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ASME/STLE 2012 International Joint Tribology Conference
October 7-10, 2012
Westin Denver Downtown, Denver, Colorado

*Work supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Freedom Car and Vehicle Technologies Program, under Contract DE-AC02-06CH-11357.

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Proceedings of the ASME/STLE 2012 International Joint Tribology Conference
IJTC2012
October 8-10, 2012,
Denver, Colorado, USA

IJTC2012- 61062

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ABSTRACT

In this work, the friction and wear of poly-alpha-olefin (PAO10) base oil with 3 wt. % boron nitride (BN), and molybdenum disulfide (MoS_2) nanoparticles were studied. The formulations were tested using cast iron cylinder-liner segments reciprocating against aluminum alloy piston-skirt segments at 20, 40, and 100°C. The results showed that at a load of 250 N and reciprocating frequency of 2 Hz BN did not lower friction, whereas MoS_2 nanoparticles were very effective at reducing both friction and wear, compared to the base oil. Raman spectroscopy showed the formation of an aligned MoS_2 layer on the cast iron liner surface, which functioned as a tribofilm. In the case of the cast iron liner tested with BN nanolubricant there were no traces of BN that could be related to tribofilm formation. The effect of surfactant was also studied and it was found that not only it was beneficial in dispersing the nanoparticles in oil, but also produced some reduction in friction and wear even as stand-alone additive in PAO10.

INTRODUCTION

The piston skirt contribution to the total mechanical friction losses of the piston/cylinder system in the internal combustion engine is significant [1]. Reduction in friction and wear can be achieved through optimization of the surface topography of the piston rings or cylinder liner, coating the piston and piston rings with low friction films, or through introduction of additive packages to lubricant formulations [2, 3].

The dispersion of nano-sized materials in oils is an emerging concept in lubrication. Nanomaterial additives may help counteract friction and save energy. There are reports in the literature demonstrating tribological improvements due to the addition of nanoparticles, but no clear mechanisms for the improvements are proposed. While well-known solid lubricants such as graphite, h-BN, and transition metal dichalcogenides owe their lubricity to a unique layered structure, solid nanoparticles can engage additional lubrication mechanisms. In this work, segments from a commercial piston/cylinder system were tribologically tested using a reciprocating test rig. An investigation of surfactant ability to stably suspend BN and MoS_2 nanoparticles was conducted and the surfactant's contribution to viscosity and tribological properties was studied. The cast iron samples subjected to friction tests at three temperatures were studied with Raman spectroscopy to identify chemical changes on the surface. Formation of tribofilms observed with Raman spectroscopy was correlated to the reduced friction and wear for some nanolubricant formulations.

EXPERIMENTAL PROCEDURE

The specimens used in this work were extracted from commercial heavy-duty diesel engine components. During all machining operations the original surfaces of both piston and liner were protected in order to retain the original surface roughness and pattern. The skirt specimens, made of an aluminum alloy, were 19 mm x 19 mm x 6. 35 mm, and the gray cast iron liner segments were 50 mm x 38 mm x 8.5 µm. Circumferential grooves were present on the surface of the skirt specimens from the original manufacturing of the piston. The liner was plateau honed. The cylinder liner was mounted onto a reciprocating table on the bottom of the test rig while the piston skirt was stationary. A small amount of oil (0.3 ml) was applied at the interface of the samples at the start of each test. The tests were conducted at a reciprocating frequency of 2 Hz. A normal load of 250 N was applied with a pneumatic spring and measured with a force transducer while the friction force was measured using a different force transducer. Each test was 3 hours-long in order to get a representative evolution of friction over time.

Nanolubricants were prepared from PAO10 basestock oil with 3 wt. % nanoparticles and 1 wt. % of benzethonium chloride, a known surfactant (S). Boron nitride (BN) and molybdenum disulfide (MoS_2) nanoparticles with nominal sizes 70 nm and 50 nm, respectively, were used. The BN nanoparticles were fairly spherical with individual particle sizes ranging between 50-300 nm, while MoS_2 powder had a significantly wider range of sizes between 50-2000 nm. The same skirt and liner segments were used for each formulation at the three different temperatures.

RESULTS AND DISCUSSION

The coefficient of friction as a function of time was measured at 20, 40, and 100°C for PAO10, PAO10+S, PAO10+BN with and without S, and PAO10+MoS_2 with and without S. The coefficient of friction assumed values of approximately 0.1 for the formulations without the addition of S. Morphological changes (wearing off the topmost features) in the surface were responsible for a slow and gradual decrease in coefficient of friction in the tests with pure PAO10 at 20°C. The same trend in friction behavior was observed in PAO10+S; however the values of coefficient of friction were lower than in pure PAO10. It is suggested that interactions between the surfactant and the sample cause formation of a tribochemical film that in addition to the slight viscosity increase of the formulation due to the presence of surfactant contributes to the reduction in the coefficient of friction. The trend was observed both at 20 and 40°C. Introduction of BN nanoparticles did not change the values of coefficient of friction significantly, but eliminated the gradual decrease of coefficient of friction observed in pure PAO10. This result might be attributed to physical mechanisms of nanoparticles filling out the liner voids and valleys, thus providing a hydrodynamic effect and preventing morphological changes responsible for a decrease in coefficient of friction similar to that observed in the tests with pure PAO10. Adding the surfactant to the PAO10+BN mixture resulted in better stability of the suspension, and also changed the friction behavior. However, the effect of the surfactant on friction was stronger than the effect of BN nanoparticles.

The coefficient of friction at 100°C for all formulations is shown in Figure 1. In the majority of tests its value was higher than the lower temperatures. This is due to a viscosity decrease with temperature. An exception was observed for the formulations with MoS_2. A significant decrease in the coefficient of friction was observed in PAO10+MoS_2 formulation. At this temperature the contact is in the boundary lubrication regime. MoS_2 is a well-known solid lubricant with a layered structure which can significantly reduce boundary friction. At lower temperatures this was not observed because viscosity is higher and therefore the oil plays a dominant role. It is also possible that there is thermal activation leading to the lubricity of MoS_2, which is most likely related to the chemical interaction with the rubbing surfaces and formation of a tribohemical film. Formulations with both MoS_2 and surfactant demonstrated interference of the surfactant effect with the MoS_2 effect. The surfactant stabilizes nanoparticle suspensions through the adsorption onto the nanoparticles, and by preventing agglomeration and settling of inorganic additives. The surfactant layer may also prevent interactions of MoS_2 nanoparticles with rubbing surfaces, therefore hindering the formation of a tribofilm and resulting in higher coefficient of friction than MoS_2 alone.

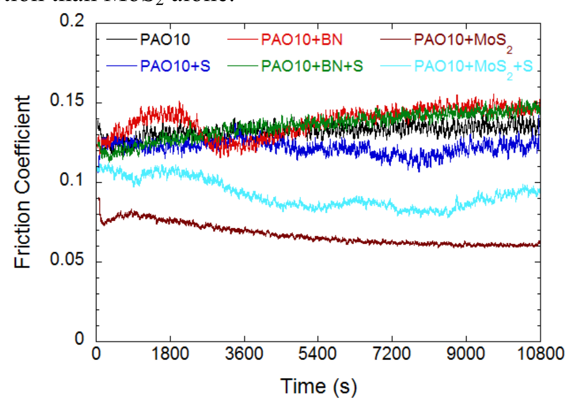

Figure 1 – Graph showing coefficient of friction as a function of time for PAO10 and PAO10 containing BN and MoS_2 nanoparticles at 100°C

For pure PAO10 and PAO10+BN+S the skirt profile measurements were conducted after each of the 3 hour friction tests at 20, 40, and 100°C. The sharp ridges of the original skirt sample wore off during the friction tests. After a run-in period, during which the topmost asperities were worn, the same plateaus were observed in both lubricants at 20 and 40°C. This result is most likely related to the high lubricant viscosity at these temperatures limiting the severe asperity interaction. At 100°C though, clear differences in wear were seen between the samples tested with pure PAO10, PAO10+BN, and PAO10+BN+S. The analysis of wear on the samples after 3 hours of friction tests at 100°C (9 hours of total friction test time) are presented in Figure 2.

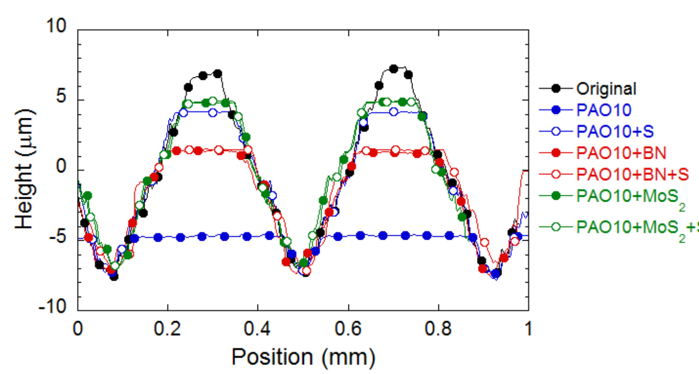

Figure 2 – Graph showing wear profiles for skirt segments

The largest wear (12.5 µm) was observed with pure PAO10 as a lubricant. Addition of only the surfactant resulted in wear of approximately 3.0 μm, which indicates that the surfactant provides protection as a stand-alone additive. Addition of 3 wt. % of BN nanoparticles resulted in 5.0 μm of wear with and without surfactant. MoS_2 appeared to provide the best protection against wearing off ridges, resulting in wear of approximately 2.0 μm with and without surfactant.

The effect of nanoparticles added to PAO10 was further investigated using Raman microscopy. The Raman spectra of friction-tested cast iron samples with BN and MoS_2 along with the corresponding lubricant formulations are shown in Figure 3.

The Raman spectrum of PAO10+BN showed no specific Raman sensitive features except for periodic intensity oscillation between 800 and 2000 cm^{-1} that is typically attributed to vibration coupling of alkane and alkene groups in long-chain PAO molecules. Resonance bands appear in both BN and MoS_2 nanolubricant formulations in the range of 800-1600 cm^{-1}. Peaks near 1300±10 cm^{-1} and 1450±10 cm^{-1} are referred to in-phase wagging and deformation of (CH_3-) and (-CH_2-) groups; the series of peaks between 843 and 891 are due to out-of-plane hydrogen modes for olefins (H-C=) and the bands between 1064 and 1079 cm^{-1} correspond to C=C=C stretching [4].

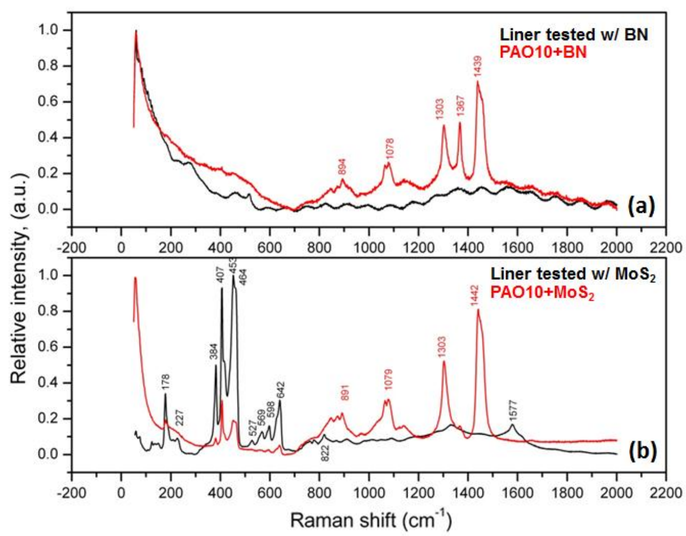

Figure 3 – Raman spectra of samples used in this work

Hexagonal boron nitride has only one Raman-active high energy band at 1366 cm^{-1} [5], which is well defined in the spectrum of BN nanoparticle suspension in PAO10. However, this peak is absent on the spectrum of cast iron tested with BN nanolubricant. Minor peaks on this spectrum may be indicative of chemical interactions between BN and cast iron, but they cannot be attributed to any of the original compositions. Therefore, it can be concluded that BN is not present at the tested cast iron interface. That might be the reason why a positive frictional effect was not observed for the tests performed with lubricant containing BN.

The Raman spectra of the MoS_2 based nanolubricant showed bands in the range between 100-800 cm^{-1}. These bands indicate that a MoS_2 tribofilm formed on the surface of the cast iron liner, which might be responsible for the lower coefficient of friction observed.

CONCLUSIONS

The tribological effects of BN and MoS_2 nanoparticles added to polyalphaolefin oil in piston skirt/cylinder liner tests were studied. The results showed that BN did not offer any improvement in friction under the tested conditions, while MoS_2 nanoparticles was very effective in reducing both friction and wear compared to the base PAO10 oil. Furthermore, the use of surfactant was not only beneficial in suspending the nanoparticles in the solution, but also lowered friction and wear by itself. The analysis of Raman spectra showed that MoS_2 nanoparticles added to PAO10 oil form an aligned MoS_2 tribofilm, which assisted in significantly lowering the coefficient of friction and reducing the wear.

ACKNOWLEDGMENTS

The Raman Microscopy was conducted at the Center for Nanoscale Materials, at Argonne National Laboratory, a U. S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

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