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PCMO Lubricant Friction Modifier Performance Durability - Extended Tribology Studies

Lubrication Fundamentals IV: Lubricant Additives

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Introduction: Designing friction modifiers (FM) resistant to performance degradation is important to meet future demands for increased fuel economy, by using low viscosity oils and longer drain intervals. Whether studying organic or organometallic FM-additives, tribological research can help increase our understanding of friction modifier surface-adsorption and performance retention, focusing on how the coefficient of friction (COF) changes with contact time. In this study we measured the performance characteristics of glycerol monooleate (GMO) industry standard organic FM, Molybdenum dithiocarbamate (MoDTC), common known FMs [1, 2], and an experimental organic friction modifier (EXP-OFM) with performance retention.

For these studies passenger car motor oil (PCMO) was formulated with Group III oil base stocks and a full range of additives meeting the viscometric requirements for a 5W-30 and 5W-20 finished oil. These additives include: viscosity and pour point improvers, calcium sulfonate detergents, polyisobutylene succinimide dispersant, amine and phenolic antioxidants, zinc dialkyldithiophosphate (ZDDP) anti-wear, silicone anti-foam, and the friction modifiers. To monitor changes in the COF with time (performance retention), the Cameron Plint TE-77 tribological testing instrument and PCS Instruments Mini-Traction-Machine were utilized in non-routine extended tribology test methods. Two types of friction modifier tribology studies were then carried out to measure retention of performance. The first study measures initial FM performance (COF-decrease) in oil held for an 60 minutes (after standard testing 50 °C to 160 °C) to insure tribofilm formation. Following this hold stage and after draining and refilling test cell with non-friction modifier oil (heated to 160 °C), the COF is monitored for ninety minutes. Finally, after draining and refilling the test cell with the original friction modifier containing oil, the COF (at 160 °C), is monitored for an additional ninety minutes. An example of the results is given in the figure below in Figure 1. These tests measured the memory of the tribofilm initially formed and ability for it to be refreshed to its original state with subsequent FM containing PCMO. The results indicated the 5W-30 oil with GMO at (1 % wt.) treat rate gave an initial friction reduction of -29% COF and retained a reduction of -18% COF on switching to non-FM oil. This could then be completely refreshed to -29% COF after the second oil switch back to GMO containing oil. The same base formulated 5W-30 with Exp-OFM at (1 %wt), had an initial friction reduction of -45% COF, retained -31% COF with non-FM oil, and was then refreshed back to a -44% COF reduction. In contrast, although MoDTC at (1 %wt) shows a stronger initial friction reduction of -70% COF, during the first hold period, before oil switches, this degrades up to -45% COF. In addition, after the non-FM oil switch, it degrades further all the way up to only -13% COF reduction. Finally, following the second MoDTC (1 %wt) oil switch, the COF again first drops to -70% COF and then degrades up to a -44% COF reduction.

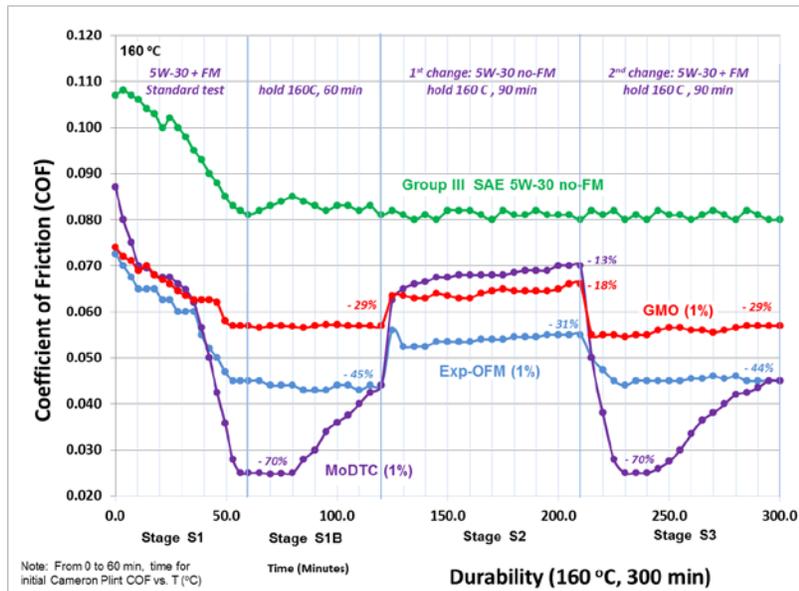


Figure 1. Durability Study (FM / non-FM / FM) – Cameron Plint TE77. The percent reduction in the coefficient of friction is shown relative to the oil without friction modifier at each point.

The oil change results sparked further investigation into additional friction modifier durability studies to now extended hold tribological testing. At the end of standard test temperature the testing is now continued isothermally for several hours. Specifically, first samples of fully formulated 5W-30 oil with and without a friction modifier are tested by the standard tribology testing with the Plint TE77 (50 °C to an end-temperature of 165 °C, 120 °C, or 135 °C), and Mini-Traction-Machine Stribeck curves (at 150 °C). At the final elevated end-temperature of 160 °C, 120 °C, or 135 °C (Plint TE77) or 150 °C (MTM), the tribological measurements are then *continued* for 50 h, 150 h, and 100 h, (TE77-hold respectively) and 48 h (MTM hold) to record the COF vs. time. The changes in the reduction in COF can therefore be analyzed with time (simulated mileage accumulation) Figure 2. When no further COF change occurs the test is stopped.

These tests were performed to determine the extent of retention of tribobilm boundary layer friction reduction with time, and as expected showed considerable difference between organic friction modifiers and MoDTC. Specifically, GMO performance was lost after 35h at (160 °C hold testing) giving a *sharp COF rise*, while its performance was stable for 150h at 120 °C hold testing. The Exp-OFM in comparison showed stable friction reduction retention *at all temperatures*, from 120 °C to 160 °C. In sharp contrast, the MoDTC *lost* all its performance completely in 10h at (160 °C), and in 130h at (120 °C) both showing a *very sharp COF rise to or greater than that of the starting oil with no-FM*. It appears that increase temperature accelerates the breakdown in FM performance of the MoDTC and to further investigate influences to this breakdown, the level of ZDDP as (%P) was then varied and studied. It appears that an increase in ZDDP delays the MoDTC FM performance breakdown. The combination then of lower temperatures and high levels of ZDDP will function together to extended time before MoDTC performance breakdown.

Tribology hold experiments were also performed with the Mini-Traction-Machine ball-on-disc Stribeck curve hold study at 150 °C, 30 Newton (N) load, a 50% side-roll-ratio, at 5 mm/s entrainment speed.

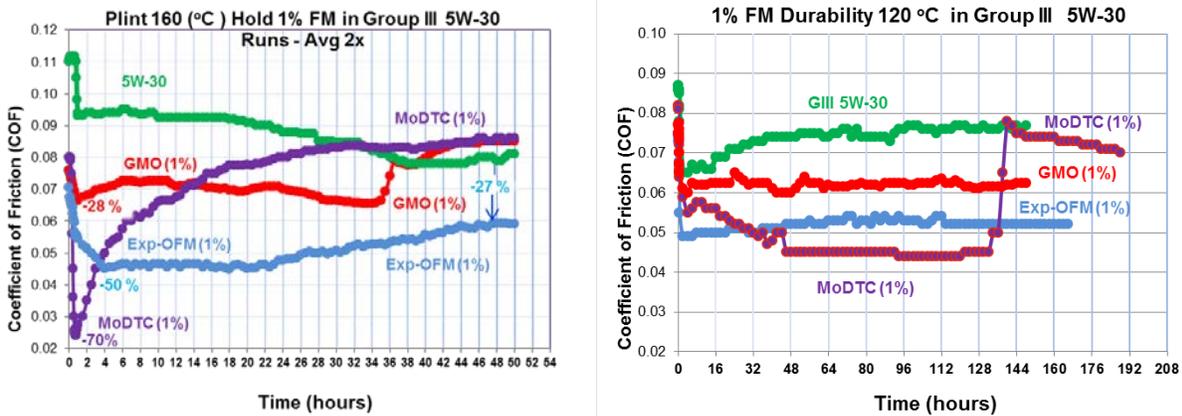


Figure 2. Cameron Plint TE-77 Extended hold tribology experiments. Left, held at 160 oC, Right, held at 120 oC, both with 100 N applied load to cylinder on disc friction testing experiment.

These hold experiments compared test oils with Exp-OFM (1 %wt), and MoDTC (1 %wt) to the same formulated 5W-30 oil without any friction modifier. The results with the MTM test again show the rapid degradation of performance with MoDTC FM and sustained performance retention with the Exp-OFM. The non-FM t5W-30 gave a flat (40 h) COF = 0.104, 1% Exp-OFM (48h) COF = 0.06, while for MoDTC in (2.5h) COF increased to 0.12, and on average higher than 5W-20 no-FM. The support data showed the same difference in tribology BL performance retention as the Cameron Plint TE77 tribology hold data. The durability studies suggest that the tribofilm generated by MoDTC breaks down with sufficient time and therefore analysis of the surface of the specimen at the end of the Plint TE77 should indicate a loss of Molybdenum and sulfur from (Mo-S₂-Mo) breakdown. In order to explore this idea further Scanning Electron Microscopy x-Ray fluorescence analysis was conducted on the contact surface of the MoDTC hold tribology plate specimen, gently rinsed with heptane, to remove any residual surface oil. The results show large multiple areas deplete of Mo, and S and only minor patches on the surface where the elements Mo & S were detected. Further characterization by micro-FTIR on the same specimen indicates very little overall absorbance (hydrocarbon or oxidation products), and the only areas of oxidation that do occur, are at the boundaries of the rubbing path of the dowel on plate. It is as if the oxidized hydrocarbon generated during the hold testing for 50 h is moved in the testing process as it develops, to the extreme boundaries of the sliding contact, giving the appearance of a debris field.

Finally, to see if there is a reasonable correlation between the tribology bench test measurements of COF and engine fuel economy, Sequence VID Engine Fuel Economy tests were performed on a Chemtura blended 5W-20 PCMO and compared to the Plint TE77 tribology hold testing at 135 °C. The formulated 5W-20 oil again contained all the additives including ZDDP at 0.07%P, and was measured isothermal in the Cameron Plint TE77 at 135 °C, and 100 N load for 100 hours. The 5W-20 oil and (1 %wt) treat rates of both Exp-OFM and GMO were tested by the Plint TE77 hold method. On average over the 100 hours the COF for oil with Exp-OFM (1 %wt) was COF= 0.0495; still significantly less than the 5W-20 non-FM oil with a COF=0.09. For oil with GMO (1 %wt) there were significant changes with time. The run began at a COF= 0.06 but after 28h begins to rise to a COF=0.087 at 100h, thus losing most of its performance. For comparing the COF improvement from Exp-OFM (1 %wt) to fuel economy improvement, the Sequence VID fuel economy test was performed on the same oils. The results showed the Fuel Economy Increase (FEI) for the 5W-20 non-FM oil gave a FEI (Sum) = 1.37%, with FEI2 = 0.8%; while 5W-20 + Exp-OFM (1 %wt) gave FEI (Sum) = 2.00%, and FEI-2 = 0.91%. This indicates, relative to the same oil without Exp-OFM, there was a 45.6% better Fuel Economy Increase gained from the Exp-OFM. If we compare the average COF values of 0.0495 for Exp-OFM (1 %wt), and COF 0.089 for non-FM 5W-20, we can calculate a reduction in the COF of -44.4% COF. The 44.4% benefit compares with the overall 45.6% improvement in FEI (Sum) from the engine test. These results are given below in Table 1 and Figure 3.

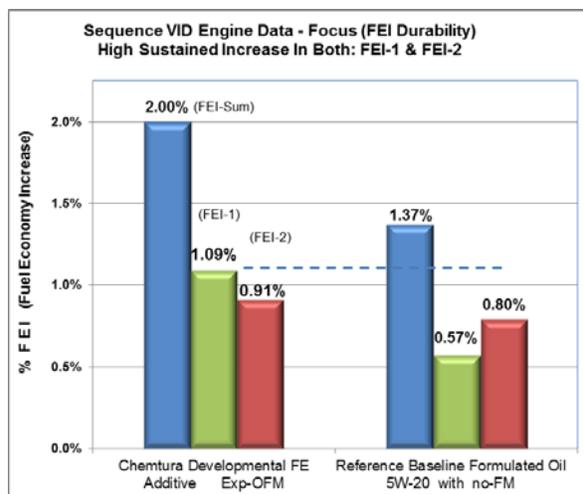
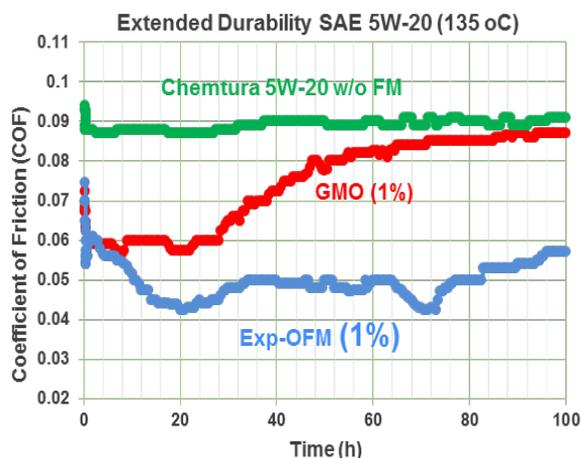


Figure 3. Left, Cameron Plint TE77 extended hold of Chemtura formulated 5W-20 held at 135 °C for 100h. Right, Sequence VID engine fuel economy test results of the same Chemtura 5W-20 with no FM and with a treat rate of (1 % wt.) Exp-OFM.

Sequence VID Fuel Economy Improvement - Engine Test / Extended Tribology 135 °C					
Oil Formulation	FEI(Sum)	FEI2	% FEI (Sum) Improvement	Avg. COF (Extend 135 °C)	% Avg. COF Improvement
5W-20 non-FM	1.37 %	0.80 %	----	0.0891	----
5W-20 + 1% Exp-OFM	2.00 %	0.91 %	45.6% better	0.0495	44.4% better

Table1. Sequence VID Fuel Economy Engine Test Data & Tribology Hold COF data.

In summary, these combined tribology and engine studies supports the concept that the extended hold COF studies, may guide new friction modifier development in relation to engine fuel economy increase benefits. In addition, these studies agree with the close values of Seq. VD, FEI-1 (1.09%) & FEI-2 (0.91%) with 83.4% fuel economy retention, $(FEI-R) = (FEI-2/ FEI-1) \times 100$, for oil treated with Exp-OFM at (1 %wt).

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References:

[1] J. Crawford, A. Psaila, S.T. Orszulik. In R.M. Mortier and S.T. Orszulik, eds. *Chemistry and Technology of Lubricants, Miscellaneous Additives and Vegetable Oils*, 2nd Ed., London, 1997, pp 181-187.
 [2] D. Kenbeck, T.F. Bunemann. In L.R. Rudnick, ed. *Lubricant Additives Chemistry and Applications, Organic Friction Modifiers*, 2nd Ed., Taylor and Francis, Boca Raton, FL, 2009, pp 195 -209.

Key words: Organic Friction Modifier, Tribology, Glycerolmonooleate (GMO), Molybdenum dithiocarbamate (MoDTC), Sequence VID, Fuel economy increase, SEM X-Ray, Fourier Transform Infrared (FTIR) micro-spectroscopy