

FRICION MODIFIER ADDITIVES

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ABSTRACT

The need for energy efficiency is leading to the growing use of additives that reduce friction in thin film boundary and mixed lubrication conditions. Several classes of such friction modifier additive exist, the main ones being organic friction modifiers, functionalised polymers, soluble organo-molybdenum additives and dispersed nanoparticles. All work in different ways. This paper reviews these four main types of lubricant friction modifier additive and outlines their history, research and the mechanisms by which they are currently believed to function. Aspects of their behaviour that are still not yet fully understood are highlighted.

Keywords: Friction; lubricant additives; OFM; molybdenum additives; functionalised polymers; nanoparticles; boundary lubrication

1. INTRODUCTION

In order to reduce energy consumption and thus CO₂ emissions it is necessary to increase the energy efficiency of mechanical systems and an important way to achieve this is to design lubricants that give low friction in machine components. One design approach is to optimise liquid lubricant rheology so as to minimise hydrodynamic shear, churning and pumping losses. In practice this often means reducing lubricant viscosity to the lowest possible value consonant with maintaining fluid or mixed film lubrication. Another approach is to add small proportions of friction modifier additives to the lubricant in order to reduce friction in the boundary and mixed lubrication regimes. In practice both of these approaches are best applied concurrently since, as lubricant viscosity is progressively reduced, contacts are separated by thinner and thinner hydrodynamic films and so operate increasingly the regimes where friction modifier additives are effective.

Although in practice many polar organic species and solid particles dissolved or dispersed in base oils produce measurable reductions in boundary friction, there are four main classes of material that have been deliberately developed and applied as additives in liquid lubricants to reduce friction and may thus be formally termed *friction modifier additives*.

The first of these is the group of compounds based on amphiphilic surfactants now usually called *organic friction modifiers* (OFMs). The first of these were free fatty acids derived from fats and vegetable oils, discovered almost exactly a century ago. OFMs are key additives in modern engine oils and are also employed in fuels.

The second class are the oil-soluble, organo-molybdenum compounds, developed initially as antiwear additives but recognised in the 1980s to be very effective in reducing boundary friction. They are currently used in many engine oils and, more recently, in gear oils.

In the last few years, attention has focused on functionalised polymers tailored to adsorb specifically on polar tribological surfaces and these have been shown to markedly reduce friction in some contact conditions. The fourth class of friction modifier additive encompasses dispersed nanoparticles. Some such particles have been shown to reduce boundary friction but, so far as the author is aware, they have not yet found widespread employment in this role in practical applications. However they have the potential to become a valuable class of friction modifier additives. Fig. 1 shows a timeline to indicate when each of these main classes of friction modifier was identified, as well as showing the first introduction of the other main classes of lubricant additive.

This paper outlines both the history and our current understanding of the mechanisms of action of all four of the above classes of friction modifier additive. It is inevitably imbalanced given that the quantities of research carried out on the four are very different, so consideration of adsorbing polymers is much shorter than that of organic friction modifiers. It should be noted that this review does not attempt to examine other ways to reduce friction, such as the use of low friction solid coatings or of micron-sized dispersed particles as presently employed in many greases. Nor does it attempt to provide a complete account of all

suggested possible friction modifier structures - such an account can be found in a very comprehensive review of friction modifier additives in the recent literature [1]. The principle objective of the current paper is to provide an assessment of the state of our understanding of the mechanisms by which friction modifier additives work.

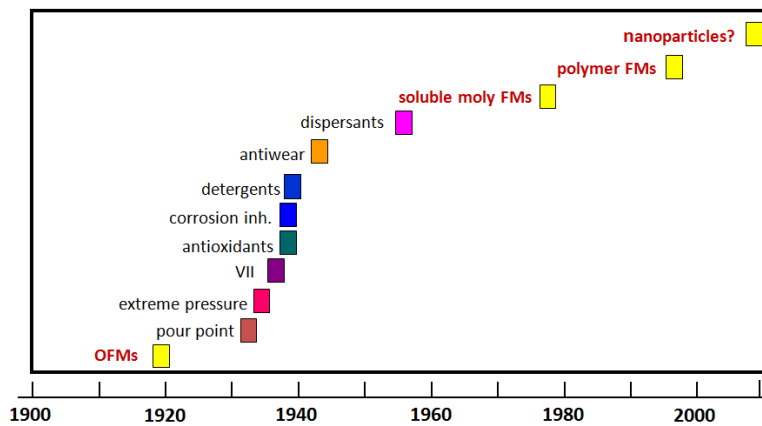


Figure 1. Timeline for development of lubricant additives including friction modifiers

2. ORGANIC FRICTION MODIFIERS

2.1 History of OFMs

In 1886 Osborne Reynolds published his seminal paper on hydrodynamic lubrication [2]. This demonstrated the key role of lubricant viscosity in forming a separating lubricant film between rubbing surfaces and, since viscosity is the only lubricant property that appears in Reynolds' equation, it implied at the time that only viscosity mattered in lubrication – *i.e.* all lubricants having the same viscosity should be equally effective. However this was contrary to the experience of many practising engineers of the day who knew that natural oils based on plant and animal oils and fats generally gave lower friction and wear than corresponding mineral oils. To explain this difference, a mysterious lubricant property known as *oiliness* was invoked.

It is clear that oiliness was a significant issue in the period and aroused considerable passion. Thus in 1918, upon being shown evidence that the difference in lubrication properties between natural and mineral oils had chemical origins, the famous automotive engineer F W Lanchester wrote [3];

"I am sure that to-day it is impossible to dispute the existence of a property of oiliness apart from the ordinary physical properties of a lubricant and, so far as this view is only of recent acceptance amongst scientific men, so far we may take the period from 1886 until today as a measure of the time it has taken to recover from an overdose of Osborne Reynolds."

In the same year of 1918, Wells and Southcombe submitted a patent which showed that a low concentration of vegetable oil-derived free fatty acid when dissolved in mineral oil was able to impart the latter with oiliness, *i.e.* to make it as effective as a vegetable oil in reducing friction and wear [4]. They ascribed this effect to an improvement in wetting properties of the oil. Other researchers proposed alternative mechanisms including *"an intensified viscosity in that part of the fluid within the region of the surface molecules of the metal"* [5] and *"the unsaturated molecules of the lubricant enter into a firm physicochemical union with the metallic surfaces, thus forming a friction surface which is a compound of metal and oil."* [6]

However the early 1900s was the heyday of research on monolayer surfactant films at air-liquid interfaces and this concept was readily transferred to the solid-liquid interface so that by the 1920s many scientists believed that oiliness resulted from single layers of surfactant adsorbed on solid surfaces. Langmuir in 1920 described the deposition of a monolayer of oleic acid on a glass surface and its dramatic influence in reducing friction [7], while in 1922 Hardy showed that fatty acids and alcohols produced a progressively lower friction on glass and steel surfaces as their chain length was increased [8]. Hardy proposed that friction reduction was produced by vertically oriented, single monolayers of these surfactants on each surface and coined the term "boundary lubrication".

Thus by the early 1920s both the concept and a mechanism of behaviour of organic friction modifiers had been developed – that they adsorb from solution or "self-assemble" on solid surfaces and that sliding occurs within the low shear strength plane

between methyl groups on opposing, adsorbed, vertically oriented monolayer films. Hardy's very simple model of boundary lubrication is shown schematically in Fig. 2a while Fig. 2b summarises a later development of this model by Bowden and Tabor, who measured localised solid-solid adhesion events during sliding and suggested that OFMs only partially separate opposing surfaces but that as a result they inhibit metallic junction growth and thus reduce the extent of solid adhesion [9].



Figure 2 (a) Hardy and (b) Bowden and Tabor models of OFM mechanism

It is important to note, however, that these models based on the concept of vertically oriented monolayers were (and still are) by no means universally accepted. In 1936 Hersey listed six general hypotheses that might explain the origins of oiliness [10] while, as indicated by Allen and Drauglis [11], there was still considerable debate even in the 1970s as to whether the boundary lubricating films formed by organic friction modifiers consisted of single monolayers or were much thicker.

2.2 Main types of OFM

The first OFMs were fatty acids but by the 1930s these were found to cause high levels of corrosion of some bearing metals such as copper, cadmium, lead and tin [12][13] and they were gradually replaced in most applications by less corrosive amphiphiles such as amides, amines and esters [14-16] or by more complex organoacid-based compounds that gave insoluble metal salts and thus formed passivating layers [17].

Figure 3 illustrates three OFMs in use today. These are examples with relatively well-defined molecular structures although it should be noted that the glyceryl monooleate (GMO) in practical use as a lubricant and fuel additive generally contains considerable proportions of other esters. All are based on amphiphiles having a predominantly linear alkyl chain with one or more functional groups at one end.

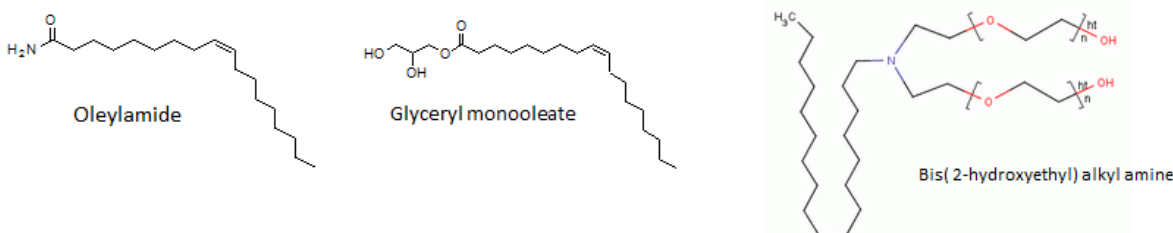


Figure 3. Three commercial OFMs

In practice, many commercial OFMs derive from natural fats and oils and thus contain complex mixtures of mainly unsaturated alkyl chains, while others are prepared *via* oligomerisation of unsaturated surfactants to give quite poorly defined mixtures of products such as the dimer acids. A recent theme is the design of OFMs with multiple functional groups to promote chelation and thus adsorption, for example tartrate and citrate derivatives [18][19].

In addition to the corrosive action of some carboxylic acids there are other constraints on the polar head group. For example primary amines may inhibit the film forming behaviour of antiwear films and also promote degradation of elastomers. It should be noted that there is considerable concurrence between the structures of OFMs and rust inhibitor additives, especially in terms of head group type; thus GMO was patented as a rust inhibitor considerably before its friction-reducing properties were recognised [20].

Although most OFMs are based on molecules containing only C, H, O and N atoms, some researchers categorise organophosphorus compounds such as dialkylphosphites as OFMs, especially when they are used in automatic transmission fluids [21][22], and even some sulphur and boron-based amphiphiles [1][23]. However these also show antiwear and EP

properties and are rarely used solely for their friction reducing properties. For the sake of brevity they will not be discussed in the current paper.

2.3 Early research on OFMs

Throughout the 1930s to 1980s there were many studies of the nature and properties of the friction-reducing properties of model OFMs and in particular of saturated fatty acids. A useful review up to about 1950 is given by Bowden and Tabor [9]. Two key problems in understanding the films formed by this type of friction modifier is that they are (i) extremely thin and, (ii) in many cases only very weakly bound to the surfaces and thus fragile when extracted from the liquid phase. In practice this has meant that until recently it was generally not possible to study them within rubbing contacts or even *ex-situ* on rubbed surfaces. The vast majority of early research was therefore limited to measuring the friction behaviour of solutions of OFMs and observing how this varied with operating conditions such as applied load, temperature and sliding speed, with concentration of additive, nature of solvent, additive molecular structure and substrate material. The presence and nature of the self-assembled OFM films were then inferred from the observed friction behaviour.

In a classical study in 1940, Bowden and Leben investigated the ability of stearic acid monolayers deposited by the Langmuir-Blodgett technique to reduce friction of a steel/steel contact [24]. They found that a single monolayer of stearic acid deposited on the steel was able to reduce friction down to the same level as that produced by immersion of the contact in a solution of the same fatty acid in paraffin oil. However this friction-reducing effect was lost after only 2 to 3 passes and was durable only when multilayers were deposited, indicating the importance of there being a supply of stearic acid to repair the initial monolayer. This reflects what is now recognised to be a key feature of friction modifier, and indeed other surface-active additives such as antiwear and extreme pressure additives, that they must be able to replenish surface films as these are worn away or otherwise damaged during rubbing.

In general it was found that OFMs start to produce a reduction in friction between a wide range of metal-metal tribo-pairs when their concentration reaches about 0.00001M, above which friction decreases progressively to level out when concentration reaches *ca.* 0.01M [25-27]. This range is equivalent to approximately 2 to 2000 ppm. Figure 4 shows friction measurements for hexadecylamine solutions with stainless steel [25].

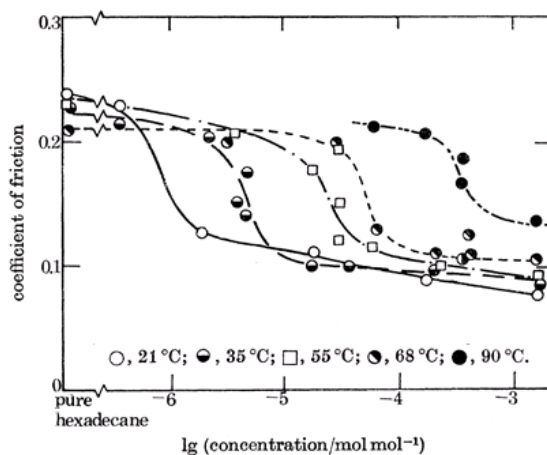


Figure 4. Change in friction coefficient with concentration of hexadecylamine in hexadecane on stainless steel [25]

Several researchers have explored the impact of chain length on friction for homologous series of amphiphiles such as carboxylic acids and alcohols [28-33]. All found that significant friction reduction only occurs for alkyl chains of more than 4 carbon atoms and that friction then decreases progressively as chain length increases. Jahanmir [32] found that friction continued to decrease to the maximum chain length tested of 16 carbon atoms but most other researchers observed a leveling out in friction above 10 carbon atoms.

The effect of head group has been studied extensively to show that on ferrous substrates, carboxylic acid and amine groups are generally more effective (*i.e.* their amphiphiles reduce friction at lower additive concentrations and/or reach lower friction values at high concentrations) than alcohol, ester, nitrile or halide groups [26][34,35]. Studies have shown friction being proportional to load, *i.e.* constant friction coefficient, except at very low loads when friction coefficient increases [28][36]. This was later explained by Deryagin *et al.* as resulting from friction depending on a two term expression, the first pressure independent of and

the second varying linearly with pressure [37]. This was subsequently confirmed from friction measurements on Langmuir-Blodgett films in a mica-mica contact by Briscoe and Evans [38] who derived an expression for the shear strength, τ , of the film;

$$\tau = \tau_o + \alpha p \quad (1)$$

where τ_o is a pressure-independent shear stress term, p the pressure and α is a constant. Since τ_o is quite small, of order 1 MPa, at high pressures the second term dominates and the friction coefficient is simply α .

The effect of sliding speed will be discussed later in this review. Friction may increase or decrease with temperature at moderate temperatures but a number of studies have indicated that the effectiveness of OFM films can be lost quite suddenly, as evinced by a rapid rise in friction or the onset of severe stick slip, when a critical temperature is reached [39,40]. In some cases, for example for alcohols, this temperature corresponds approximately to the melting point of the OFM but in others, in particular for fatty acids, it is higher, suggestive of a chemical reaction between additive and substrate to form a metal soap [8]. It should be noted that much of this early work used pure OFMs as lubricants rather than dilute solutions [39,40] although more recent work has confirmed similar behaviour for additive solutions [31].

Although the head group is critical in determining the effectiveness of OFMs, it was soon recognised that the strength of a monolayer OFM film, *i.e.* its ability to support load, is determined at least for saturated chain additives by the cumulative, short range van der Waals forces between the methylene groups of neighbouring close-packed alkyl chains [41,42]. The importance of these lateral side-chain interactions may explain why short chain OFMs are less effective than long chains, especially on hard substrates where high contact pressures are reached, and also why linear chains are more effective than branched ones or ones whose polar group is not at the end of the molecule [27][43].

The above friction studies were accompanied by numerous studies of the adsorption of OFMs on solids. Due to a lack of suitable surface analysis methods most of these used radio-tagged OFMs [44-47], ellipsometry [48] or estimated adsorption from the depletion of solution concentration as OFM adsorbed [25][32][49-51]. The last approach required powdered solids to provide enough surface area to give a measurable concentration change.

Such studies showed that saturated fatty acids generally gave Langmuir-type, monolayer adsorption isotherms to reach levels indicative of vertical orientation on many metals (or more accurately metal oxides) including iron, steel, aluminum and nickel, but the slow formation of more than a single monolayer on others such as copper, zinc and cadmium [44][50-52]. This difference in behavior may be related to whether metals form wholly insoluble and thus passivating soap films, or soaps that are weakly soluble. The presence of water led to much thicker films on many metal oxides [52]. Adsorption of alcohols, esters and amines gave monolayers on all metals studied, but the adsorption was weaker than for the acids and did not always increase monotonically with concentration [49]. Desorption studies showed only partial loss of adsorbed films of acids and amines on iron and steel, suggesting a mix of physical and chemical adsorption [25][47]. Few studies have examined systematically the rate of adsorption, but ellipsometry has been used to show that dilute solutions of fatty acid can take several days to form complete monolayers on aluminium oxide, while radiotracing has shown the rate of monolayer replacement by a deuterated fatty acid to be equally slow [48].

One aspect of OFM behaviour that has appeared intermittently in the literature is that of "chain matching". This is improved performance in terms of friction reduction, wear and seizure when the number of carbon atoms and thus the chain length are similar for both the OFM and solvent; for example it was found that that palmitic (C16) acid can give lower friction than C14 or C18 acid in hexadecane. This phenomenon was originally highlighted in the 1960s by Cameron and co-workers [53][54] but has also been reported in later studies [55,56], although other research has found no such effect [57]. It is conjectured to arise from the presence of intercalated solvent molecules aligned within the vertically oriented OFM monolayer such that chain matching maximises lateral side chain bonding while also giving a smooth plane of methyl groups that promotes easy slip. It should be noted that adsorption studies thus far carried out have not directly detected solvent molecules within adsorbed monolayers of OFMs, though it has been shown by pressure-area measurements that mixed stearic acid/hexadecane films on water form stable, incompressible monolayers even when there are three times as many hexadecane as stearic acid molecules present [42].

2.4 OFM research 1990s to present

In the 1980s new experimental techniques were developed with sufficient resolution to enable the very thin films formed by OFMs to be studied directly, both on surfaces *ex situ* and within contacts. These include the surface forces apparatus (SFA) [58-61], atomic/lateral force microscope (AFM/LFM) [62-65], quartz crystal microbalance (QCM) [66], ultrathin film interferometry (UTFI) [67], neutron reflectometry [68,69] and various surface-specific vibrational spectroscopies [70-72]. Methods were also

developed to generate model close-packed monolayers by chemical grafting of self-assembled alkylthiols and alkyl siloxanes on solid surfaces [73][74].

These “nanotribology” techniques have been applied quite extensively to study films formed by model OFMs. SFA has confirmed that saturated alkyl chain OFMs adsorb from solution to form vertically oriented monolayers on mica [59,61] and also cobalt surfaces [58,60] while QCM has shown that oleic acid molecules appear to adsorb parallel to the surface on iron [66]. In AFM/LFM a sphere or sharp tip is rubbed against a substrate to provide a reasonably close analogue of a high pressure sliding asperity contact. Most work has used very smooth mica or silicon wafer substrates and examined three types of surface film; deposited Langmuir–Blodgett films [75], grafted alkylthiol and siloxane monolayers [76][77] and films of OFMs adsorbed from hydrocarbon solution [78]. Clearly the last of these is most relevant to understanding OFMs but the first two provide better-characterised, close-packed monolayers. These studies have confirmed the important influence of chain length and packing density on friction and also provided some estimates of film strength [79-81]. Most AFM work has studied films on substrates withdrawn from the liquid phase (*i.e. ex situ*) but recently liquid cell AFM, in which the whole AFM contact is immersed in liquid, has been carried out to provide a closer approximation to an actual lubricated contact. Fig. 5 compares a topography map of a mica surface immersed in hexadecane with the same surface immediately after injection of stearic acid solution in hexadecane [82]. The surface immersed in hexadecane is almost featureless, but upon injection of the acid solution irregular islands, which are about 1.6 nm thick (corresponding to tilted, vertically oriented monolayers) and have low lateral force (the paler regions) compared to the inter-island regions, form very rapidly. Interestingly the islands were progressively removed by successive scanning, suggesting that they are too weak to withstand the very high pressure present in the AFM contact. The liquid cell can be heated and this showed reversible loss of the adsorbed islands above about 40°C.

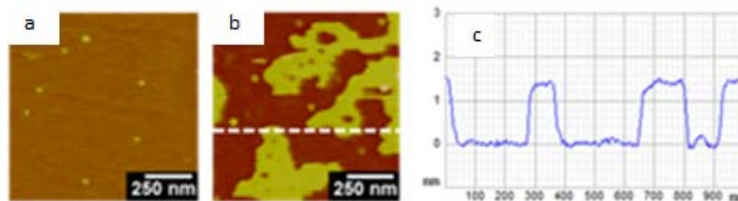


Figure 5. AFM height images of mica in hexadecane before (a) and after (b) injection of 0.001 M stearic acid solution. Also profile of surface after injection [82]

The technique of ultrathin film interferometry can study boundary films in actual rubbing contacts and this confirmed that stearic, oleic and isostearic acid solutions form 2 nm thick films in dry conditions [67][83]. However exposure to water vapour for an extended period resulted in stearic acid forming a significantly thicker film (Fig. 6) [67]. This thicker film was formed only when a bearing steel ball was employed, not a stainless steel ball, suggesting a chemical reaction to form ferrous or ferric stearate. A limitation of the ultrathin film interferometry method is that it cannot be used to study OFM films in high pressure, high sliding contacts since the coatings used for interferometry are easily damaged under these conditions.

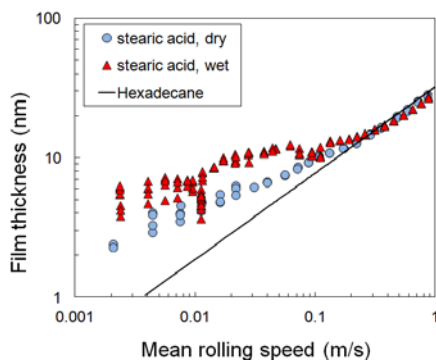


Figure 6. Film forming behaviour of 0.1% wt. stearic acid solutions in hexadecane at 25°C. Adapted from [67]

A variety of reflection-based vibrational spectroscopies including IR, Raman and sum frequency generation (SFG) have been applied to study adsorbed or reacted surfactant films on surfaces [84,85]. Most work has focused simply on exploring the

structure of these films on immersed surfaces, to map features such as molecular tilt or the linearity of the alkyl chain [86], but a few studies have been applied to observe film behaviour within rubbing contacts [87][88]. Beattie and co-workers studied a Langmuir-Blodgett film of zinc arachidate in sliding sapphire/quartz contacts and found that film order was maintained during sliding but some film was transferred from the monolayer to the opposing surface [87]. In a recent study by Koshima *et al.* the friction coefficients of solutions of a range of model OFMs were correlated with the SFG spectral characteristics of their self-assembled films on iron, suggesting that OFMs that give the most ordered surface films also show the lowest friction [72].

Another quite new technique is neutron reflectometry in which a low angle beam of neutrons is bounced off a surface and analysed to calculate the location of the various interfaces from which it is reflected and thus the thickness of any layers present. This has been used to determine the thickness of acetic acid films adsorbed on iron and copper from polyalphaolefin (PAO) [69] and of palmitic acid adsorbed on iron oxide [68] and DLC [89] from hexadecane and PAO respectively. Films indicative of tilted monolayers were detected on the metals and most DLCs. An advantage of the approach is that it can measure very thin films on surfaces covered in oil. Two disadvantages are (i) to distinguish the base oil from additive one of these has to be deuterated and (ii) it appears to require extremely smooth surfaces of sub-nanometer roughness – for example of iron deposited on silicon wafers. To date the method has been used only to study adsorbed films on surfaces and not those within rubbing contacts. In principle the latter is possible but the need for very smooth surfaces may limit the amount of rubbing that can be applied.

From the above it should be evident that while some of these new techniques provide useful insights, few are able to probe contacts operating under the conditions experienced by OFM films in real rubbing systems. QCM and neutron reflectometry have been used only to study films on surfaces out-of-contact, although immersed in liquid. SFA, vibrational spectroscopies and interferometry can look into actual lubricated contacts but only in “mild” contact conditions involving low pressure or very little sliding. AFM can match the pressures experienced within contacts but to date has been used mainly on mica and very rarely on metal or metal oxide surfaces.

The last few years have also seen new work on OFM films using the more conventional approach of measuring friction in macro-scale contacts under very controlled conditions. An interesting recent observation is that many OFMs require some rubbing action in order to initiate or complete their friction reduction. This has been seen using optical interferometry [90] and also slow speed ball on disc friction tests [35]. Fig. 7 shows friction traces for three concentrations of stearic and oleic acid in hexadecane [35]. It is evident that friction reduces in two stages, one immediately and the second only after the disc has rotated once against the ball. Similar, though less pronounced behaviour was seen with amine solutions. Three possible reasons for this behaviour are (i) that rubbing “activates” the adsorption/reaction process in some way, (ii) that it accelerates adsorption by forcing convection or (iii) that it helps “order” the film in a similar fashion to the “ironing” process used to form liquid crystal display surfaces [91].

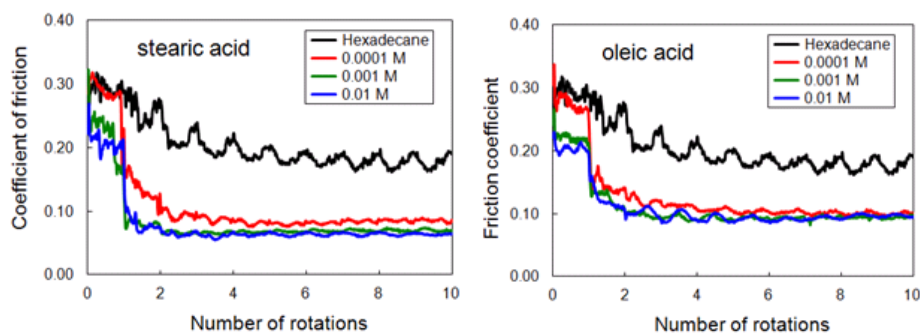


Figure 7. Friction during first ten rotations in a slow speed ball on disc rig; solutions in hexadecane at 35°C [35]

There is considerable research in the literature which suggests that stearic acid can give greater friction reduction than oleic acid when the two are compared at similar concentrations [27][61], even though SFA shows that both form similar film thickness on mica surfaces [57], while optical interferometry indicates that they also both form monolayers in steel/glass contacts [67]. Recent work has compared friction coefficients of three model OFMs, stearic acid, oleic acid and elaidic acid [92]. The last of these is a geometrical isomer of oleic acid where the carbon atoms on the single double bond are arranged in a trans configuration rather than the cis one of oleic acid. Although a very small difference, this has a profound effect on the shape of the molecule in that elaidic acid can adopt a linear arrangement while the oleic acid molecule always has a kink in the middle. As a result elaidic acid can form closer packing, as evidenced by its higher melting point than oleic acid. Figure 8 compares

friction/sliding speed behaviour for 0.01M solutions of stearic, oleic and elaidic acid solutions in hexadecane using a ball on disc apparatus [92].

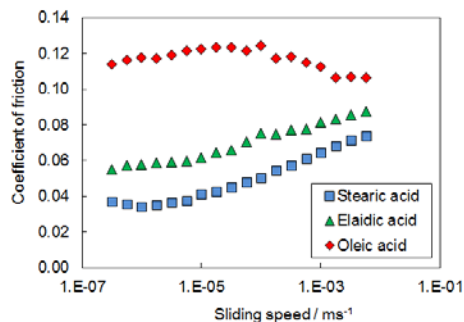


Figure 8 Friction *versus* sliding speed for three 0.01M fatty acid solutions in hexadecane at 100°C [92]

It can be seen that stearic and elaidic acid give very low friction at low speeds that increases approximately linearly with log(speed). However oleic acid gives very different behaviour – the friction is still reasonably low but is almost constant with speed. These results suggest that the types of film, and thus the friction behaviour, seen with molecules that can adopt linear configurations and thus close-pack easily are very different from those seen with molecules than cannot so easily close-pack.

Most research on OFMs has studied their behavior on metals or ceramics but in the last few years it has been recognised that OFMs are generally used in lubricants that contain other tribofilm-forming additives including antiwear additives. These are known to react with rubbed surfaces to form layers of zinc and iron phosphate, so to be effective in a formulated oil an OFM must form a low friction film on such a surface [93]. As well as their effectiveness in reduce friction of tribofilms, there has also recently been considerable interest in the ability of OFMs to lubricate diamond-like carbon (DLC) surfaces. Some DLCs give inherently low boundary friction and these are not significantly improved by addition of OFM to the lubricant [94]. However one specific type of DLC, non-hydrogenated and having mainly sp³ C-C bonding (ta:C), was found to give particularly low friction with GMO. It has been suggested that glycerol in GMO reacts with the ta:C surface to form OH groups and that the low energy of these, combined with the high hardness of ta:C, gives very low friction [95]. Recently the use of GMO containing the stable isotope ¹³C in combination with TOF-SIMS has been used to confirm that molecules of GMO (and not just oleic acid formed from it) adsorb on DLC surfaces [96]

Another area of growing research in the last few years has been the application of molecular dynamics simulation to model OFM behaviour. Initial work focused mainly on the sliding of opposing, densely packed monolayers to explore factors such packing density, chain length, types of energy dissipation, mixed alkyl chain lengths and fluorination [97-101]. Most of these studies used coarse grain approaches where methyl and methylene groups were simulated by individual point masses even though early work suggested that it was important to include the contribution of hydrogen atoms[102]. Relatively little attention was generally paid to the way the head group bonded to the substrate. More recently simulations of specific OFMs have been carried out both to study how their packing on surfaces influences friction [103] and also how monolayers behave when separated by a high pressure/high shear rate film of base oil [104]. A limitation of all work to date is that because of the very small time steps needed to model molecular motion accurately and the relatively slow rate of molecular diffusion [105], it is not yet possible to simulate the process of self-assembly to form an adsorbed film or the equilibrium between solution and surface film. Instead, at present molecules have to be positioned on or adjacent to surfaces such that the outcome depends to a considerable extent on the assumptions made by the modeler.

2.5 Origins of monolayer-monolayer friction

Various models have been suggested to explain the origins of friction between opposing, vertically oriented monolayers. Cameron [106] and Drauglis *et al.* [107] estimated friction as the force required to move alkyl chains on a vertically oriented monolayer from one stable equilibrium position to an intermediate minimum position against an opposing monolayer. They calculated the potentials involved from the van der Waals and repulsive interactions of individual methyl groups with all the neighbouring and opposing methyl and methylene groups. Sutcliffe *et al.* extended this approach to allow for rocking and tilting of the chains and add a second term to represent the work done in lifting methyl end groups over those on the opposing surface [108].

In 1981 Tabor simplified Sutcliffe's approach and obtained a two-term expression for shear stress similar to Equ. 1 [109]. The first term was pressure-independent and resulted from the tangential force required to displace a methyl end group to its next equilibrium position and the second, proportional to pressure, represented the work required to lift the plane of methyl groups over the opposing plane.

Briscoe and Evans adapted a stress-induced, thermal activated slip model due to Eyring to explain why friction increased linearly with $\log(\text{sliding speed})$ for Langmuir-Blodgett films of saturated fatty acids [38]. This behaviour is shown for stearic and elaidic acid solutions in Fig. 8 and is often seen in boundary lubrication [110-112]. In this model the energy required for methyl groups to traverse the potential energy barriers created by the methyl groups on the opposing surface is provided by a combination of the work done and thermal energy. Briscoe and Evans also used this model to explain their observed linear increase of friction with pressure for monolayer sliding against monolayer [38].

Based on AFM measurements Drummond *et al* developed a model of boundary friction based on the local forming and breaking of bonds between opposing monolayers [113]. This results in four stages of friction-speed dependence. At very low sliding velocities friction is proportional to sliding speed and then it increases logarithmically with speed, in response to a thermal activation model very similar to Briscoe and Evans. At still higher speed friction becomes independent of speed since there is no longer time for any thermal activation to occur; applied stress provides all the energy needed to break the bonds. Finally, at very high velocities bonds do not have time to reform so friction reduces.

Yoshizawa *et al.* have suggested that friction correlates with and is fundamentally related to adhesion hysteresis since both originate from the same energy-dissipating processes between interdigitated chain molecules [114], while Salmeron has used a combination of AFM, SFA and SFG to explore the generation of defects such as chain tilt and terminal and gauche distortions in monolayer films during sliding and the contribution of this to friction [83].

2.6 OFMs; slip at the wall

Although the monolayer model is the most widely used to describe the behavior of OFMs in full boundary lubrication conditions, *i.e.* when hydrodynamic film formation is negligible, there is growing interest in the possibility that OFMs can also reduce friction in full film hydrodynamic conditions by promoting fluid slip and thus reducing hydrodynamic friction [115][116]. It is suggested that the planes of methyl groups formed by vertically adsorbed monolayers of OFMs provide smooth, low wetting surfaces against which liquids can slip [117]. OFMs films are known to form oleophobic monolayers which are not easily wetted by alkanes [118]. Research has shown that the formation of self-assembled monolayers on very smooth surfaces can markedly reduce Couette friction in low pressure, hydrodynamic contacts and that a similar response is seen when stearic acid is added to a hydrocarbon base fluid [119]. What is still not yet known is whether this mechanism plays a significant role in reducing friction in actual engineering components such as transmissions and engines, where surfaces are generally rougher.

2.7 Current state of knowledge on OFMs

As described above, the classical mechanism proposed to explain the friction-reducing properties of OFMs is that their amphiphilic molecules self-assemble on polar solid surfaces to form vertically oriented, close-packed monolayers. These reduce friction since there is easy slip between the resultant, opposing methyl end groups. The films are strong and able to withstand high applied pressure because of cumulative van der Waals forces between the methylene groups on the closely packed alkyl chains. The polar group serves to locate the molecules of the solid surfaces and its bonding can be reversible or, especially with carboxylic acids, involve soap formation and is thus irreversible.

This simple model is certainly present in the idealised conditions generally used in research and has been supported by numerous experiments using Langmuir-Blodgett films, thiolate and siloxane monolayers and the adsorbed films formed by model, saturated chain OFM solutions. Of particular value in this context has been the studies carried out using atomic and lateral force microscopy which are able to measure simultaneously the thickness and friction of the film present. However there still are some issues with the close-packed monolayer model even for saturated chain amphiphiles. Thus Briscoe *et al.* have shown considerable differences between the friction properties of monolayers of some fatty acid soaps and their corresponding fatty acids, including quite different friction-speed behaviour [120] and, at high speeds much lower friction for the soaps than the acids [121].

More importantly it has not yet been demonstrated definitively that monolayers are actually present and are solely responsible for reducing friction in real engineering contacts. There is some evidence that when metal is rubbed against metal in heated, damp conditions, thicker, possibly soap-based films are formed by carboxylic acids. But it is not known if these thicker films

influence performance or whether they are displaced under moderate conditions so that friction is eventually determined by the final monolayers present.

A significant limitation of our current research methods is that, while it is possible to determine either film thickness or film composition, it is not yet possible to do both at once. Optical and mechanical-based techniques - for example UTFI, AFM, ellipsometry and SFA - can measure film thickness, while techniques that detect molecules such as solution depletion, radiotracer methods and vibrational spectroscopy can measure film composition. But at present none can reliably do both and thus monitor, for example the mixed solute and solvent composition of films as they form. In principle it would be possible to combine two measurement techniques to achieve this.

Apart from the major question of whether OFM monolayers actually control boundary friction in real engineering components there remain two outstanding research issues concerning OFMs that have not been fully addressed.

One is that the vast majority of research has studied saturated chain OFM; much less work has looked at unsaturated chain ones. The limited research published on the latter suggests that they form quite different and possibly more disordered films than saturated chain compounds and also show different friction behaviour, as indicated in Fig. 8. Since the majority of commercial OFMs are based, for cost and solubility reasons, on mainly unsaturated alkyl chain compounds we need to understand much more about their boundary film forming and friction properties. Another complication is that with many OFMs it is not clear whether friction reduction is produced by the original material or by a breakdown product. Long chain fatty acids are effective at reducing friction but their use as additives is constrained by their corrosivity to bearing metals. It has been suggested that some OFMs such as glyceryl monooleate act by releasing fatty acid rather than adsorbing to form protective films in their own right [1]. However an immediate reduction in friction by GMO has also been noted [35]. Both of these issues are further discussed later in this paper.

3 OIL-SOLUBLE ORGANOMOLYBDENUM FRICTION MODIFIERS

3.1 History of molybdenum additives

Colloidal molybdenum disulphide (MoS_2) was first patented as a lubricant additive to reduce friction in 1939 [122], though it was only produced commercially in the late 1940s [123]. After this, the use of colloidal MoS_2 in oils and particularly greases grew rapidly, both to reduce friction [124] and to help control wear and scuffing [125,126]. Throughout the 1960s and 1970s there was also considerable effort made to use colloidal MoS_2 in crankcase lubricants to reduce engine friction, with variable degrees of success [123].

To overcome the problem of keeping MoS_2 in dispersion in liquid lubricants, oil-soluble organomolybdenum additives were first proposed in 1955, initially in the role of extreme pressure additives [127][128]. Their use to reduce friction was reported in 1959 [129] and 1963 [130]. Initially the most widely studied organomolybdenum friction modifier (FM) was molybdenum dialkyldithiophosphate (MoDDP), the molybdenum analogue of ZDDP, and in 1969 its ability to control scuffing, wear and friction was compared with colloidal MoS_2 [131].

Until the late 1970s, oil-soluble molybdenum FMs were envisaged primarily as EP, antiwear and antioxidant additives, but fuel shortages following conflict in the Middle East region in 1973 focused attention on fuel economy and thus friction reduction throughout the 1970s. By the end of this decade, these additives were widely recognised as enhancing vehicle efficiency by reducing friction in transmission [132] and engine oils [133][134].

3.2 Main types of oil-soluble molybdenum FM

Some typical organomolybdenum FMs are shown in Fig. 9. The two most widely studied and used types are molybdenum dialkyldithiophosphate (MoDDP) and molybdenum dialkyldithiocarbamate (MoDTC). In MoDTC the atoms shown as X can be either O or S. Most commonly the bridging X atoms are S and the double bonded ones O, but the additive is generally more reactive when the latter are S [135]. The MoDTC shown in Fig. 8 is a dimer and this is its most widely used form, but its trimer analogue is also produced.

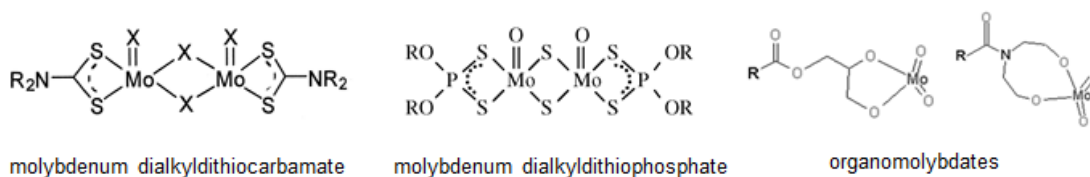


Figure 9. Three organo-molybdenum FMs

As well as those shown in Fig. 9, a wide range of other organomolybdenum additives have been developed, many of which have been reviewed by Mitchell [136]. The majority contain sulphur but some, primarily those produced by reacting amines or fatty oils with molybdic acid, are sulphur-free; examples are shown in Fig. 9. Typical concentrations of organomolybdenum FMs used in formulated oils are in the range 200 to 1000 ppm Mo.

3.3 Research on oil-soluble molybdenum FMs

The characteristic form of friction reduction seen with MoDTC and MoDDP is high initial friction followed by a sudden drop of friction coefficient to a value typically in the range 0.03 to 0.08, as shown in Fig. 10a for solutions of three different MoDDPs in engine oil [137] and Fig. 10b for two MoDTCs [138]. In Fig. 10a the open circles show friction of the engine oil without MoDDP, while in Fig. 10b MoDTC1 and MoDTC2 are both based on 2-ethylhexyl alkyl groups but are from different suppliers and with different levels of impurity [138]. Friction appears to drop only when solid-solid rubbing occurs and is particularly clearly seen in reciprocating contacts, where contact conditions during reversal are severe. In unidirectional sliding and mixed sliding rolling conditions it only takes place at high pressures or with rough surfaces [138][139]. Friction reduction also occurs only above a critical concentration and temperature that both depend on the MoDTC structure and purity [138].

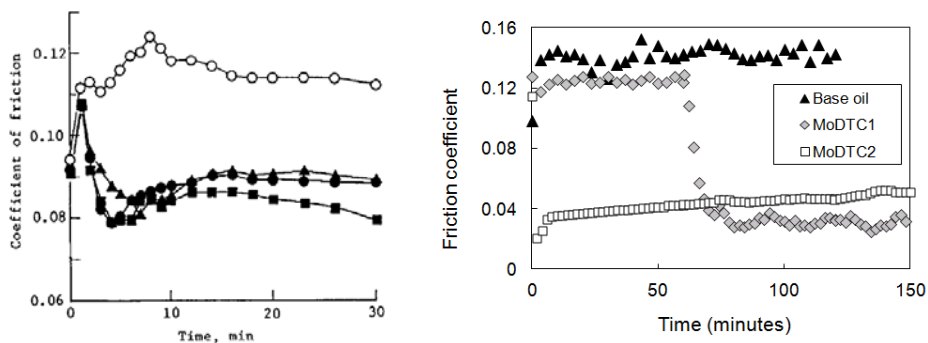


Figure 10. (a) Friction reduction by three MoDDPs [137], (b) Friction reduction by two MoDTCs [138]

The original rationale of using organo-molybdenum additives was that they would form MoS₂ during rubbing and thus offer the scuffing and wear protection and friction reduction seen with colloidal MoS₂. However it was some years after their introduction before sufficiently sensitive surface analysis became available to demonstrate this convincingly. In 1963 Feng *et al.* showed that the use of a combination of a molybdic phosphonate complex with ZDDP gave low friction and identified MoS₂ on the surfaces using electron diffraction [130]. In the 1980s, Yamamoto *et al.* used XPS to study the films formed by MoDTC and MoDDP during rubbing and concluded that the films formed when friction was reduced contained MoS₂ [135][140]. They also showed that Mo-containing additives that did not contain sulphur atoms and thus, theoretically, could not form MoS₂, were able to reduce friction so long as the base oil contained sulphur [141].

In 1998 Grossiord *et al.* combined XPS to analyse wear scars with high resolution TEM to study wear debris from friction tests using MoDTC solution [142]. Like Yamamoto *et al.* they identified MoS₂ in the wear scars with XPS. TEM revealed the presence of highly dispersed sheets of MoS₂ just a few atomic layers thick dispersed in the tribofilm wear material, as shown in Fig. 11. More recently, similar sheets have been seen in tribofilms on rubbed surfaces using focused ion beam TEM [143].

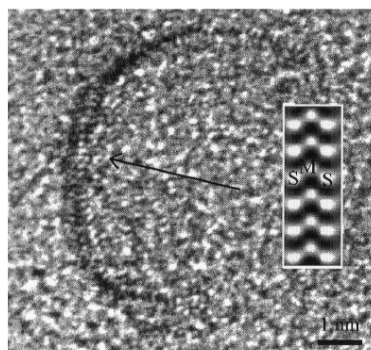


Figure 11. HRTEM image of wear debris containing chevron-like MoS₂ sheets [142]

In 2001 Topolovec *et al.* applied both AFM and Raman spectroscopy to analyse steel surfaces rubbed in MoDTC solutions [144]. Whenever a marked friction drop was observed, Raman detected MoS₂ on the surfaces and AFM showed the presence of tiny regions of very low lateral force on the rubbed surface high spots. The latter are shown in Fig. 12 and are typically about 10-40 nm across and 1-2 nm thick, suggesting that they are the MoS₂ nanosheets identified by Grossiord. XPS and Raman have subsequently become widely used tools to study organo-molybdenum additive tribofilms [145][146]

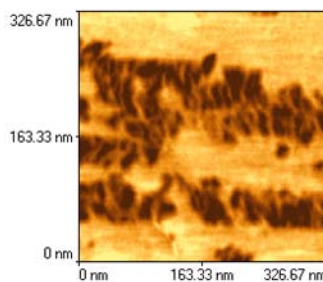


Figure 12. AFM lateral force map of surface rubbed in MoDTC solution showing low (dark) lateral force nanosheets [144]

A recurrent theme in the literature is the existence of a “synergy” between MoDTC and ZDDP, where a combination of both types of additive in solution gives lower friction than MoDTC alone and/or lower wear than ZDDP alone [137][147-151]. It is certainly the case that the rate of onset of friction reduction and in particular the longevity of friction reduction by MoDTC appears to be increased when ZDDP is present, although the actual occurrence of additive synergy, a quantitative concept based on the combined concentrations of pairs of additives [152], does not appear to have been demonstrated. The origins of the beneficial effect of ZDDP on MoDTC response has variously attributed to ZDDP promoting the formation of MoS₂ from MoDTC [147][145], ZDDP suppressing of the formation of a high friction sulphate [148], digestion of the high friction MoO₃ component of the tribofilm by the ZDDP [149] and ZDDP extending the useful life of the film [150,151].

It is noteworthy that MoDTCs and presumably other Mo-based additives can form MoS₂ on ZDDP films just as they do on steel surfaces. AFM and nanoscratch methods have shown tiny, low lateral regions formed by MoDTC at or close to the surface of the ZDDP tribofilm when ZDDP and MoDTC are used together, very similar to those formed by MoDTC on steel [153-155]. Topolovec *et al.* pre-formed ZDDP tribofilms on surfaces in a minitraction machine (MTM) and then replaced the lubricant by one containing only MoDTC [156]. Subsequent rubbing gave a drop in friction characteristic of Mo-additives, showing that MoDTC was able to form MoS₂ on the zinc phosphate and polyphosphate surfaces generated by ZDDP.

A significant practical problem associated with the use of organo-molybdenum FMs in engine lubricants is that their ability to reduce friction can be quite rapidly lost when they operate in oxidising environments at elevated temperature, such as in crankcase engines [157]. This has been variously attributed to ligand exchange between ZDDP and MoDTC resulting in loss of MoDTC [158], oxidation of the MoS₂ tribofilm to MoO₃ [159] or MoDTC in solution being used up as it acts as a peroxide decomposer antioxidant [158][160]. Hoshino *et al.* found that the addition of a heterocyclic sulphur compound extended the longevity of friction reduction by MoDTC and suggested that it prevented conversion of MoS₂ to MoO₃ under oxidising conditions

[159]. Graham *et al.* subjected MoDTC solutions to an air/NO_x oxidising environment and monitored both MoDTC concentration and friction performance [160]. They found that its friction-reducing capability ceased when the additive in solution fell below a critical concentration. Mo-additives are effective peroxide-decomposer antioxidants and Graham showed that the addition of other peroxide-decomposer antioxidants slowed the consumption of MoDTC and thus friction reduction [160].

One area of considerable interest in recent years has been the use of organo-molybdenum FMs with DLC-coated surfaces. It has been shown that MoDTC solution reduces friction in both DLC-steel and DLC-DLC contacts [161,162]. AFM has shown the formation of tiny low friction regions just as seen with MoDTC on steel [162] while TEM has also revealed the characteristic nano-sheets of MoS₂ previously seen with steel-steel contacts [161]. Unfortunately MoDTC also appears to promote very high wear of most types of DLC coatings [163-167]. The mechanism of this harmful effect is not yet clear and has been variously attributed to MoO₃ promoting the oxidation of DLC [163], abrasion of the DLC by MoO₃ particles [166] or wear *via* graphitization of the DLC surface [165]. Interestingly it only occurs with DLC/steel rubbing pairs and not DLC/DLC ones [165]. Fortunately this high wear can be suppressed, at least to some extent, by the presence of antiwear additives [164] and appears to be less pronounced for other organomolybdenum additives compared to MoDTC [167].

Despite considerable research the precise chemical reaction mechanism of MoS₂ formation from MoDTC is still unclear. Sakurai *et al.* suggested that MoDTC forms MoS₂ by a process involving homolytic fission of the Mo-S bonds linking the dithiocarbamate with the Mo atoms [134], and a very similar reaction scheme was proposed later by Grossiord as shown in Fig. 13 [142]. An alternative mechanism is cleavage of pairs of C-S bonds within the dithiocarbamate, leaving the sulphur atoms attached to Mo. Coffey *et al.* have reported the facile double cleavage of these bonds and the application of this cleavage to synthesis [168].

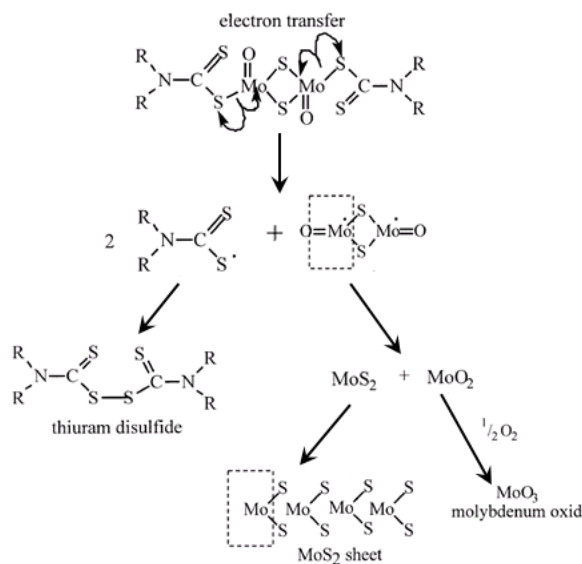


Figure 13. Proposed reaction scheme for the formation of MoS₂ from MoDTC [142]

MoDTCs often show an initial rubbing period in which there is negligible change in friction followed by a very rapid fall to a stable, low value, as shown in Fig. 10b, and it has been suggested that this may indicate that the reaction process to form MoS₂ is autocatalytic [138].

Sarin and co workers have shown that for MoDDPs the alkyl group size has relatively little effect on their friction or wear reducing properties [169], but there has been little systematic research on the effect of alkyl group size on MoDTC performance. An intriguing recent observation is that asymmetric MoDTCs, *i.e.* those having several different alkyl groups (the R groups in Fig. 9) in a molecule give lower friction than those in which the alkyl groups are all the same [170][171]. Best of all are MoDTCs made from asymmetric amines, *i.e.* having two different alkyl groups on each nitrogen atom [171].

3.4 Current state of knowledge of oil-soluble molybdenum FMs

Based on the above we are currently considerably more confident about how organo-molybdenum FMs work than we are about OFMs. Under rubbing conditions they form nano-sheets of MoS₂ on rubbing surfaces. These form only on the load-bearing asperity tips and thus have a disproportionate effect on reducing friction. Grossiord suggests that the MoS₂ single sheets form by degradation of the MoDTC molecule by electron transfer mechanisms activated by the friction process but this reaction scheme is not yet confirmed. One striking observation is that MoDTC appears to form films and reduce friction on a very wide range of surfaces, including DLCs, the tribofilms formed by ZDDP [156] and ceramic coatings [162]. This suggests that the formation of the friction-reducing MoS₂ sheets does not involve a chemically specific reaction with metal or metal oxide but may rather be an intramolecular reaction stimulated by applied stress.

There remain several quite important aspects of organomolybdenum FMs that are not well understood. One is why an asymmetric arrangement of alkyl groups in MoDTC appears to improve performance: one conjecture is that this asymmetry may influence the stress experienced by the bonds that must break in order to form MoS₂, or perhaps it may influence adsorption. Nor has the mechanism by which MoDTC promotes DLC wear been convincingly proved.

On a more general note, there has been a great deal of research on the mechanism of action of MoDTC but far less in recent years on other Mo-based additives. Recent work showed that one S-free Mo additives reduced friction only in the presence of ZDDP and formed MoS₂ [173,174], but it would be helpful both in understanding the mechanisms of Mo-additive behaviour and from the practical point of view to explore precisely how non-S containing organomolybdenum additives extract sulphur from other additives present.

4 FUNCTIONALISED POLYMERS

4.1 Early functionalised VM research

Polymeric additives are routinely added to engine and transmission oils as “viscosity modifiers” (VMs) in order to increase viscosity index. More recently it has been recognised that the temporary shear thinning displayed by VM solutions plays an important role in reducing friction in hydrodynamic conditions. Although these are considered to be their two main roles, in the early 1960s Okrent also found that some VM solutions reduced friction and wear of engines in a fashion that could not be explained solely by their impact on viscosity [175,176]. This effect was especially evident for a “multifunctional” polymer and one explanation suggested by Okrent was that the polymers interacted with surfaces to give anomalous rheological properties in thin film conditions.

In 1994 ultrathin film interferometry was applied to measure the film thickness of dilute solutions of polyisoprene in PAO in a rolling ball on flat contact. This showed the presence of thicker than expected elastohydrodynamic (EHD) films at low speeds [177]. The study indicated the presence of boundary films of thickness ranging from 2 and 20 nm depending on the polymer molecular weight. These thicknesses corresponded to approximately twice the diameter of the polymers in their random coil arrangements in solution and were similar to the thicknesses of immobile films formed by the corresponding polymer melts in a surface forces apparatus [178].

This research was extended in 1995 to study solutions of a range of commercial VMs in mineral oil using optical interferometry. It was found that most VMs showed conventional EHD behavior down to film thicknesses of less than 2 nm but that three formed boundary films of thickness *ca* 15 to 30 nm, similar to those previously seen with polyisoprene. [179,180]. These films persisted at temperatures up to 150°C as shown in Fig. 14 for one of the polymers. It was noted that, while the non-boundary film-forming VMs were based on non-polar monomers, the three boundary film-forming polymers contained some polar monomers, likely to adsorb on polar surfaces. For example the one shown in Fig. 14a was a copolymer of olefin and a nitrogen-containing monomer having dispersant properties. The proposed mechanism of boundary film formation is shown in Fig. 14b. It was suggested that the polymer molecules adsorb on the two solid surfaces to give surface layers that have a higher polymer concentration than the bulk solution and thus are much more viscous. At low speeds this viscous surface film fills the contact inlet and thus controls the amount of fluid entrained. However at higher speeds, when the EHD film thickness formed by the bulk solution is significantly greater than the viscous layer thickness, the adsorbed polymer no longer enhances fluid entrainment.

Further research showed that these thick VM boundary films were also formed and markedly reduced friction in mixed rolling/sliding conditions [181]. The dependence of friction on entrainment speed was measured and correlated with film thickness measurements. This showed that the viscous surface films formed by the VMs had the effect of delaying to slower speeds the onset of mixed and boundary lubrication since all friction results collapsed on the same curve when friction coefficient

was plotted against film thickness [181]. A high pressure SFA technique was also applied to compare the rheology of thin adsorbed films of functionalised and non-functionalised polymers and showed that the latter formed much more compact and uniform films in a confined contact [182].

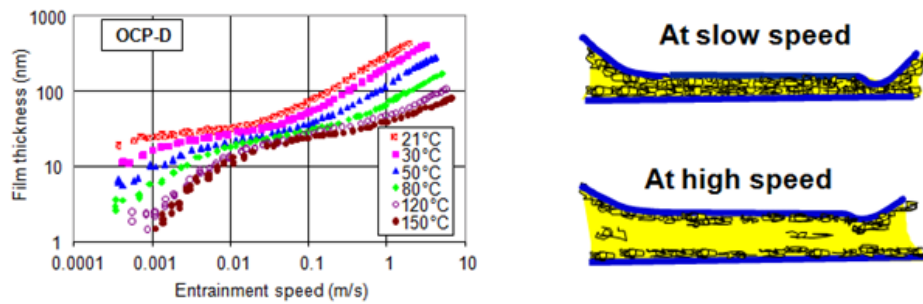


Figure 14. (a) Boundary film formation of a functionalised polymer solution and (b) the proposed mechanism [180]

4.2. Recent research on functionalised polymer additives

A considerable limitation of most early research was that it was based on commercial viscosity modifiers whose precise composition was not available for proprietary reasons and whose molecular weight distribution was very broad. This made it difficult to explore the relationship between polymer structure and boundary film-forming ability. In subsequent research a series of polymethacrylate polymers (PMAs) were synthesised using controlled radical polymerization methods to give very narrow molecular weight distribution copolymers of alkylmethacrylate with various functionalised methacrylates [183][184]. For each polymer, 10% of the monomers were functionalised with a variety of structures including aminic, acidic, hydroxyl and ethoxy groups. Fig. 15 shows some of these structures, together with non-functionalised alkylmethacrylate.

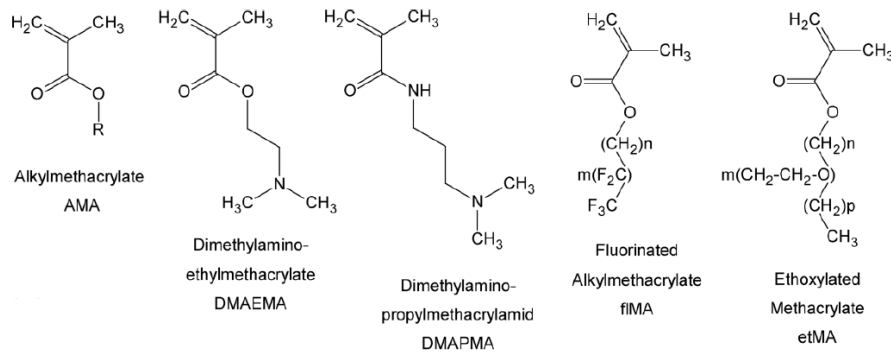


Figure 15. Polymethacrylate monomers used to make functionalised PAMs [183]

It was found that the functionalised PMAs only formed boundary films when they had block copolymer architecture, *i.e.* all of the functionalised monomers were linked together as a block at one end of the overall polymer rather than being randomly distributed along the whole polymer chain. This is probably because several functional monomers grouped together in a block copolymer molecule adsorb much more rapidly than when the functional groups are scattered throughout the polymer chain in random copolymers and also give higher coverage since the non-polar block segment can stretch away from the surface eventually to form a “brush” configuration [185][186].

Research has shown that linear polymer molecules can adsorb on surfaces in three configurations; “pancake”, “mushroom” and “brush”, as illustrated in Fig. 16 [187]. In the pancake arrangement the polymer molecules are arranged across the surface and this type of arrangement might be expected when there are several bonding positions along the chain – for example with statistically distributed functionality. When polymers have all their functionality located at one end of their molecules, as with functionalised block copolymers, in good solvents they initially adsorb to form mushrooms but at higher adsorption densities

they elongate to form brushes. Good solvents are ones in which the non-functionalised polymer chain segments are fully soluble; in poor solvents all adsorbed polymers will tend to form the collapsed, pancake configuration.

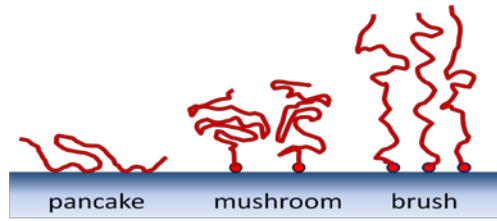


Fig. 16. Three adsorbed polymer chain configurations

Fig. 17 compares the friction behaviour of two statistically distributed functionalised copolymer solutions with two corresponding block copolymer structures at 120°C. The reduction in friction of the block copolymers is evident.

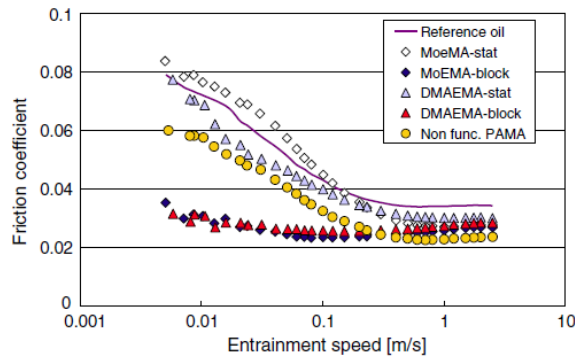


Figure 17. Comparison of friction coefficient versus entrainment speed for statistically distributed and block copolymers. Test temperature 150°C [184].

One limitation of these adsorbing polymers was that, while they reduced friction very effectively in unidirectional rolling-sliding where mixed lubrication was present, they appeared to be less effective in the more severe boundary lubrication conditions present in reciprocating contact [181][188]. The behaviour of the copolymers with other additives commonly present in lubricants was also studied [189]. In general the functionalised PAMAs combined in a complementary fashion with other additives but were less effective at reducing friction when amine-based dispersants or corrosion inhibitors were present. This probably results from competition for surface adsorption sites by the latter additives.

The above polymers generally combine VM and often dispersancy properties with a friction modifier response. It is interesting to note however that commercial functionalised polymer additives have recently been designed which are intended solely as friction modifiers [190].

In addition to the research on oil-soluble polymers described above there has also been research interest concerning the use of adsorbing polymers in aqueous systems to reduce friction, both with respect to bio-lubrication and also with a view to designing improved water-based lubricants. Spencer and co workers have explored the boundary friction properties of one water soluble copolymer system, poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), in some detail [191-193]. This polymer has a backbone of polylysine in which some of the monomers have a free primary amine group. This means that this backbone adsorbs horizontally and strongly on polar surfaces. However some of the monomers are bonded to polyethylene glycol chains and these extend out into the supernatant water to form a brush configuration. Aqueous solutions of the polymer markedly reduced friction in rolling-sliding conditions but were less effective in slow speed, pure sliding conditions [194].

The frictional properties of adsorbed polymer films have also been studied quite extensively by Klein and co-workers using a SFA to measure the thickness and friction of end-functionalised polymers adsorbed on mica from various solvents [195-197]. In good solvents very low friction was observed. Molecular dynamics simulation suggested that this was because the polymer brushes on the two opposing surfaces showed very little interpenetration even in static conditions due to osmotic pressure within the brush system; the surfaces were therefore held apart by the extended polymer chains [195]. When sliding occurs, the chains stretched along the sliding direction to reduce this overlap still further and in consequence friction was very low. At

higher pressures friction was found to increase as greater interpenetration occurred and eventually the polymers were detached from the surfaces [198]. Electrolytic polymers in aqueous solution have also been studied and these showed low friction up to higher contact pressures than uncharged ones. This is because hydration forces between the water molecules and the ions of the polymer strongly resist collapse of the polymer brushes [197].

4.3 Current state of knowledge of polymer-based friction modifiers

It is clear that functionalised VM polymers can adsorb on solid surfaces to markedly reduce friction and that they appear to do this by separating the surfaces with a pressurised fluid film at much lower entrainment speeds than is possible by the base oil alone. This behavior has been interpreted as resulting from an increase in viscosity close to the surface, though it is not known if there is also a viscoelastic contribution. Nor do we know the tethered density of these films or whether they have mushroom or brush configuration. There is evidence that the polymers fail to reduce friction effectively in severe reciprocated contact conditions but the friction and film thickness of functionalised VMs have not yet been studied at slow enough entrainment speeds to explore the true boundary lubrication properties of the adsorbed films. Some insights may be gained from SFA studies of end-functionalised polymers which suggest that these polymers adsorb to form quite stiff, brush-like adsorbed films that tilt and stretch under shear, resulting in very little interpenetration and thus very low friction at low pressure, but give higher friction and eventual tearing from the surface at high pressure. Adsorbed VM polymers may follow a similar progression in low entrainment speed conditions, though the contact pressures in the SFA are much lower than those normally found in engineering components.

One limitation of adsorbing polymers is that, unlike OFMs it is very difficult for them to form very dense packing. This is because, as the polymer molecules adsorb they sterically hinder further polymer molecules from reaching the surface. This problem increases with molecular weight and means that the VM functionalised polymers may actually operate in the mushroom rather than brush regime. One solution is to grow polymers on surfaces by polymerization from initiators pre-attached to the surface, so-called "grafting-from". Very dense polymer films can be formed in this way and these show low friction in both high and low speed conditions [199,200]. Unfortunately this approach does not provide the replenishment process generally required of lubricant additives and is thus a surface treatment rather than being delivered and maintained by the lubricant.

Almost of the work described above is based on amphiphilic polymers having a polar segment at one end and oil-soluble segment at the other and thus able to adsorb on surfaces to form a mushroom or brush configuration. However it should be noted that some of the earliest research outlined above showed that polyisoprene forms thick boundary lubricating films [177,178] and this has been confirmed by other research [201]. In polyisoprene the functional C=C double bonds are distributed throughout the polymer chain and it is of interest to question how such polymers bond to the metal oxide surfaces present and how the resulting adsorbed, presumably pancake configuration can form a separating lubricating film.

5. NANOPARTICLES

5.1 Rationale and early research

In recent years there has been growing interest in the possibility of using colloidal solid particles in the size range 1 to 500 nm as friction modifier and also antiwear additives. In principle such particle sizes are small enough both to remain dispersed in liquids by Brownian motion and to pass undisturbed through filters used in oil systems. This interest has been fuelled in particular by the recent development of fullerenes and inorganic fullerenes, whose graphitic-like structures resonate with the concept that layer-lattice materials can reduce friction. However, as will be described below many other types of nanoparticle have also been suggested as friction-reducing additives, including metals and inorganic salts. The main potential advantages of using nanoparticles as lubricant additives are envisaged as; (i) the ability to use chemistries that are insoluble in non-polar base oils; (ii) since their activity is limited to their surfaces they should show less interaction with other additives present in a lubricant; (iii) since their film formation is largely mechanical they may form films on many different types of surface; (iv) because their films form mechanically they need to be less chemically reactive than normal additives and so will be more durable and less likely to react with other additives; (v) they are likely to be highly non-volatile and thus not lost in high temperature conditions.

Nanoparticles have in fact been used as additives in lubricants for many years in the form of overbased detergents [202,203]. These are tiny particles of calcium or magnesium carbonate (typically 5 to 50 nm diameter) stabilised by a sulphonate, salicylate or phenate salt with the matching cation. In these additives, the organic salt acts as a detergent to solubilise polar oxidation material and prevent deposit/varnish formation while the carbonate core neutralizes inorganic acids formed during fuel combustion. It has long been recognised that the overbased detergents possess some antiwear properties [204] and recent work

using optical interferometry and AFM has shown that they form thick (100 nm+) films of CaCO_3 or MgCO_3 on rubbing surfaces [205]. The films are much thicker than the original size of the nanoparticles, so the particles must have fused together on the surface to form a thick layer of calcium carbonate. The effect of these particles on boundary friction is controlled by the type of surfactant employed, with long, linear alkyl chains giving low friction and branched ones high friction, as would be the case with OFMs. Thus, with the appropriate stabilising surfactants, overbased detergents can reduce boundary friction. Unfortunately, because their thick surface films are rough, they show enhanced friction in mixed lubrication conditions [205].

Apart from the overbased detergents it is difficult to chart the precise introduction of nanoparticle additives in lubricants since dispersed micron-sized particulate additives have been in use since the 1900s and it is not always clear whether these included a proportion of smaller particles. The use of colloidal MoS_2 was described earlier in this paper. In 1977 Bennington and co-workers showed that three unidentified colloidal additives reduced friction in engines [206] while Reick describes the preparation and use of dispersed 50 nm-sized PTFE in oil in the early 1980s [207,208].

5.2 Nanoparticle additive research; 1990 to present

Reviews of the use of nanoparticles in lubricants can be found in [209-211]. Many different types of material have been examined as colloidal additives to reduce both friction and wear, but the most common are metals, metallic oxides, borates and phosphates, fullerenes, inorganic fullerenes, boron oxide and nitride and recently graphene.

Considerable research on metal nanoparticles has been carried out. It has been shown that both copper [212] and nickel [213] nanodispersions reduce friction as well as improve antiwear and seizure performance in sliding contact conditions. Optical interferometry has been used to investigate the film-forming properties of dispersions of gold and silver nanoparticles [214,215]. The particles formed monolayer films on rolling–sliding surfaces but these were quite easily dislodged under high speed conditions.

Metal oxide nanoparticles have also been quite widely investigated as possible boundary lubricating additives. Titanium and iron(III) oxides were found to be only moderately effective [216][217], but $\text{La}(\text{OH})_3$ showed quite good friction and wear-reducing performance [218]. Very recently it was shown that CuO and ZrO_2 nanoparticles dispersed in a formulated engine oil were effective in reducing both friction and wear [219]

A recent area of great interest is the possible use of fullerenes and related carbon structures dispersed in lubricants as potential boundary lubricating additives. Gupta *et al.* [220] studied the influence of dispersed fullerene (C60-rich) powder on friction and wear and found similar performance to dispersed graphite or MoS_2 . The authors reported that the improvement in wear was due either to the formation of a transfer film in the contact area or to the C60 clusters acting as “tiny ball bearings”. Ginzburg *et al.* [221] analysed the tribofilm formed by fullerene using mass spectrometry, wide angle X-ray diffraction and TEM. They proposed that the film consists of a network of fullerene molecules linked by polyolefin chains formed during rubbing. Joly-Pottuz *et al.* have studied dispersed carbon nano-onions and found these to reduce friction at least as effectively as graphite particles [222]. Based on TEM-EELS analysis of the rubbed surfaces they suggested that the carbon particles may stabilise maghemite, a low friction form of iron oxide. Carbon nanotubes have also been investigated as potential boundary lubricant additives and found to reduce significantly both friction and wear [223,224]. In the last few years there has been considerable focus on graphene as a potential lubricant, including its use as an additive dispersed in oil. Graphene particles do not disperse in hydrocarbon but they can be stabilised by treatment with a surfactant such as a fatty acid. Several studies have shown that such dispersed particles reduce friction in boundary lubricating conditions [225-228].

A very widely studied class of nanoparticulate additives are the “inorganic fullerenes” (IFs). These are lamellar, inorganic compounds which have a similar spherical or tubular structure to fullerenes and carbon nanotubes. They have an onion-like structure built up of concentric layers of material and are usually solid although sometimes hollow [229]. The IFs of main interest in tribology to date have been molybdenum and tungsten disulphides (IF- MoS_2 , IF- WS_2). Both of these have been shown to have friction-reducing and antiwear properties [230,231]. *In situ* high resolution SEM has identified three different mechanisms by which they reduce friction, as summarised in Fig. 18 [231]. At low pressures, particle rolling can occur depending on the particles’ shape and hardness. At intermediate pressures the particles remain intact but slide against the bounding surfaces. At still higher pressures the particles are crushed to form a low shear strength layer-lattice film. The onset of exfoliation of IF- MoS_2 has also been observed using *in situ* TEM [233]. Because of this pressure-dependent exfoliation, IF particles give lower friction coefficient at high than at low pressure [231].

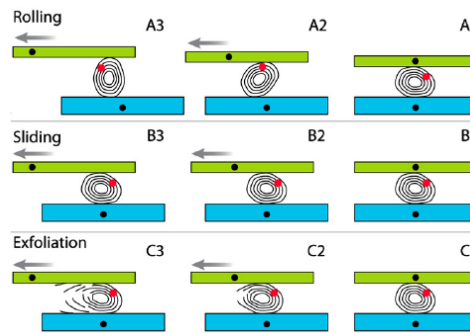


Figure 18. Three friction mechanisms of IF nanoparticles, (A) rolling, (B) sliding, (C) crushing/exfoliation. Red dot is gold marker reference point [232]

The inorganic fullerenes have a layer lattice structure which, once exfoliation occurs, is believed to provide low shear strength sheets that adhere to the surfaces to reduce sliding friction in a similar fashion. Other nanoparticulate solids also having layer lattice structure, such as hexagonal boron nitride [224,235] and boric acid [236], have also been shown to reduce friction, probably by a similar mechanism.

5.3 Discussion – nanoparticle additives

The friction-reducing properties of nanoparticles are disparate and still quite poorly understood. One problem in interpreting their effectiveness as additives lies in distinguishing the benefits of the particles themselves from those of their stabilising surfactant since in much of the published work, performance is compared to a nanoparticle-free lubricant rather than a blend containing only stabiliser. Another problem is that, unlike dissolved additives, for nanoparticles the delivery and adhesion of particles to the rubbing surfaces is strongly dependent on the mechanics of the rubbing contact and the presence of any separating fluid films. This means that the performance of nanoparticles as additives is likely to be very system-specific and in consequence, very different performance is likely to be seen in different tests and test conditions. Figure 19 shows two friction traces for a dispersion of IF-MoS₂ in a reciprocating test rig. In one test the oil in the test holder was stirred for the first and third hour. The unstirred sample showed almost complete loss of friction reduction after about half an hour while in the other stirring enabled friction to remain low and even to recover friction reduction after this was lost during an unstirred period [237].

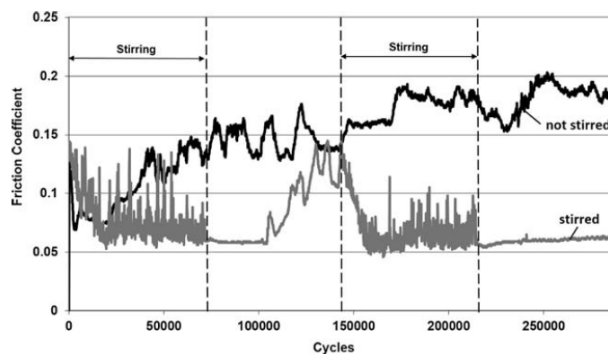


Figure 19. Loss of IF-MoS₂ friction reduction during rubbing and its recovery by stirring [237]

For a nanoparticle to be effective in controlling friction three requirements must be fulfilled; (i) the dispersed particles must enter the contact in sufficient quantities; (ii) once between the surfaces the particles must impart low friction; (iii) some adhesion of the particles to the surface is probably necessary.

The need to ensure that dispersed solid particles enter a lubricated contact to be effective is an issue with all colloidal lubricants. As liquid lubricant approaches a sliding or sliding-rolling contact, almost all undergoes reverse flow or is deflected round the sides; very little passes through the contact and solid particles may be deflected [238]. It is possible that carbon nanotubes may be more effective than spherical fullerene particles simply because their shape makes them more likely to be trapped in the

contact inlet [239]. It has also been shown that external mechanical excitation of the contact can increase the access of nanoparticles in a lubricated contact [240].

How the particles reduce friction once they are in the contact is more problematic. Particles may roll or slide as individuals. But based on the number of particles present this may not reduce friction significantly. Consider a circular contact of radius R lubricated by a dispersion of concentration C vol.% of nanoparticles of radius r . Suppose the film thickness is $2r$ (just enough to be bridged by the undeformed nanoparticles). Assuming that all particles enter the contact unhindered by flow, a simple calculation yields the number of particles present in the contact at any one moment to be $1.5CR^2/r^2$ and the fraction of the contact area covered by particles to be simply $1.5C$. For a quite high nanoparticle concentration of 1% vol. this implies that only 1.5% of the contact area will be covered by particles at any given time, probably insufficient to hold the surface apart. This suggests that to separate the surfaces effectively, either particles must become more concentrated in the contact inlet or some adhesion of particles to surface the rubbing is required to accumulate the requisite film.

To date, although there has been a great deal of research on nanoadditives, this has generally not been translated into practical use in commercial liquid lubricants. This is probably because there have to be clear performance and/or cost benefits in introducing such additives, especially since there are likely to be some concerns about the long term stability of nanoparticulate dispersions. It is possible that such additives will only become widely used if they can address problems that current, soluble additives cannot solve.

A final important question when considering nanoparticle additives is whether they might harm other aspects of the lubricant performance. One type of nanoparticle that cannot be avoided in engine oils is soot, formed by incomplete combustion of hydrocarbon fuel, and some of which accumulates in the lubricant. This soot is known to be promote wear of engine parts and it has recently been shown that one mechanism by which this occurs is that the carbon particles abrade the tribofilms normally formed by antiwear additives [241]. In consequence lubricants that contain both antiwear additive and carbon nanoparticles actually give faster wear than when the antiwear additive is left out. The key to this phenomenon is that the hardness of the nanoparticles, although less than the steel substrate, is greater than that of the antiwear film. It has been shown that other hard nanoparticles also remove antiwear films, while nanoparticles that are softer than antiwear films such as CuO do not [234]. It has also recently been reported that carbon nanoparticles can prevent MoDTC from reducing friction to an extent dependent on the particle size [342]. Clearly it is very important to ensure that nanoparticle additives do not damage beneficial tribofilms formed by other additives present in the lubricant.

6. GENERAL DISCUSSION

This paper has reviewed the four main classes of friction modifier additive in current use or under consideration, focusing on research that investigates the mechanisms by which they reduce friction. It must be stressed that it does not cover all possible types of friction modifier additives; for example it has also been suggested that ionic liquid additives, boron and phosphorus compounds may also reduce friction [1].

Two of the friction modifiers classes, OFMs and functionalised polymers act by adsorbing on polar solid surfaces to form low shear strength films that separate the solid sliding surfaces. However the thickness and strength of their adsorbed films are very different.

OFMs are low molecular weight amphiphiles that, at least when their alkyl structure permits a linear configuration, form close packed, vertically oriented monolayers with strong, inter-chain van der Waals bonding. This bonding confers strength and stiffness to the monolayers while the opposing alkyl groups provide a plane of low shear strength. However such strong, close-packed monolayers have been seen almost exclusively with long, straight, saturated chain molecules with small head groups - molecules that are often insufficiently soluble or too expensive for commercial application. A key practical as well as scientific question is thus how much unsaturation and/or branching and/or larger head group can be tolerated before molecules no longer pack sufficiently closely to support load and reduce friction effectively. A larger head group leads to a lower maximum adsorption coverage but this can be accommodated to some extent by tilting of the alkyl chains to increase their packing density, as indicated by molecular simulation [243]. Recently it has been shown that in mixtures of saturated and unsaturated chain acids, the unsaturated chains reach the surface first and effectively block it from saturated chains, to the detriment of low friction [105].

It has also been suggested that OFMs may form relatively thick viscous or paste-like metal soaps on rubbed steel surfaces, especially when water is present and that these may contribute to friction reduction. Such soaps would, however, only be

expected to result from OFMs based on fatty acids. This raises the important issue of whether OFMs such as esters and amides hydrolyse or otherwise break down during use to give free fatty acids and whether these species are actually responsible for some or all of the friction reduction seen with these additives. There appears to be no published research to measure the persistence of molecules of ester and amide OFM additives in actual use in machines. In a recent study the friction properties of 0.01 M solutions in hexadecane of the two esters, ethyl stearate and stearyl acetate, have been compared at 100°C in a high frequency reciprocating rig (HFRR). If ethyl stearate decomposes it should form stearic acid, which ought to be a very effective OFM, while the structurally quite similar stearyl acetate should give stearyl alcohol, a relatively poor OFM. The results are shown in Fig. 20, together with the friction of 0.01M stearic acid and 0.01M stearyl alcohol.

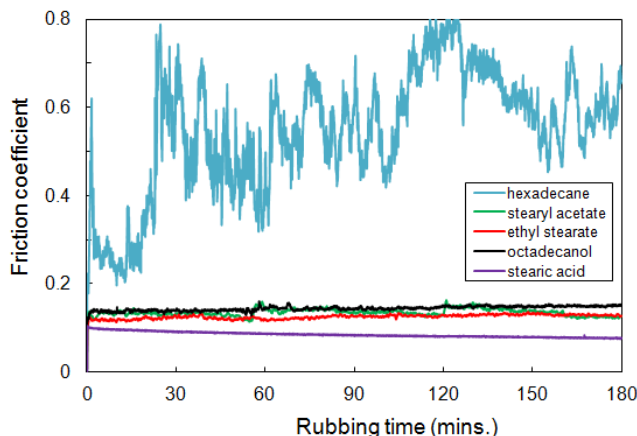


Figure 20. Comparison of friction of two esters in a prolonged reciprocating test at 100°C (Campen, S.M. to be published)

Both solutions give modest friction reduction, typical of an ester or alcohol but much less effective than stearic acid, suggesting no significant free acid production during the three hour tests. This approach is not conclusive since it does not allow for the presence of water and strong acid that might promote hydrolysis in some machine components. But it does show that fatty esters do adsorb on steel surfaces to reduce friction and also that rubbing alone does not promote ester breakdown.

Functionalised polymers also adsorb on polar surfaces so long as the functionality is located at one end of the molecule. This can give rise to adsorbed films that are tens of nanometers thick. Steric constraints mean that polymer packing density is relatively low, so there is no strong inter-chain bonding as is present in OFM monolayers. This means that the boundary lubrication properties of these polymers in high pressure conditions may be limited; though how limited has not been fully explored. However the adsorbing polymers do create thick surface layers of high effective viscosity which help separate the surfaces and thus give low friction in less severe, mixed lubrication conditions.

From the scientific point of view it might be of interest to bridge the gap between the boundary film-forming and friction properties of OFMs and functionalised polymers by exploring the impact on adsorption and friction of progressively increasing the OFM chain length.

The friction-reducing properties of the organo-molybdenum FMs and especially MoDTC are quite well understood in that they form the low shear strength, layer-lattice compound MoS₂ on rubbing surfaces. The main practical interest is performance longevity; how long the additives survive in solution and under what conditions does the surface film transform to high friction MoO₃. Unfortunately, the many oxidation states of molybdenum make its compounds susceptible to oxidation. The philosopher's stone would be an additive that reacted to form a layer lattice on rubbed surfaces similar to MoS₂ and the other molybdenum and tungsten chalcogenides, but which was not susceptible to oxidation. There is no obvious candidate, though boric acid may be a possibility.

As outlined above, many types of nanoparticle have been studied as potential lubricant additives. Of these, most are more suited to reducing wear than friction since the films that they form do not have very low shear strength. In terms of friction reduction, the most promising have 2D sheet structures; the various carbon-based graphitic materials and the inorganic fullerenes. These show low friction in boundary lubrication conditions in laboratory tests. The challenge is to transfer this behaviour reliably to operating machine component lubricants and to demonstrate better performance than alternative friction modifier classes.

A final question is whether the different classes of friction modifier additive work well together; whether combinations give the advantages of both types of additive or whether they are antagonistic. There is relatively little published work on this. Solutions containing both functionalised PMA and organo-molybdenum additives were found to provide the low mixed friction of the PMA and the low boundary friction of the molybdenum compounds; the best of both worlds [189]. However functionalised PMA reduced the boundary friction reducing properties of an aminic OFM. Very recently it was shown that the addition of small amounts of MoDTC to an OFM solution reduced boundary friction to lower values than either additive alone in a ZDDP-containing lubricant [244].

7. CONCLUSIONS

The mechanisms of action of the four main classes of friction modifier additive have been reviewed. Considerable research over many years has provided a quite clear understanding the conditions under which these additives work and, in the cases of organo-molybdenum and functionalised polymer additives, how they work. Organo-molybdenum additives react on rubbing asperities to form low shear strength MoS₂ nanosheets, though the precise driver and mechanisms of this is not yet clear. Functionalised polymer molecules adsorb to form high viscosity surface films that enable surfaces to remain separated in low entrainment speed conditions, thus postponing the onset of mixed lubrication. The mechanism of nanoparticle friction is more problematic since there are many types of nanoparticles and they may work in different ways. Here a critical issue is to ensure that the particles enter rubbing contacts and adhere to surfaces. Remarkably, the class of friction modifiers about which we know least in terms of mechanisms is the OFMs, even though they have been in use for almost a century. Much academic research has shown how model OFMs can behave in model conditions - by forming vertically oriented absorbed monolayers on polar surfaces. But it is not yet proven that this is the actual mechanism that prevails in real machine components such as found in engines. There is also a mismatch between OFMs studied in academia, mostly straight, saturated alkyl chain, small head group amphiphiles, and the largely unsaturated and/or larger head group ones more commonly employed in formulated lubricants.

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