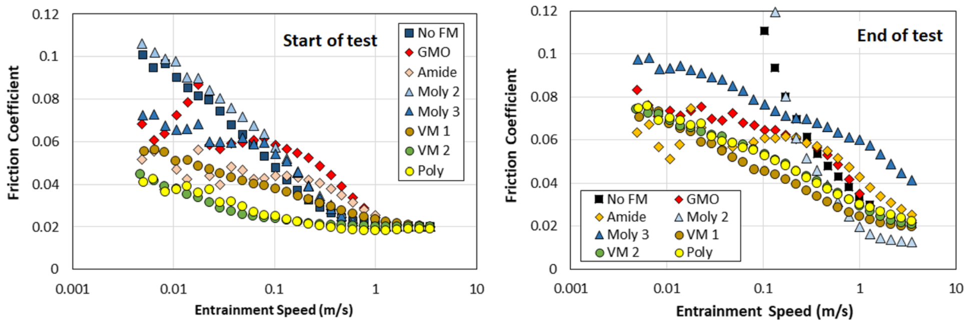
At the end of 2 h slow speed rubbing, all FMs have become less effective, though most still reduce friction to some extent, compared to the FM-free base oil and the Moly 2 solution that both show very high boundary friction. This is probably because the roughness of the ball and disc have increased, as is evident from the friction coefficient at high entrainment speeds. In the Stribeck curves taken at the start of the tests this is low at 0.02 and is the same for all test fluids; it represents full EHD lubrication. However, the Stribeck curves after 2 h rubbing suggest that full EHD film lubrication is barely reached even at the highest entrainment speed. Thus, for most FM solutions, the difference between the start and end of test Stribeck curves effectively represents a shift to higher speed caused by an increase in roughness and thus increase in proportion of boundary lubrication at a given speed. The reason for the very low EHD friction of Moly 2 at end of test is not known.

5.2 FMs in Formulated Engine Oil

Figure 7 shows HFRR friction results for the FMs in formulated engine oil. In this case Moly 1 is soluble at the concentration used. The behaviour of the various FMs follow broadly the same pattern as in GTL4, with the OFMs being quite effective, two of the MoFMs very effective and the two functionalised VMs ineffective. The main differences are (i) Moly 3 is now showing a significant friction reduction; MoFMs are generally found to work better when ZDDP is present in the oil as is almost certainly the case here, and (ii) Poly is much less effective, probably because of competition for the surfaces by other additives present in a formulated engine oil.

Figure 8 shows slow speed pin-on-disc results for the FM solutions in engine oil. It should be noted that the y-axis scale is quite different from that of the results in GTL4 in Fig. 5 since the FM-free engine oil has much lower boundary friction than FM-free base oil, as might be expected

Fig. 6 MTM Stribeck curves for individual FM solutions in GTL4



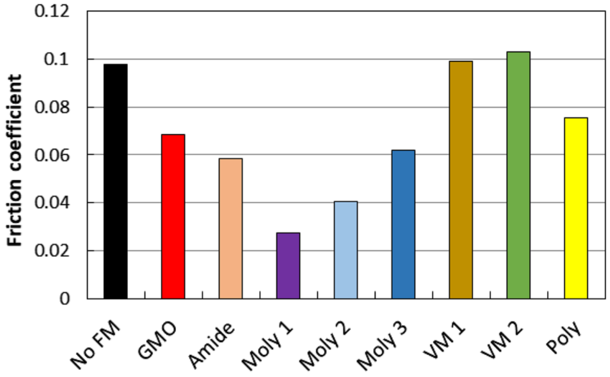


Fig. 7 HFRR mean friction values for individual FM solutions in formulated engine oil

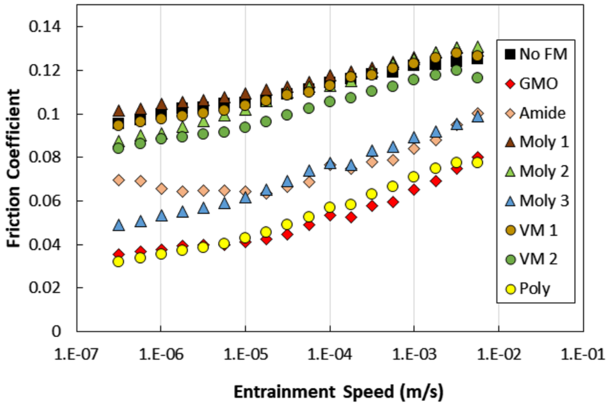


Fig. 8 Slow speed unidirectional sliding friction tests for individual FM solutions in engine oil

since the engine oil contains surface active additives that will adsorb to some extent. When this scale difference is allowed for, the slopes of friction versus sliding speed for most of the FM blends in engine oil are actually quite similar to those in GTL4 shown in Fig. 5.

In engine oil the two functionalised polymers are now quite ineffective in reducing boundary friction as are Moly 1 and Moly 2. The two OFMs, which were not very effective in GTL4, are now able to reduce boundary friction, especially GMO. Poly retains its ability to reduce friction when dissolved in formulated engine oil. Moly 3 reduces friction at very slow speed. The shape of this response, where friction increases with sliding speed, is more reminiscent of OFM behaviour that that normally seen with MoFMs and may represent adsorption rather than reaction to MoS_2.

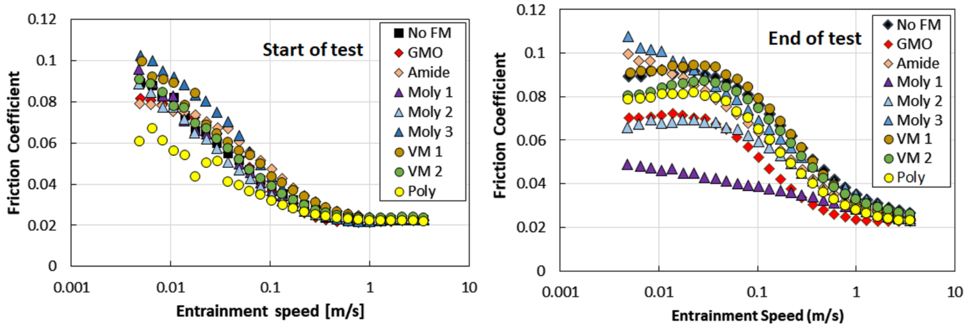
Figure 9 shows MTM Stribeck curves at the beginning and end of 2 h of rolling–sliding at low entrainment speed. Unlike in base oil, at the start of the test the functionalised polymers show almost no ability to reduce slow speed friction while the OFMs are only marginally effective. Only Poly provides significant friction reduction. Presumably the other additives present in an engine oil, in particular the dispersant and detergent, are interfering with the various FMs. The end-of-test Stribeck curves show very clearly the effect of growth of a ZDDP film, which is well known to produce a rough tribofilm that inhibits fluid entrainment; hence much extending the boundary lubrication regime [27–29]. GMO and Moly 2 clearly reduce the boundary friction of this ZDDP tribofilm while Poly and VM 2 do so to a lesser extent. Moly 1 gives a remarkably low boundary friction that has the effect of reducing friction across the whole boundary and mixed part of the Stribeck curve.

6 Results: Blends of Two FMS

The three types of friction test were carried out on all six FM combinations listed in Table 2. Within a given test there were few examples of synergy or antagonism. An example of apparent antagonism is seen in Fig. 10, where a combination of Moly 2 with both of the OFMs gave higher friction that any of the three additives alone, in both GTL4 and engine oil. It is possible that the OFMs are slowing the adsorption of Moly 2 on the rubbing surfaces while the MoDTC is hindering formation of a close-packed OFM film.

Figure 11 shows that GMO and Poly are synergistic in GTL4 when tested in the CETR at very low sliding speed. In this case the GMO, while ineffective on its own, is able to improve Poly's ability to reduce boundary friction. No such

Fig. 9 MTM Stribeck curves for individual FM solutions in engine oil



effect is seen in engine oil, but here other polar additives such as detergent probably play a role.

Figure 12 shows that a combination of GMO and Poly in GTL4 is also synergistic in MTM tests. At the start of a test, Poly gives very low friction and GMO high friction, while the combination gives the same low friction as Poly alone. However, after 2 h rubbing, Poly alone has become much less effective, but when combined with GMO it retains its ability to deliver low friction. Here GMO may be helping protect the surfaces, or the Poly boundary film, from damage during rubbing.

Most commonly, additive pairs gave friction values that lay between those of the two individual additives concerned, or that matched the behaviour of either an effective or ineffective FM, as can be seen in Fig. 12 at the start of MTM tests. Figure 13 shows that the blend of Moly 2 and VM 2 largely retains Moly 2's ability to reduce HFRR friction in both GTL4 and engine oil, while Fig. 14 shows that blends of Amide and Poly with GMO in GTL4 inherit GMO's somewhat high friction rather than the lower Poly and Amide friction coefficient values.

In some cases, friction performance of blends was intermediate between those of the two individual FMs, as illustrated for Amide and Moly 2 in GLT4 in CETR tests in Fig. 15.

Thus far, the performance of FM blends has been compared with those of the individual FMs in single types of friction test. Another type of possible synergy is when the blend gives lower friction than either of its individual FMs across more than one friction test. For example, as can be seen in Fig. 16, the combination of Moly 2 and Poly gives low friction equivalent to Moly 2 on its own in the severe conditions of the HFRR, but low friction equivalent to Poly alone in the MTM test. Such an ability to span a range of contact conditions is of practical significance; for example, the HFRR might be considered analogous to the

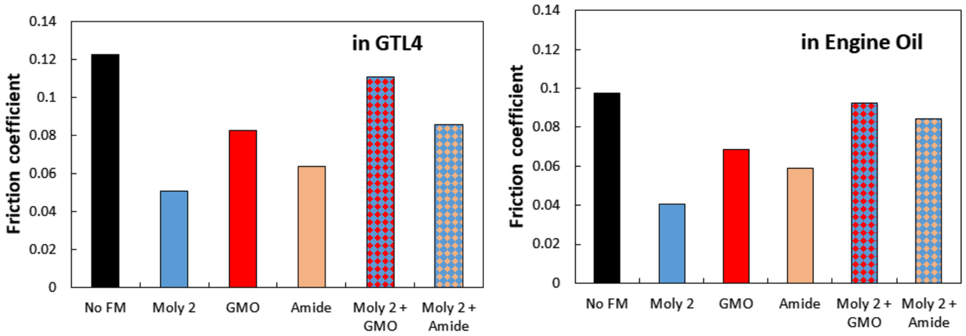


Fig. 10 Antagonism between two OFMs and a MoDTC in HFRR friction tests

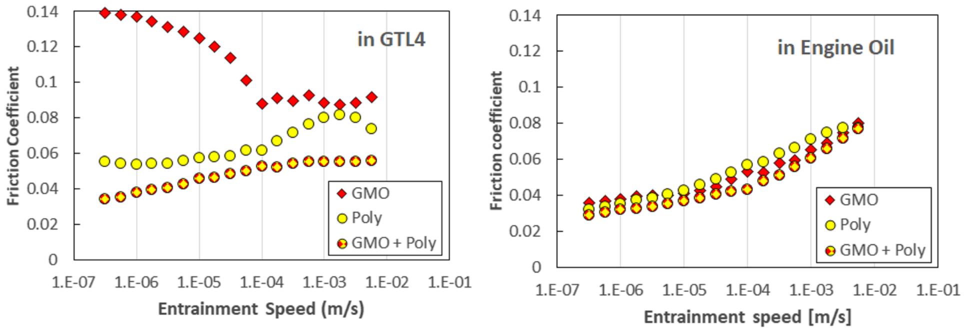


Fig. 11 Synergism between GMO and Poly in CETR friction tests

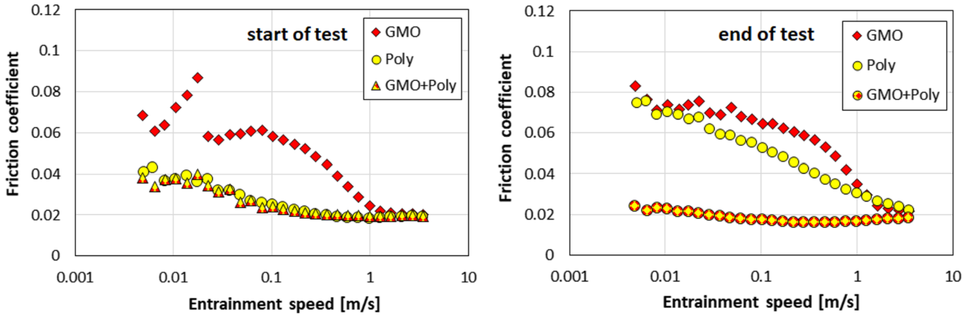


Fig. 12 Synergism between GMO and Poly in MTM friction tests after 2 h rubbing

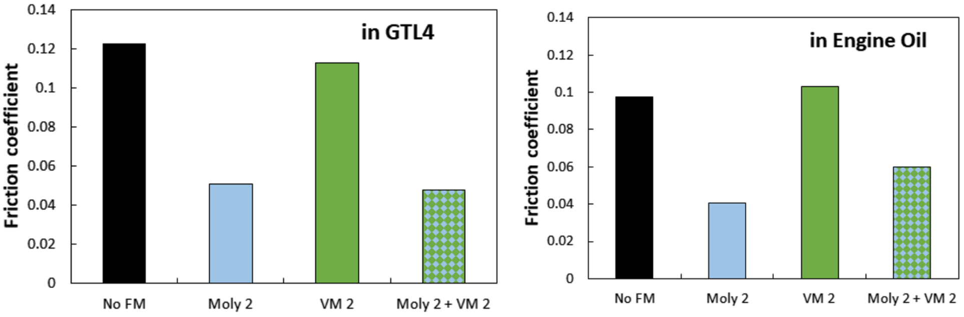


Fig. 13 Moly 2 and GMO blends in HFRR friction tests

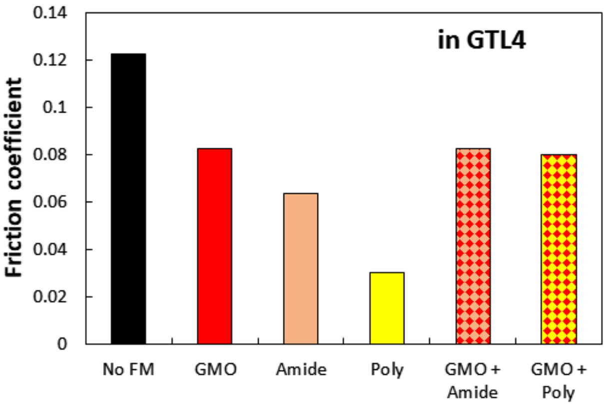


Fig. 14 Blends of Poly with OFMs in HFRR friction tests

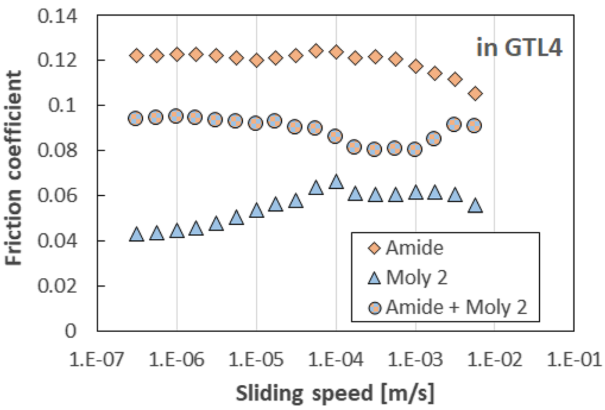


Fig. 15 Amide, Moly 2 and their combination in CETR friction tests

piston ring-liner contact while the MTM rolling–sliding test matches more closely a sliding cam-follower. This pattern of synergy can be categorised as a graded response as outlined in the Background to this paper.

7 Discussion

Figure 17 summarises the boundary friction response of the individual additive solutions in GTL4 in all three tests. In the slow speed sliding CETR test, the values are those measured at 0.001 m/s, while in the MTM they are values obtained by averaging the friction values from entrainment speed 0.005 to 0.01 m/s (the four lowest speed measurements). The additives are shown in order of effectiveness. It is evident that different additives behave differently in the various test conditions, though there are some clear patterns. Thus, Moly 2 is effective when significant sliding asperity contact occurs, as in the HFRR and CETR, but not so in rolling–sliding conditions. By contrast, VM 1 and VM 2 give lower friction in mild, rolling–sliding MTM conditions than in pure sliding contacts. The polymeric FM Poly is effective in all tests, while Amide in particular shows a very wide range of responses. This study shows clearly the importance of not relying on just one type of test condition to assess the effectiveness of an FM in machines that have several machine components.

Solution in engine oil rather than GTL4 exposes FMs to two major new influences, competition from other polar additives such as the dispersant and detergent, and formation of a ZDDP or ZDDP/overbased detergent tribofilm. The

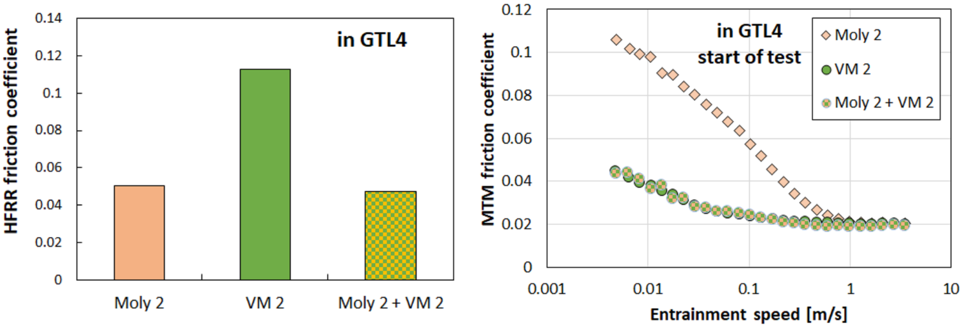


Fig. 16 Moly 2, VM 2 and their blend in HFRR and MTM tests

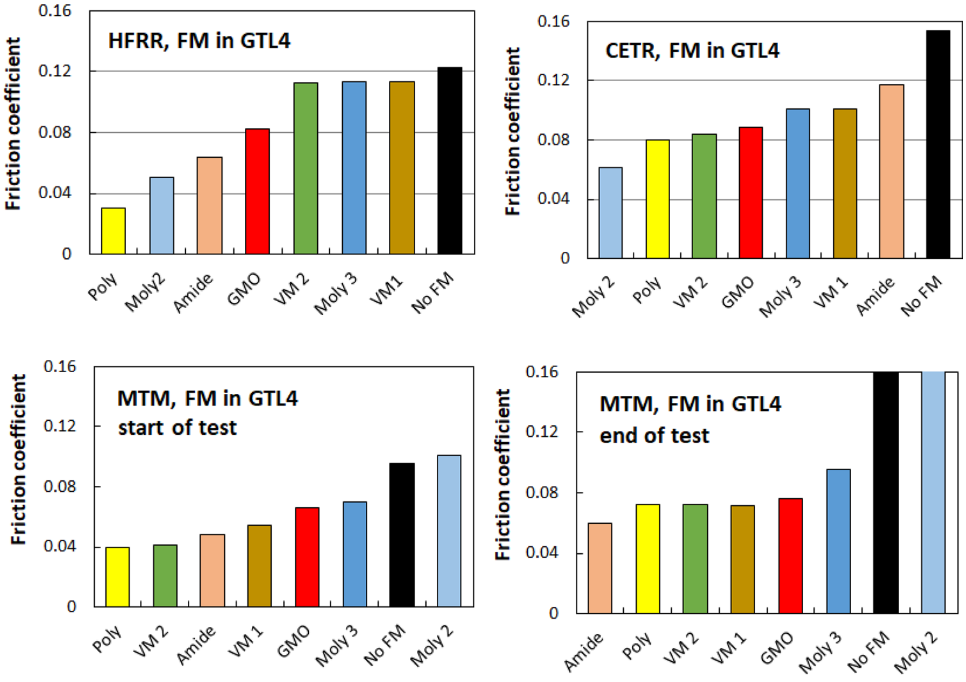


Fig. 17 Summary of friction-reducing properties of individual FMs in GTL4 (CETR is friction coefficient at 0.001 m/s. MTM friction is averaged up to an entrainment speed of 0.01 m/s). Friction coefficients at end of MTM test are 0.27 and 0.32 for No FM and Moly 2 respectively

latter means that to be effective the FM must adsorb or react on a phosphate or phosphate/carbonate film rather than a ferrous oxide surface [26]. Figure 18 summarises friction performance of the individual FMs in engine oil in all three tests. The results are more disparate than in GTL4. Moly 1 and Moly 2 are very effective in the HFRR and at the end of MTM tests. It is well known that MoFMs form films rapidly when ZDDP is present [30–32], possibly because the increase in roughness as the ZDDP film develops create the high local stresses needed for MoS_2 formation or because the ZDDP film helps the MoS_2 nanocrystallites survive. This is seen in the HFRR tests and at the end of MTM tests. However, Moly 1 and Moly 2 are quite ineffective in the CETR, probably because other polar additives in the oil inhibit access to the steel surface. The two functionalised VMs are less effective in engine oil than in GTL4 in MTM tests, most likely because of competition from the aminic dispersant. It has been shown previously that succinimide dispersants can

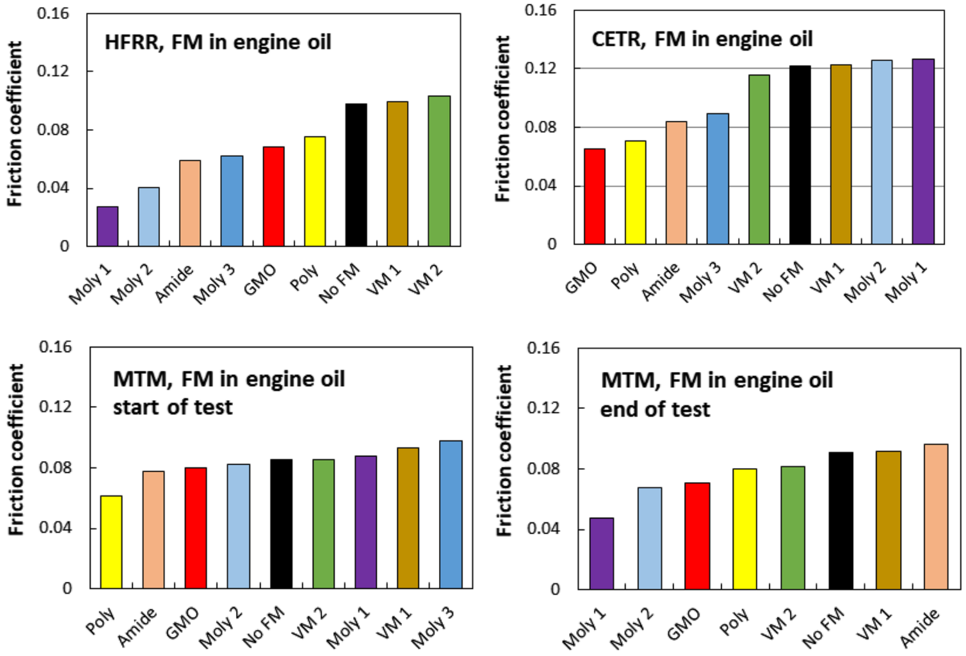
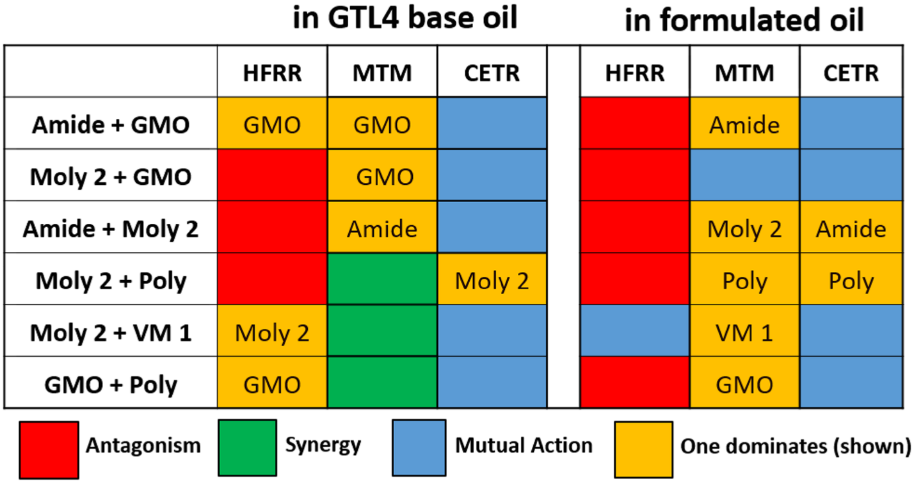


Fig. 18 Summary of friction-reducing properties of individual FMs in engine oil (CETR is friction coefficient at 0.001 m/s. MTM friction is averaged up to an entrainment speed on 0.01 m/s)



	in GTL4 base oil				in formulated oil		
	HFRR	MTM	CETR		HFRR	MTM	CETR
Amide + GMO	GMO	GMO	🟦		🟥	Amide	🟦
Moly 2 + GMO	🟥	GMO	🟦		🟥	🟦	🟦
Amide + Moly 2	🟥	Amide	🟦		🟥	Moly 2	Amide
Moly 2 + Poly	🟥	🟩	Moly 2		🟥	Poly	Poly
Moly 2 + VM 1	Moly 2	🟩	🟦		🟦	VM 1	🟦
GMO + Poly	GMO	🟩	🟦		🟥	GMO	🟦

🟥 Antagonism 🟩 Synergy 🟦 Mutual Action 🟨 One dominates (shown)

Fig. 19 Summary of FM interactions. Where the individual response of one of the FM pair is dominant this is shown in the relevant box

inhibit the friction-reducing ability of some functionalised PMAs in the MTM [22]. Poly appears to be less effective in the engine oil than base oil, again probably because of competition by other engine oil additives. The OFMs reduce friction in all conditions except at the end of the MTM test.

Figure 19 summarises the behaviour of the FM combinations in the three tests, the MTM response being at the start of the test. There are four alternative types of interaction at each test condition: (i) mutual antagonism where the friction of the combination is higher than that of either component; (ii) synergy, where the friction of the combination is lower that either individual FM; (iii) mutual action where friction is intermediate between the two FMs alone; (iv) cases where the friction is practically the same as one of the two individual FMs. In the last case, the dominant FM is shown. In general, antagonisms are most common in the HFRR, though the caveat should be noted that these tests compare blends in which each FM was at a lower concentration than in the solutions of the individual additives. Mutual action is most prevalent in the slow speed sliding CETR contact. To avoid any antagonism while benefitting from synergy, the best combinations appear to be Moly 2 + VM1 and GMO + Poly in base oil.

8 Conclusion

The ability of eight friction modifier additives (FMs) and some of their combinations to reduce boundary and mixed friction has been studied in three friction tests, a very slow speed, unidirectional sliding test, a reciprocating sliding test and a rolling–sliding test. FMs have been studied in both a base oil and a formulated engine oil.

Individual FMs behave quite differently in the different tests, illustrating the importance of assessing the friction-reducing ability of FMs in more than one type of contact. Organomolybdenum FMs (MoFMs) require solid–solid contact to form their friction-reducing derivative, MoS_2, and thus reduce friction in severe boundary lubrication conditions such as are present in the HFRR test. They are also effective in combination with ZDDP in less severe rolling–sliding contact conditions. Organic friction modifiers (OFMs) and polymeric friction modifiers (PFMs) act by adsorbing on polar surfaces and are generally effective in mixed sliding–rolling conditions and in slow speed sliding.

When two different friction modifiers additives are combined in solution several outcomes are possible. The most common is for one of the additives to predominate, to give friction characteristic of that additive alone, while in some cases friction lies between the values produced by either additive on its own. In a few cases, the additives behave antagonistically so that the combination gives higher than either additive by itself. In a few cases true synergy is observed, where a combination of two additives produces lower friction in a given test that either individual component at the same overall concentration. Another, and possibly more important synergy can also occur, however, when a pair of FMs works more effectively over the range of test conditions present in different friction tests than does one single additive. This form of graded response is particularly seen with combinations of PFMs and MoFMs which function via very different mechanisms and thus perform well in very different contact conditions. This study suggests that optimal combinations of FMs may provide a means of reducing boundary friction and thus increasing the efficiency of machines, especially if these combine a range of lubricated machine components that operate with different types of tribological contacts.

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