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A review of recent developments of friction modifiers for liquid lubricants (2007–present)

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ABSTRACT

Due to the increasing demand of low emission and fuel economy, friction modifiers have been widely used in lubricating compositions to adjust friction and wear properties of lubricants. Recent achievements in the application of friction modifiers for liquid lubricants (2007–present) are reviewed in this paper. There are three types of friction modifiers for liquid lubricants: organomolybdenum compounds, organic friction modifiers, as well as nanoparticles. The tribological properties and lubrication mechanisms of these friction modifiers are discussed. The problems and some suggestions for the future directions of research on friction modifiers are proposed.

1. Introduction

It is well known that lubrication can be classified into four different regimes: boundary lubrication, mixed lubrication, elastohydrodynamic lubrication and hydrodynamic lubrication. Among them, friction and wear are particularly high in boundary and mixed lubrication, leading to high machine wear and energy loss. In such conditions, there are not enough liquid lubricants in the contact area to prevent direct metal/metal contacts. Friction modifiers are the lubricant additives that commonly used in boundary and/or mixed lubrication conditions to adjust friction characteristics and improve the lubricity and energy efficiency. Friction modifiers which reduce the coefficient of friction are used in lubricating compositions such as gear oils and engine oils, while friction modifiers which raise and maintain friction to a certain level are used in lubricating compositions such as automatic transmission fluid (ATF).

Typically, there are two main types of friction modifiers for liquid lubricants: organomolybdenum compounds and organic friction modifiers [1]. The former friction modifiers can be divided into three families: sulfur- and phosphorus-containing compounds, such as molybdenum dialkyldithiophosphates (MoDTP); sulfur-containing and phosphorus-free compounds, such as molybdenum dithiocarbamates (MoDTC); and sulfur- and phosphorus-free compounds, such as molybdate ester [2]. The latter are generally long chain surfactants with polar end groups, including carboxylic acid, ester, alcohol, amine, amide, imide, borate, phosphate, ionic liquid and their derivatives. Their polar end groups either physically adsorb onto the metal surfaces or chemically react with the surfaces, while the hydrocarbon chains extend into the lubricants. As nanoscience and nanotechnology advance, it has been widely accepted that the application of nanoparticles as effective friction modifiers for lubricants [3]. Due to the increasing demand of reducing emission and improving fuel economy, friction modifiers have been attracting growing interests and they have developed rapidly in the last few years. This review will summarize the recent achievements in friction modifiers for liquid lubricants during the past few years.

2. Organomolybdenum compounds

2.1. Mechanism of organomolybdenum compounds

Organomolybdenum compounds were first introduced into lubricants in 1950s, and began to be recognized as friction modifiers in the late 1970s [4–6]. Since then, they have become one of the most important classes of friction modifiers, especially for automotive crankcase engine lubricants to improve fuel efficiency. It is widely believed that organomolybdenum compounds act by forming tiny platelets of the low shear strength, layer-lattice compound

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molybdenum disulphide (MoS_2) on rubbing asperities, and result in reduced friction [6,7]. Previous studies on the triochemistry of additives showed the chemical process for the formation of MoS_2 from organomolybdenum compounds such as MoDTC (Fig. 1) [8]. MoS_2 is generated together with molybdenum oxides from the degradation of MoDTC in the contact by the tribochemical reaction. It has been suggested that the formation of MoS_2 from MoDTC is promoted by the presence of anti-wear additive zinc dialkyldithiophosphate (ZDDP) which provide the sulfur atoms to complete the sulfuration of oxysulfide ($MoS_{2-x}O_x$), and the formed lamellar sheets of MoS_2 cover the asperity tip and efficiently reduce friction [9–11]. However, if the concentration of ZDDP is low, the sulfuration is reduced and the contact is dominated by molybdenum oxides which have a negative effect on the anti-wear and friction reduction properties, and thus not reducing friction efficiently [12,13].

2.2. Overview of organomolybdenum compounds

Organomolybdenum compounds have been widely used in lubricants as friction modifiers for many years because they can efficiently reduce friction and wear in the boundary lubrication regime [5,14]. Due to its special lamellar-type structure and low shear strength, MoS_2 is a very useful lubricant additive that provides excellent friction reduction especially in high-pressure contacts, and a number of papers have been published [15–19]. Zhou et al. reported that the MoS_2 microspheres exhibited much better extreme pressure, anti-wear and friction reduction properties in base oil than commercial colloidal MoS_2 [20]. However, the application of MoS_2 is limited by its poor solubility and easily oxidation when the temperature is higher than 673 K [12,13]. So, surface modification was proposed to improve the solubility in nonpolar hydrocarbon oils. The synergistic effect of surface-modified nanoparticles of molybdenum trisulfide (nano-MoS_3) and ZDDP was demonstrated [21].

The most extensively investigated organomolybdenum compounds are MoDTC and MoDTP. They can be used independently to reduce friction and wear by the formation of protective films containing MoS_2 and other molybdenum oxides, or used in combination with ZDDP with better anti-wear performance [7,22–24]. The highly sulfurized molybdenum oxysulfide dithiocarbamates (**1**, Fig. 2) can be efficiently produced with high sulfur contents and low corrosive action, which can be used in either grease or lubricating oils as friction modifiers, anti-wear agents, extreme pressure agents and anti-oxidants [25]. Very recently, the synergetic effects of MoDTC and overbased liner alkyl benzene synthetic calcium sulfonate (OBCaS) were also studied, and the results showed that these two kinds of additives with a certain range of concentration could improve the tribological properties as compared with MoDTC alone [26]. The phosphorus-free organo-imido molybdenum complexes (**2**) [27], organomolybdenum compound (**3**) [28,29] and dicyclopentadienyl molybdenum crosslinked complexes (**4**) [30] exhibited a low friction coefficient and can be used as friction modifiers for various types of energy-saving engine lubricating oils, and compound **3** showed a lower coefficient of friction when compared with other Mo-based friction-reducing agents with the same Mo content in the oil.

Despite significant advantages of friction reduction with steel surfaces, it becomes necessary to investigate the tribological behaviors of friction modifiers in lubricants with other friction materials, such as diamond-like carbon (DLC) and chromium nitride (CrN) surfaces that have been used on machine components with excellent properties. The film formation behaviors of MoDTC on all the main types of DLC (a-C, a-C:H, a-C:H:W, a-C:H:WC, Si-DLC, ta-C, ta-C:H) were obtained, and it showed that MoDTC improved the wear resistance of DLC/DLC contacts but not DLC/steel contacts [31]. The friction modifier MoDTC formed a tribo-film on both DLC surfaces, but with lower friction on the graphitic than on DLC one [32]. Similarly, the combination of ZDDP and moly dimer gave a positive effect for both low friction and anti-wear performances in CrN/cast iron system [33]. When the anti-wear additive (ZDDP) was used along with moly dimer (MoDTC) or moly trimer (**5**), moly trimer (**5**)/ZDDP gave lower wear than MoDTC/ZDDP on the DLC coating because the former provided higher MoS_2 that offered higher load bearing capability and lower MoO_3 abrasive particles [34–36].

It is not surprising that the environment-friendly sulfur- and phosphorus-free organic molybdate ester (**6**) alone was not effective in reducing wear scar diameter (WSD) and friction coefficient because it is free of sulfur and no MoS_2 can be formed. However, it can effectively improve friction-reducing and anti-wear properties when combined with ZDDP due to the formation of MoS_2 on the

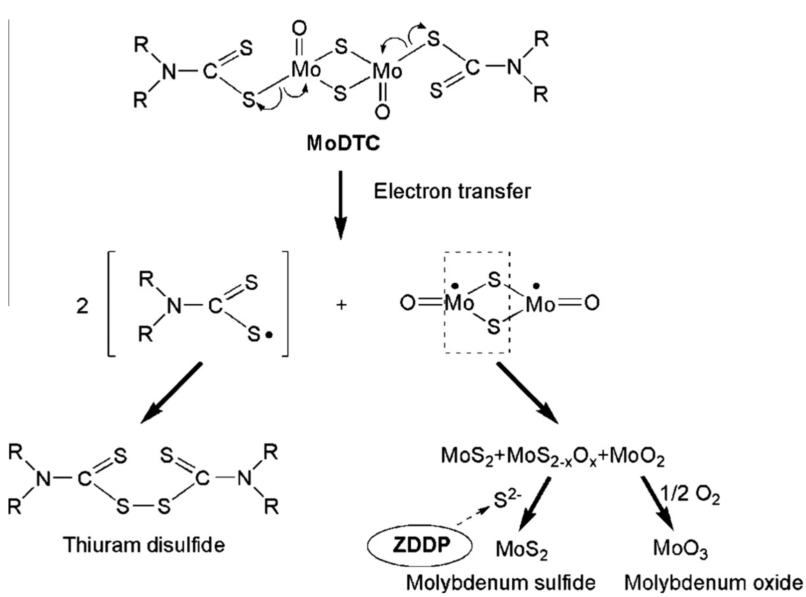

Fig. 1. Chemical process for the formation of MoS_2 from MoDTC [8].