

Frictional Properties of Molybdenum-Based Lubricating Oil Additives Using Green Chemistry

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ABSTRACT

In this study, a green process was developed to synthesize a novel molybdenum disulfide (MoS_2) based friction modifier (FM) for improving fuel economy performance of lubricants. These new materials were synthesized using less hazardous elemental sulfur as opposed to other sulfur sources like hydrogen sulfide (H_2S) and carbon disulfide (CS_2). Using various bench and motoring friction torque tests, it was shown that friction reduction was benefited by utilizing low molecular weight organic backbone when designing molybdenum FMs. Also, it was shown that newly synthesized molybdenum based FMs were comparable to other well known MoS_2 precursors.

INTRODUCTION

Friction is found in engines wherever there are surface interactions such as sliding, rolling and tapping. A recent study by Argonne National Laboratory identified 16 areas of friction in engines, with the biggest friction culprits being piston rings and cylinder liners, valve trains, bearings, seals, and some auxiliary components (Figure 1).¹

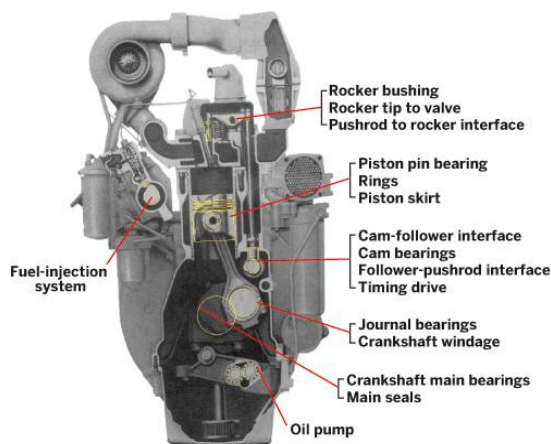


Figure 1 Schematic of an engine showing 16 points where friction occurs.

Friction contributes to wear and tear in the engine; in boundary conditions where there is metal-to-metal contact, surfaces will eventually wear out and parts will fail in a long run. Friction also consumes about 10% of a car or truck's fuel, which works out to about 1.4 million barrels of oil wasted per day in the United States. At \$60 per barrel, that is almost \$31 billion worth of petroleum lost in automobile engines every year. Therefore, much effort has been put heavily on coming up with ways to reduce friction in automobile internal combustion engines around the world.

Good friction reduction and fuel efficiency can be achieved by two ways in any engine. The first option is choosing a low viscosity engine oil, which is dependent on the properties of the base oil. This is generally a viable choice in situations where the engine primarily operates in the elastohydrodynamic regime (fluid lubrication) such as in bearings (Figure 2). Recently, it was demonstrated that by using lower viscosity oil (5W-30 vs. 15W-40) fuel economy improvement can be improved in a heavy duty diesel engine.² It is also important when choosing base oils to select one with a low pressure viscosity coefficient, since with a low pressure viscosity coefficient there will be low friction in the contact. Other required base oil properties include low kinematic viscosity, high viscosity index and low "high temperature high shear" (HTHS) viscosity; although it should be noted that one often has to adjust additive formulations to enable the use of lower viscosity base oils and provide acceptable wear, oxidation, deposit control, etc.

The second option of reducing friction is by utilization of a friction-modifying additive, i.e., friction modifier in a formulation. The friction-modifying agents for automotive engine oils are meant to reduce friction in both mixed and boundary lubrication regimes. The friction modifiers which help in the mixed lubrication regime that are commonly used in the industry today are long chain organic carboxylic acid derivatives, especially long chain amides, organic partial esters (glycerol monooleate, GLYMO), organic polymers, and phosphoric and phosphonic acid derivatives.

These organic friction modifiers are believed to stack in an orderly fashion, with the polar heads anchoring to the engine surface while the alkyl chains aligning upon each other, forming smooth sliding films, thus reducing friction (Figure 2).

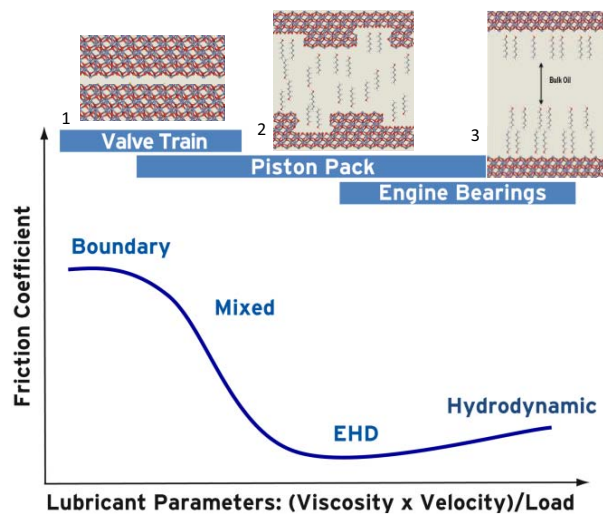


Figure 2 Stribeck Curve for various regimes: (1) boundary regime showing MoS₂ layers, (2) mixed regime showing ordered monolayers, and (3) elasto-hydrodynamic regime showing bulk oil properties.

Apart from organic friction modifiers mentioned above, some inorganic ones are also commonly used which are based on layered sheet structure, as shown in Figure 3. Under applied loads, these sheets tend to slip and slide across each other, because of their weakly held van der Waal's force between them, thus reducing friction. MoS₂, WS₂, and graphite are some common examples which are effective in the boundary lubrication regime. Some examples of MoS₂ based friction modifiers include molybdenum dithiophosphate (MoDTP), molybdenum dithiocarbamate (MoDTC), and MoS₃/MoS₂ nanoparticles, etc., which are well known in the industry and have been a topic of review³. MoDTP, phosphoric or phosphonic acid derivatives, however, are not the first choice due to a desired reduction of phosphorous in engine oils.⁴

Selecting molybdenum and sulfur source is an important criterion from its manufacturing and safety perspective. Different raw materials can have different chemical risks or exposures. Materials with minimal chemical hazards (such as spills, releases, explosions) should be chosen as suggested by the twelve principles of green chemistry.⁵ Molybdenum sources don't offer high risk as compared to some of the sulfur sources such as hydrogen disulfide (H₂S) or carbon disulfide (CS₂). Hence, this paper evaluates the performance of novel molybdenum based complexes using elemental sulfur and offers green alternatives to well known MoS₂ precursors.

Secondly, a lot of discussions have been carried out on the mechanisms of organic friction modifiers, whereas there are very few hypotheses in regards to metal containing FMs.⁶ We therefore carried out a simple structure-activity relationship which could lead to improvement in frictional properties of these novel molybdenum based friction modifiers.

In essence, this paper tries to address the following questions: a) Do molybdenum based materials synthesized using elemental sulfur reduce friction effectively?, and b) What structural modifications could be introduced to enhance the frictional properties of these novel friction modifiers?

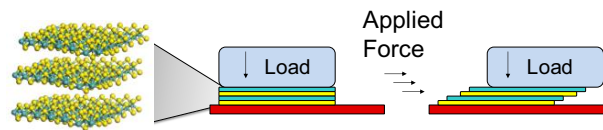


Figure 3 Schematic showing: (1) layered structure of MoS₂ and (2) layered structure of MoS₂ slipping under load.

EXPERIMENTAL

MATERIALS

"High molecular weight succinimide molybdenum oxysulfide" (H1MW) complex was obtained from Oronite Company LLC. Various molybdenum oxysulfide complexes were synthesized as shown in Figure 8.⁷ Some examples used throughout this paper are abbreviated as follows: "Low molecular weight succinimide molybdenum oxysulfide" (L1MW) and "low molecular weight amide molybdenum oxysulfide" (L2MW), respectively. MoDTP and MoDTC samples were obtained commercially.

Two different, fully formulated oils with different viscosity grade were evaluated for this study, namely the 0W-20(η1) and 5W-30(η2) without containing any friction modifier. Other additives such as wear inhibitors (zinc dialkyldithiophosphate), ashless dispersants, detergents, antioxidant, viscosity index improver (VII), etc., were included. These are designated NoFM(η1) and NoFM(η2). The above materials (H1MW, L1MW, L2MW, MoDTC, and MoDTP) were blended at different metal concentrations in the above-mentioned baselines and designated appropriately. For example, 500 ppm of H1MW in 0W-20(η1) was coded as H1MW(η1). The other oils along with their kinematic viscosity (KV) at 40°C and 100°C are summarized in Table 1. These oils were either blended or obtained from Chevron Oronite Company LLC.

BENCH TESTING

Bench testing is often used as a quick and cost-effective way to screen a property of the oil. Often these are used to screen various oil formulations to understand the structure activity relationship of diverse chemistries.

Table 1 Properties of oils.

Oil	NoFM(η_1)	H1MW(η_1)	L1MW(η_1)	L2MW(η_1)
SAE Viscosity Grade	0W-20			
Base Oil Type	Group III			
FM Type	NoFM	H1MW	L1MW	L2MW
Mo Concentration, ppm	--	500	500	500
Kinematic Viscosity (40°C), mm ² /s	39.47	40.48	--	40.70
Kinematic Viscosity (100°C), mm ² /s	8.38	8.50	--	8.51

Oil	NoFM(η_2)	H1MW(η_2)	L1MW(η_2)	L2MW(η_2)
SAE Viscosity Grade	5W-30			
Base Oil Type	Group III			
FM Type	NoFM	H1MW	L1MW	L2MW
Mo Concentration, ppm	--	1000	1000	1000
Kinematic Viscosity (40°C), mm ² /s	73.74	75.09	--	73.62
Kinematic Viscosity (100°C), mm ² /s	12.44	12.67	--	12.42

Tests on High Frequency Reciprocating Rig (HFRR)

An HFRR supplied by PCS Instruments was used to measure boundary lubricity (Figure 4). In testing, a ball of 6 mm diameter is used as the upper specimen and a highly polished disk with a 10 mm diameter and 3 mm in thickness as the lower specimen. The following test conditions were applied to screen the oils: frequency of 20 Hz, stroke of 1000 μ m, and a load of 400 g (1.03 GPa), temperatures of 80, 100, 120, 140, 160, and 180°C, respectively, for 10 minutes. HFRR tests were performed in duplicate to verify the repeatability of the trends. The friction coefficient of the two repeated test runs were averaged.

**Figure 4** High Frequency Reciprocating Rig (HFRR)

Tests on Mini-Traction Machine

The Mini-Traction Machine (MTM) (Figure 5) was also chosen for its capacity of a wide variety of loads and speeds and, therefore, being able to simulate the operations of engine parts in almost of all the lubrication regimes such as hydrodynamic, mixed, and boundary lubrication.

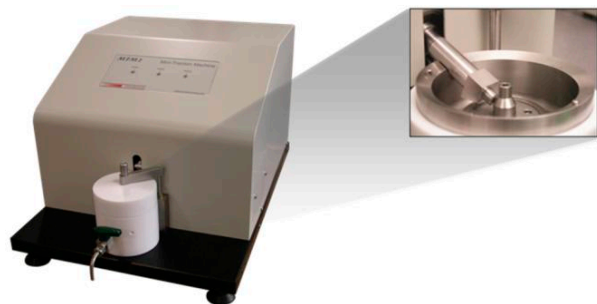
Friction tests in mixed/boundary lubrication regimes

The compositions described above were also tested for friction performance in mixed/boundary regime on the MTM bench test supplied by PCS Instruments, as

shown in Figure 5. The test was operated in the following conditions: a ball (3/4-inch 52100 steel ball) is loaded against a rotating disk (52100 steel), and the test was run under a load of 10 N (0.64 GPa), speed of 500 mm/s, and temperature of 120°C for 60 minutes. The test was repeated two times and coefficient of friction was averaged for the last 10 minutes of the rubbing process (in a stable stage).

Friction tests in multi-lubrication regime

Another test was carried out in multi-lubrication regimes, ranging from hydrodynamic to boundary lubrication on the MTM machine. The test was run at a load of 10-30 N (0.64-0.94 GPa) with a speed ranging from 10 mm/s to 2000 mm/s at a temperature of 125°C to generate Stribeck curves. In this test, the total area under Stribeck curve was used as a measure of friction performance of oil samples. The effects of various friction modifiers were then evaluated by comparing the total area of the Stribeck curve generated with the "baseline formulation with a friction modifier" with the "baseline formulation." The difference between the two Stribeck curves was reported. Lower total area values correspond to better friction performance of the oil.

**Figure 5** Mini Traction Machine (MTM)

Motoring Friction Torque Test

A motored friction torque test was designed with the valve train without piston and crankshaft, as shown in Figure 6. The camshaft is contacted with the rocker arm. The friction torque was measured by the torque meter located between the motor and camshaft. Oil temperature was controlled by the heating unit. The