TRIBOLOGICAL BEHAVIORS AND MOLECULAR SPECTROSCOPIC CHARACTERIZATION OF LUBRICATED PISTON RING–CYLINDER BORE SLIDING CONTACT UNDER STEPWISE HEATING CONDITIONS

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SUMMARY
Frictional behaviours of Mo alloy coated piston ring against cast iron cylinder bore was recorded as a function of temperature using a reciprocating tribotester and a fully formulated engine oil, SJ/CF/5W-30, with and without a friction modifier, molybdenum dialkyldithiocarbamate (MoDTC). It was observed that, as temperature was increased in a stepwise mode from 150 ºC to 400 °C, friction coefficients in the presence of MoDTC presented two local minimal values respectively at 285 – 300 ºC (µ = 0.045) and at 390 – 400 ºC (µ = 0.05), with only one minimal value at 340 – 355 ºC (µ = 0.065) in the absence of MoDTC. Chemical characterization of worn tracks of the cylinder bore with reflected FTIR spectroscopy, Raman spectroscopy and ESCA indicated that, as temperature ramps up stepwise, both the base stock and the tribological additives, ZDTP and MoDTC, experienced tribochemical reactions yielding MoO_3, MoS_2 and carbonaceous matters. MoO_3 and MoS_2 are partially responsible for the local minimal friction coefficient at the lower temperature and ratio of the ordered carbons accounts partially for that at the higher temperature.

Keywords: Piston ring-cylinder bore assembly, MoDTC, molecular characterization, stepwise heating, tribochemistry

1 INTRODUCTION
Variations in the tribofilm compositions and structures, which affects friction coefficient and wear rate, can arise either from the chemistry of triboelements such as lubricant basestock, tribological additives and tribomate materials, or from the combined effect of mechanical action and frictional heating [1 - 3]. In tribochemical research, much attention has been paid to the chemistry of tribological additives and their tribochemical reactions with tribomaterials, and to correlating qualitatively observed tribochemical performances with the tribomaterials chemistry, tribofilm chemistry and formation mechanisms [4 - 7]. During friction and wear process, especially when the tribosystem is operated at higher temperatures, the lubricant basestock will undergo tripyrolysis and polycondensation, and such chemical changes will exert important effects on tribometric outputs. It is thus necessary to investigate the chemical and physical changes of lubricant basestocks during friction and their possible contributions so as to understand more comprehensively the overall tribological characteristics.

2 EXPERIMENTAL
Tribological experiment was conducted on an Optimal-SRV tribotester under a stepwise heating scheme shown in Figure 1. The upper specimen is cut directly from real piston rings of plain steel substrate sprayed with Mo + NiCrBSi, and the lower specimen is worked with practical cylinder liner materials of plain grey cast iron. Before each test run, 40 µL of lubricating oil, a fully formulated synthetic engine oil (SJ/CF/5W-30) with or without 3 wt% molybdenum dialkyldithiocarbamate (MoDTC), was supplied onto the contact area.

![Figure 1: Stepwise heating scheme](image)

Worn tribosurfaces of the lower specimen corresponding to specific points on the friction coefficient curves as a function of temperature were chemically characterized with reflected Fourier- transform infrared (FT-IR) spectroscopy, laser Raman spectroscopy and electron spectroscopy for chemical analysis (ESCA).

3 RESULTS AND DISCUSSION
3.1 Friction Coefficient (µ)
Variation of friction coefficient with temperature under lubrication of SJ/CF/5W-30 with or without MoDTC is shown in Figure 2.
For both SJ/CF/5W-30 and MoDTC-modified SJ/CF/5W-30, valley effects were identified for friction coefficient as temperature ascends. An important difference is that lubrication with MoDTC-modified SJ/CF/5W-30 presents two friction coefficient valleys, one occurring at a lower temperature (285 - 300 °C) and the other at a higher temperature (390 - 400 °C) as contrasted with the unmodified oil which has only one valley at a temperature in-between (340 - 355 °C). More importantly, either of the local minimal µ in presence of the modified oil is invariably lower than that attained just with the unmodified oil, justifying the effectiveness of MoDTC in friction improvement.

3.2 Infrared Spectroscopic Characterization

The molecular chemistry of worn surfaces at specific points on the friction coefficient versus temperature curve (Figure 2) was characterized with reflected FTIR, as plotted in Figure 4, and compared with the IR spectrum of the new API SJ/SAE 5W-30 displayed in Figure 3.

Through a combination of tribological and thermal effects (i.e. tribo-thermo effect), both the ester base stock and tribological additives, ZDTP and MoDTC, have experienced great changes in terms of molecular chemistry. At point a, peaks characteristic of the functional groups, P-O-C (aliphatic group) (ν=998 and 1059 cm⁻¹) and P=S (ν=723 cm⁻¹) of ZDTP and MoDTC cannot be identified, and only some weak peaks (ν=1744, 1463, 1378 and 1159 cm⁻¹) characterizing the ester type engine oil survive. As the temperature increases with the accumulation of tribo-thermo effect, these peaks become fewer in number and grow weaker in intensity. At point b and point c in particular, the peaks designating the ester type engine oil become even weaker, and almost just methylene groups (2928 and 2857 cm⁻¹) of decreased quantity can be detected. Further at point d and point e, no peaks are observed at all and the maximum slope of the spectral baseline is reached. It is inferred that severe degradation of the lubricating oil has occurred. One dominating mechanism of this tribological process is the desorption of the weakly bonded films of MoDTC and ZDTP and the conversion of their tribochemical decomposition products into tribochemical films due to higher contact temperature. Another major mechanism is the tribopyrolysis and tribocondensation of base stock. As temperature goes high, both mechanisms proceed in different manners and co-contribute to the generation of the tribochemical reaction films for friction reduction.

A further inference is that there have occurred on the contact area not only tribochemical reactions that lead to formation of inorganic species via organics, but also physical state changes of the yielded species as suggested by variations of the slope of the spectral baseline. Such changes are presumed to be due to evaporation of oil components and phase transitions of the accumulated species on the contact area. Friction reducing characteristics as shown in Figure 2 (friction versus temperature curve) are co-contributed by both the formation of inorganic/organic species and their physical states.
3.3 Raman Spectroscopic Characterization

Raman spectroscopy was employed to characterize the carbonaceous residua from mainly decomposition and condensation of pyrolysed base stock species on the contact area. As shown in Figure 5, no Raman active species have been detected on tribosurfaces at points a and b. This indicates that the lubricant has not been pyrolysed into carbonaceous matters in spite of its obvious molecular structure changes as shown by the FT-IR results. With the enhancement of tribo-thermo effect afterwards (from state c via state d and finally to state e), two types of carbonaceous matters come into occurring, as evidenced by the D peak (1370 cm\(^{-1}\)) and the G peak (1580 cm\(^{-1}\)). These facts imply that at tribo-state a and b, contribution of carbonaceous matters to the local minimal \(\mu\) can be negligible, while at tribo-state c, d and e, the pyrolysed carbonaceous matters play parts in the frictional behaviours of the tribosystem.

![Figure 5: Raman spectra for the lower worn surfaces at points a through d on the \(\mu\) curve](image)

It is believed that D line and G line represent two different carbon modes in the carbonaceous matters, the former indicating disordered carbons and the latter ordered carbons which are frequently referred to as graphitic carbons for it assumes the same peak position as natural graphite \cite{8}. The stronger the D-line peak, the greater the proportion of the disorder-induced defects in the carbonaceous matters. While the stronger G-line peak denotes the abundance of the ordered carbon in the carbonaceous tribofilms.

The ratio of peak intensities between G-line and D-line \(I_G/I_D\) corresponding to points c through e was best fitted considering Lorentzien line shapes, as displayed in Table 1. It is evident that the maximal \(I_G/I_D\) value is attained at point d. As point d assumes the local minimal \(\mu\)-value, it is suggested that the proportion of the ordered carbonaceous matters on the contact area can contribute to the effective improvement of the frictional behaviours. This finding is in agreement with the reportage of Jin et al \cite{9}.

<table>
<thead>
<tr>
<th>Typical points</th>
<th>(I_G/I_D)</th>
</tr>
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<tbody>
<tr>
<td>c</td>
<td>0.66</td>
</tr>
<tr>
<td>d</td>
<td>0.85</td>
</tr>
<tr>
<td>e</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*Table 1: \(I_G/I_D\) ratios of carbonaceous matters at typical points*

3.4 ESCA Characterization

Existence of carbonaceous matters, the ordered in particular, is evidently not the only chemical species responsible for the frictional behaviours observed. As implied by IR identifications in Figure 4 and inferred by the chemistry of the friction modifier MoDTC, there should exist other chemical species on the tribosurfaces accounting for each of the five tribo-states on the \(\mu\)-curve. To identify the chemical states of the friction reducing species especially derived from MoDTC, ESCA analysis of every worn lower tribosurface was conducted. In Table 2 are listed the major chemical species of element Mo from MoDTC and their contents.

<table>
<thead>
<tr>
<th>Tribo-states</th>
<th>Chemical species</th>
<th>Content (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>MoO(_3), Mo(CO)(_4)</td>
<td>0.06, 0.03</td>
</tr>
<tr>
<td>b</td>
<td>MoO(_3), MoS(_2)</td>
<td>0.21, 0.10</td>
</tr>
<tr>
<td>c</td>
<td>MoO(_3)</td>
<td>0.27</td>
</tr>
<tr>
<td>d</td>
<td>MoO(_3)</td>
<td>0.35</td>
</tr>
<tr>
<td>e</td>
<td>MoO(_3)</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*Table 2: Calibrated results for Mo3d peaks*

It is noticed that MoO\(_3\) is the common Mo species that exists at every specific tribo-states on the \(\mu\) curve. From Tables 1 and 2 it is suggested that, in terms of chemistry, MoS\(_2\) and MoO\(_3\) contribute to the global minimal \(\mu\)-value at lower temperature (point b), and MoO\(_3\) and the ordered carbonaceous matters accounts for the local minimal \(\mu\)-value at higher temperature (point d). It can thus be concluded that MoS\(_2\) confers anti-friction performances at lower temperature and the ordered carbonaceous matters do at higher temperature.

As there is no consistent correlation between the atomic concentrations of chemical species on the tribosurfaces and the observed frictional behaviors, it is suggested that tribofilm-specific chemistry, including both types and quantities of chemical species, e.g., MoS\(_2\), MoO\(_3\) and carbon species, is not the sole factor responsible for friction improvement. The physical structures of these tribochemically induced species will also account for variations of the friction coefficients.

To conclude, the holistic improvement of the friction performance under lubrication of MoDTC-modified SJ/CF/5W-30 engine oil, which is demonstrated by two \(\mu\) valleys with both of the minimal \(\mu\) values lower than that of only one \(\mu\) valley under lubrication with just the SJ/CF/5W-30 engine oil, is partially contributed by the
formation of Mo\(\text{S}_2\) and Mo\(\text{O}_3\) for the first minimal \(\mu\) valley at the lower temperature and partially by the deposition of the ordered carbons for the second minimal \(\mu\) valley at the higher temperature.

4 CONCLUSIONS

(1) Formulation of a friction modifier MoDTC into commercial API SJ/SAE 5W-30 engine oil can benefit for improved frictional behavior of a sliding pair using the Mo sprayed piston ring against cast iron bore. In the presence of the MoDTC-modified engine oil, two valleys of low friction coefficient are observed as temperature rises in a stepwise mode. One occurs at 285-300°C (\(\mu=0.045\)) and the other at 390-400°C (\(\mu=0.05\)), as contrasted with only one valley at 340-355°C (\(\mu=0.065\)) when the sliding part is lubricated just with the unmodified engine oil under identical sliding conditions.

(2) Both the base stock and the tribological additives, ZDTP and MoDTC, have undergone pronounced tribocatalytic reactions under the set tribotest conditions. The base stock will be tribocatalytically pyrolyzed into carbonaceous matters. The ratio of the ordered and disordered carbons determined by Raman spectroscopy depends on temperature and relates to friction coefficient. The maximum ratio corresponds to the local minimal friction coefficient.

(3) Tribocatalytically degraded products of MoDTC and its reactions with tribocoatings present chemical species Mo\(\text{O}_3\) and Mo\(\text{S}_2\). While Mo\(\text{O}_3\) is invariably identified at all specific tribostates, occurrence of Mo\(\text{S}_2\) is observed to be dependent on temperature and related to the global minimal friction coefficient.

(4) In the present tribosystem lubricated with the MoDTC-modified engine oil, the friction behavior (friction coefficient versus temperature) at lower temperature is partially attributable to film formation of Mo\(\text{S}_2\) and Mo\(\text{O}_3\), and the lower friction coefficient values at higher temperatures are contributed a role by the higher ratio of the ordered carbon species and Mo\(\text{O}_3\) film.

5 REFERENCES