Tribology and tribochemistry of oil soluble methylene-bis-[dialkyl/alkylaryl-dithiocarbamates] as potential EP additives

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A number of blends of methylene-bis-[N,N-dialkyl/alkylaryl dithiocarbamates] in paraffin oil (0.5% w/v) were evaluated for their anti-wear, EP and friction reducing tribological properties by employing 12.7 mm diameter low carbon and chromium bearing ball specimen in a four ball test. All the additives were found to decrease wear and friction to appreciable levels and increase the load carrying capacity to very high values. In particular, the additive methylene-bis-[morpholino-dithiocarbamate] was instrumental in exhibiting lower values of wear scar diameter and coefficient of friction at lower as well as higher loads and high load carrying capacity, load wear index and flash temperature parameter values in comparison to plain paraffin oil and a reference additive. The additives also afforded lower values of wear-scar diameter in one-hour wear test. The topography of the used bearing ball specimen was investigated by scanning microscopy technique.

The automotive industry is a major market for lubricants and extensively uses additive treated lubricants in engines, manual and automotive transmission and rear axles. The automobile gear teeth often experience severe wear and scuffing under the conditions of high specific pressures and temperatures. These deleterious effects can be minimized by using EP and anti-wear additive blended lubricants.

The use of certain organic sulphur compounds as anti-wear and extreme pressure lubricant additives has been well known1-4. These compounds help to increase the mechanical efficiency and fuel economy and diminish wear and destructive heating at higher loads and also provide lubrication to the sliding surfaces by forming soft, easily sheared inorganic films on the sliding surfaces. On the other hand, the use of some nitrogen compounds has exhibited only anti-wear characteristics at lower loads by their adsorption on the metal surfaces5-7.

These abovementioned facts and the ability of certain zinc and molybdenum dithiocarbamates to function as anti-oxidation, anti-corrosion, anti-wear, antifriction and EP additives5-15 have attracted our attention for making efforts in incorporating the special tribological properties of sulphur and nitrogen elements in a single synthesized molecule.

In the present communication, a number of oil soluble methylene-bis-[N,N-dialkyl/alkylaryl-dithiocarbamates] were synthesized and evaluated for their anti-wear, anti-friction and EP properties in a four ball test by using 12.7 mm diameter low carbon and chromium alloy steel ball specimen. The topography of the used bearing ball wear spots was examined by scanning microscopy technique.

Materials and Methods

Bearing ball specimen
Low carbon and chromium alloy steel ball specimens of the following composition and hardness used were C% 0.31, Mn% 0.34, Cr% 0.33, Hardness in VHN 255.

Base lubricant
Paraffin oil was used as the base lubricant having the following characteristics: specific gravity; 0.85 at 30°C, viscosity; 81.42 cP at 40°C and 7.65 cP at 100°C, cloud point; -2°C, pour point; -10°C, flash point; 186°C, fire point; 202°C.

Additives
The additives, methylene-bis-[N,N-dialkyl/ alkylaryl-dithiocarbamates] were prepared by refluxing an ethanolic solution of appropriate sodium dithiocarbamate, and methylene chloride for four hours. Solid separated out from the filtrate, which was filtered, washed with water, dried and re-crystallized from a mixture of benzene and ethanol (Scheme 1).

\[
\begin{align*}
RR'N - C - SNa + CH_2Cl_2 & \xrightarrow{\text{ethanol}} (R R' N - CS_2)CH_2S \\
& \text{Scheme 1}
\end{align*}
\]
where \( R \) and \( R' \) = benzyl-, \( n \)-butyl-, ethyl-, methyl phenyl-, morpholino- and piperidine-groups.

The purity of compounds (Table 1) was ascertained by TLC technique and were characterized by the elemental analysis and IR spectra. 0.5% w/v blends of additives with paraffin oil were made by stirring and heating at 60°C for 30 min.

**Four ball test**

Tribological evaluation of these additives for EP and friction modifying characteristics was conducted on a four-ball machine operating at 1500 rpm [ASTM D 2783]. A series of 60 s tests were conducted until the welding point was reached. One-hour duration wear tests were also performed at 40 kg load and 1200 rpm [ASTM D 2266-67].

**Results and Discussion**

0.5% w/v solutions of methylene-bis-[\( N,N \)-dialkyl/alkylaryl-dithiocarbamates] (\( A_1 \) – \( A_6 \)) in paraffin oil were evaluated for their anti-wear, friction modifying and EP properties by using 12.7 mm. Steel ball specimen and determining wear scar diameter (\( d \)) and coefficient of friction (\( \mu \)) at initial seizure load (ISL) and just before weld load (JBWL) and weld load (WL), flash temperature parameter (FTP) and load wear index (LWI). The results were compared with plain paraffin oil and its blend with methylene-bis-[\( N,N \)-di-\( n \)-butyl-dithiocarbamate] reference additive (\( A_6 \)) and are recorded in Tables 2 and 3.

The experimental results recorded in Table 2 clearly show the effectiveness of the additives \( A_1 - A_6 \) in increasing the values of ISL, WL, LWI & FTP and lowering the values of the scar diameter and coefficient of friction at higher loads. Especially, the additive methylene-bis-[morpholino-dithiocarbamate] (\( A_4 \)) affording higher load carrying capacity and higher values of LWI (89) and FTP (398) and comparatively lower values of wear scar diameter and coefficient of friction at higher loads, indicates its overall efficiency as compared to plain paraffin oil, reference and other additives.

<table>
<thead>
<tr>
<th>Code No</th>
<th>Additive</th>
<th>Molecular formula</th>
<th>m.p. (°C)</th>
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<tr>
<td></td>
<td>Methylene-bis-[( N,N )-diethyl-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}_2\text{H}_5)\text{NCS}_2 )</td>
<td>75</td>
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<tr>
<td>( A_2 )</td>
<td>Methylene-bis-[( N,N )-dibenzyl-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}_6\text{H}_5\text{CH}_2)\text{NCS}_2 )</td>
<td>127</td>
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<td>( A_3 )</td>
<td>Methylene-bis-[( N,N )-methylphenyl-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}_6\text{H}_5\text{CH}_3)\text{NCS}_2 )</td>
<td>195</td>
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<tr>
<td>( A_4 )</td>
<td>Methylene-bis-[morpholino-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}<em>5\text{H}</em>{10})\text{NCS}_2 )</td>
<td>215</td>
</tr>
<tr>
<td>( A_5 )</td>
<td>Methylene-bis-[piperidino-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}_4\text{H}_9\text{N})\text{NCS}_2 )</td>
<td>168</td>
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<tr>
<td>( A_6 )</td>
<td>Methylene-bis-[( N,N )-di-( n )-butyl-dithiocarbamate]</td>
<td>( \text{CH}_2(\text{C}_4\text{H}_9\text{CH}_2\text{NCS}_2 )</td>
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<table>
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<tr>
<th>Lubricant</th>
<th>Observation at ISL</th>
<th>Observation at JBWL</th>
<th>WL kgf</th>
<th>FTP max</th>
<th>LWI kgf</th>
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<tr>
<td></td>
<td>Load kgf</td>
<td>( d^* ) mm</td>
<td>( \mu^{**} )</td>
<td>Load kgf</td>
<td>( d^* ) mm</td>
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<td>paraffin oil</td>
<td>100</td>
<td>0.45</td>
<td>0.047</td>
<td>200</td>
<td>2.28</td>
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<tr>
<td>paraffin oil + methylene-bis-[( N,N )-diethyl-dithiocarbamate]</td>
<td>( A_1 )</td>
<td>126</td>
<td>0.51</td>
<td>0.065</td>
<td>600</td>
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<tr>
<td>paraffin oil + methylene-bis-[( N,N )-dibenzyl-dithiocarbamate]</td>
<td>( A_2 )</td>
<td>126</td>
<td>0.51</td>
<td>0.058</td>
<td>600</td>
</tr>
<tr>
<td>paraffin oil + methylene-bis-[( N,N )-methylphenyl-dithiocarbamate]</td>
<td>( A_3 )</td>
<td>126</td>
<td>0.51</td>
<td>0.059</td>
<td>600</td>
</tr>
<tr>
<td>paraffin oil + methylene-bis-[morpholino-dithiocarbamate]</td>
<td>( A_4 )</td>
<td>126</td>
<td>0.48</td>
<td>0.058</td>
<td>600</td>
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<tr>
<td>paraffin oil + methylene-bis-[piperidino-dithiocarbamate]</td>
<td>( A_5 )</td>
<td>126</td>
<td>0.51</td>
<td>0.058</td>
<td>600</td>
</tr>
<tr>
<td>paraffin oil + methylene-bis-[( N,N )-di-( n )-butyl-dithiocarbamate] (Reference additive)</td>
<td>( A_6 )</td>
<td>100</td>
<td>0.45</td>
<td>0.067</td>
<td>600</td>
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Table 3, incorporating anti-wear test results indicates the effectiveness of all the additives [A<sub>1</sub>-A<sub>5</sub>] as anti-wear additives, however, the additive A<sub>4</sub> providing the lowest value of wear scar diameter has proved to be the best in comparison to the plain paraffin oil and the reference additive (A<sub>6</sub>) blend. Thus, the synthesized additives increasing the ISL values to a higher level, appear to be slightly better as anti-wear additives but a marked increase in the load carrying capacity, load wear index and flash temperature parameter and a decrease in the values of coefficient of friction at higher loads, indicate their

<table>
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<td>$\Delta G^o_r (1)_{ NSA}$</td>
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<tr>
<td>$\Delta G^o_r (H^+)^*$</td>
<td>-4.50</td>
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<td>$\Delta G^o_r (RH^+)^- \Delta G^o_r (RH^2)^-$</td>
<td>5.87</td>
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<tr>
<td>$\Delta G^o_r (2)_{ NSA}$</td>
<td>-1.25</td>
</tr>
<tr>
<td>$\Delta G^o_r (R^-)^- \Delta G^o_r (RH^2)^-$</td>
<td>3.25</td>
</tr>
</tbody>
</table>

* Values of $\Delta G^o_r (H^+)^*$ taken from literature<sup>24</sup>

Fig. 1—Scanning electron micrographs of paraffin oil

Fig. 2—Scanning electron micrographs of the reference additive A<sub>6</sub>.
Fig. 3—Scanning electron micrographs of the additive $A_4$

usefulness as EP and friction modifying additives in comparison to plain paraffin oil and the reference additive.

SEM Topography

Scanning electron microscopy was used to study the topography of the used steel bearing ball wear spots (Figs 1-3). The SEM micrographs of the best additive ($A_4$) were found to project smoother surfaces at ISL & JBWL in comparison to the plain paraffin oil and the reference additive ($A_6$) owing to the presence of thick reacted mixed lubricating films of FeO/FeS/Fe$_3$N at lower and very thin films at higher loads. Thus, the SEM studies confirm the utility of methylene-bis-[morpholino-dithiocarbamate] as an efficient additive.

Conclusions

From the experimental results, the following conclusions can be drawn:

1. All the methylene-bis-(dithiocarbamate) additives were found to increase the load carrying capacity, LWI & FTP values and distinctively decrease the wear and friction values at higher loads.
2. The additive, methylene-bis-[morpholino-dithiocarbamate] ($A_4$) was found to exhibit better EP anti-wear and friction modifying characteristics.
3. The additive ($A_4$) was also found to show better surface smoothening properties at lower and higher loads during SEM studies.
4. Thus, the additive $A_4$ functions as an EP and multifunctional additive.

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References