

Boosting the Friction Performance of Amine Friction Modifiers with MoDTC

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ABSTRACT

For years amine surfactants, such as primary amines, ethoxylated amines and polyamines, have been used as friction modifiers in lubricating oils in order to improve fuel economy. This paper describes how the friction performance of amine containing lubricating oils can be improved with the addition of a small amount of molybdenum dithiocarbamate (MoDTC).

Three fatty amines, tallow amine (Armeen® T), tallow propanediamine (Duomeen® T) and tallow dipropylenetriamine (Triameen® T), have been tested with Zinc Dialkyldithiophosphate (ZDDP) and with and without MoDTC in the Minitraction machine (MTM). It is shown that MoDTC improves the friction of Duomeen T and Triameen T while not for Armeen T. It is argued that the packing of Armeen T does not allow MoDTC to reach the surface and to create molybdenum disulphide (MoS₂) sheets. Duomeen T and Triameen T have more nitrogen atoms and cannot pack as closely at the surface as Armeen T which allow MoS₂ sheets to form. To validate the theory, Scanning Electron Microscopy combined with Energy Dispersive Xray Analysis (SEM-EDX) has been used to determine the amount of sulphur in the tribofilm. The SEM-EDX data show more sulphur in the tribofilm of Duomeen T compared to Armeen T which could be due to the formation of more MoS₂.

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INTRODUCTION

Molybdenum Dithiocarbamate (MoDTC) has been used as a friction modifier in engine oils for years with one of the first patents in 1966 [1]. MoDTC interacts with the surface creating molybdenum disulphide (MoS₂) sheets [2]. The MoS₂ sheets shear easily which results in low friction when MoDTC is used. The friction and wear performance of MoDTC have been studied in a number of investigations. For example, MoDTC provides low friction ($\mu=0.05$) which is kept when ZDDP is added [3]. However, the improvement in friction comes with the drawback of increased wear when MoDTC is added to ZDDP [3]. Another investigation showed that ZDDP and MoDTC had similar high friction while the blend of the two showed low friction [4]. It was also shown that the wear was not worse when MoDTC was added to ZDDP.

The chemical composition of the tribofilm can also change when friction modifiers are added. For example, surface analysis of wear films with ZDDP and ZDDP in combination with MoDTC showed that the amount of Zinc and Phosphorous in the tribofilm decreases when MoDTC is added [3]. This has been suggested to be due to competitive adsorption between ZDDP and MoDTC. The reduction in zinc, phosphorous and sulphur was followed by increased wear.

Due to the high cost of MoDTC and its effect on catalyst and blockage of particulate filter [5,6,7], the engine oil industry is looking for alternatives such as glycerol mono oleate and amine/amide surfactants. These chemistries have been studied in combination with ZDDP. For example, investigation of a range of organic FM's showed that some friction modifiers (such as amides and amines) give lower boundary friction on the ZDDP film than on steel, while others (like polycondensed fatty acid/ester) are more effective on steel [8]. However, the organic FM's do not lower the friction to the same extent as MoDTC.

The FM's may also disrupt the tribofilm in different ways, for example, the FM may adsorb to the surface faster than ZDDP, thus preventing ZDDP from adsorbing to the surface. The FM could also remove the ZDDP film after its formation. Examples of such FM are amides and amines where amides are suggested to remove the antiwear film by forming complexes with the ZDDP (Zinc components of antiwear film) after the formation of the film [8]. Amines, on the other hand, have been suggested to prevent the first step in the film formation by preventing the ZDDP to react at active sites.

Fatty amines contain only nitrogen, oxygen, carbon and hydrogen and as such proved friction reduction with low SAPS (sulphated ash, phosphorous and sulphur). MoDTC usually provides the lowest friction. For this reason, MoDTC has been investigated in combination with fatty amines to investigate if there are any synergetic effects between MoDTC and amines resulting in low friction and with less harm to catalyst and particulate filters. In the present investigation friction has been studied with a Minitraction machine (MTM). Reducing the friction between the moving parts of the engine will reduce the power loss and improve fuel economy. However, MTM is a bench test and it is usually used as a screener for friction performance with the hope that fuel economy will show similar trends. Fatty amines are tested with and without small amount of MoDTC and in some cases the MoDTC improves the performance of the fatty amines and in other not. It is argued that the reason for this is due to some fatty amines preventing MoDTC from forming MoS_2 sheets while other allowing the formation of MoS_2 sheets. Analysis of the antiwear film with SEM-EDX is used to confirm this.

EXPERIMENTAL

Minitraction machine (MTM; PSC Instruments, London, UK) has been used to determining the friction in this investigation. The MTM was run at a temperature of 100 °C, 20 N and a slide roll ratio (SRR) of 50%. A Stribeck is recorded first from a speed of 5 mm/s to 3105 mm/s. Then a two hour long time step is started with a speed of 100mm/s. In the end, a Stribeck curve is measured. In some tests space layer interferometry method (SLIM) is used to take images of the tribofilm, before and after each Stribeck curve. Material for the disc and balls are AISI 52100 bearing steel.

For cleaning the MTM a solvent has been used, Fuel extraction 95/99 (Univar, Sweden). The loose parts are placed in this solvent and run in ultrasonic bath for 5, 10, 10 minutes. The solvent is changed between each run. The cup is cleaned with heptane and whipped with paper and nitrogen blast is used to dry off any heptane left.

Scanning electron microscopy combined with Energy Dispersive Xray Analysis (SEM-EDX) has been used to determine the composition of the tribofilm. In this investigation a Leo 1550 FEGSEM from ZEISS (Oberkochen, Germany) is used, applying 15 kV acc voltage. The EDX data was collected using a Xmax (80mm²) detector from Oxford Instruments (High Wycombe, United Kingdom).

EDX data were collected of different areas in the tribofilm. For determination of the average composition of the tribofilm EDX data of 4-5 areas of 200×200 μm in the middle of the film are averaged.

It should be noted that in this way the whole thickness of the tribofilm is measured, as confirmed by the high (>50 atom%) Fe signal measured of the substrate.

High frequency reciprocating rig (HFRR; PCS Instruments, Oxford, UK) was used to create samples for the SEM tests. The parts of the HFRR was cleaned with solvent, Fuel extraction 95/99, and

ultrasonic bath for 5, 10, 10 minutes. The solvent is changed between each run. The tests are run at 100 °C and 600 gram weight for 1 hour. The ball is a ANSI E-52100 steel, with a Rockwell hardness “C” scale (HRC) number of 58-66. The disc is a AISI E-52100 steel with Vickers hardness “HV30” scale number of 190-210. The surface finish of the disc is less than 0.02μm R_a and for the ball less than 0.05 μm R_a .

Chemicals: A group III base oil, Nexbase 3043 (Neste oil, Finland), has been used. A primary/secondary blend of zinc dialkyl dithiophosphate (ZDDP; Wuxi, China) was used. The Molybdenum Dithiocarbamate used was from Adeka (Germany). The organic friction modifier used came from AkzoNobel Surface Chemistry (Sweden). Armeen T is a primary fatty amine, Tallowamine, and Duomeen T is a fatty diamine, N-Tallow-1,3-diaminopropane, and Triameen T is a fatty triamine, Tallow dipropylene triamine.

RESULTS AND DISCUSSION

In **Figures 1**, the influence of MoDTC to ZDDP is shown. When a low amount (0.1 wt%, 100 ppm Mo) of MoDTC is added to ZDDP there is no change in the friction (0.5 wt% ZDDP). When the amount of MoDTC increases the friction is lowered. However, in literature the friction of 0.5wt% of MoDTC is usually lower that what is reported here [3-4, 8].

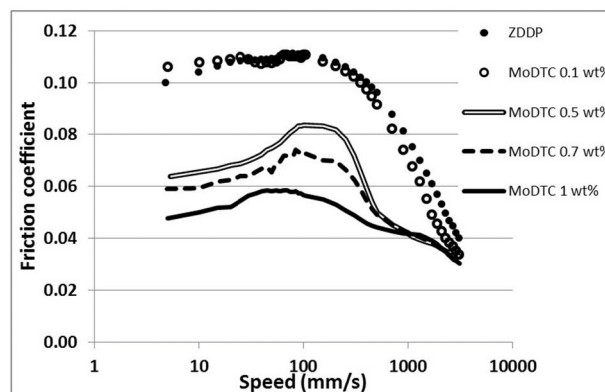


Figure 1. The Stribeck curves for different concentrations of MoDTC to ZDDP.

In **Figure 2**, **3**, **4** ZDDP and MoDTC at 0.1 wt% are added as reference. In the tests with only an amine FM and ZDDP then the concentration of FM is 0.5 wt%. In the tests where the amines have been boosted with MoDTC the amount of amine FM is 0.4 wt% and MoDTC 0.1 wt%. The amount of ZDDP is always 0.5wt% (700 ppm phosphor). In **Figure 2**, the Stribeck curves of Armeen T show that MoDTC does not improve the friction of Armeen T. Both with and without MoDTC has a friction coefficient in the boundary region of 0.08. Duomeen T without MoDTC also has a friction coefficient in boundary lubrication of 0.08 (**Figure 3**). When MoDTC is added to Duomeen T the friction coefficient is lowered, reaching a friction of 0.055. Same trend is observed for Triameen T (**Figure 4**), where the boundary friction without MoDTC is 0.09 and with MoDTC it is lowered to 0.05.