Tribological studies of some N and S heterocyclic compounds in lithium grease

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Some 5-arylamino-2-mercapto-1,3,4-thiadiazole additives, blended with lithium grease (0.5, 1.0, 1.5 & 2.0% w/w) have been evaluated as extreme pressure additives in a four-ball test. The additives lower friction as well as wear and function well even at high temperature and pressure as compared to commercially available lithium base EP grease. The blended greases were found to pass corrosion, oxidation stability as well as roll stability tests. The 2% w/w admixture of 5-p-methoxyphenylamino-2-mercapto-1,3,4-thiadiazole with lithium grease exhibited a weld load of 360 kgf, whereas, the reference lithium base EP grease and lithium grease without additive afforded the weld load values of 260 and 160 kgf, respectively. The topography and tribochemistry of the used balls after four-ball test were studied using scanning electron microscopy and EDAX techniques, respectively. The EDAX analysis showed the presence of sulphur in the wear tracks and it was found to enhance the EP activity of the additives.

Lithium greases are widely used in the industrial machineries and automobile which are formulated with various compounds, with a view to optimise the end use. Lead/zinc naphthenates and sulphurised oils have traditionally been used as EP additives for lithium base EP greases. These have shown better performance, e.g., high drop point, excellent antiwear and extreme pressure properties, better oxidation stability, pumpability as well as wheel bearing performance as compared to conventional calcium greases. The use of certain S-P and Pb-S systems in lithium grease has been on record. In view of the need for upgrading the quality of existing EP additives, we report herewith the preparation and evaluation of a few nitrogen and sulphur containing 5-arylamino-2-mercapto-1,3,4-thiadiazoles having compact and stable structures as EP additives for lithium grease.

Experimental Procedure

Additive

The additives were prepared by refluxing a mixture of 4-arylthiosemicarbazide and carbon disulphide in dimethylformamide for about two hours. The additives were characterised by elemental analysis and IR spectra. The analytical values of the additives were found to be in agreement with the calculated values within the limits and possible experimental error. The preparation of additives is shown in Fig. 1.

In a representative experiment the additive, i.e., 5-p-methoxyphenylamino-2-mercapto-1,3,4-thiadiazole was prepared by refluxing 4-p-methoxyphenylthiosemicarbazide (I: 0.01 mol) and carbon disulphide (0.01 mol) in dimethylformamide (20 mL) for about 2 h. The excess of solvent was then evaporated off. The resulting mass was purified by carrying out repeated crystallisation with ethanol, yield 70%, m.p. 164°C.

The following additives were prepared:

1. TS1 5-Phenylamino-2-mercapto-1,3,4-thiadiazole, m.p. 200°C, mol formula C6H7N3S2.
2. TS2 5-p-Methoxyphenylamino-2-mercapto-1,3,4-thiadiazole, m.p. 164°C, mol formula C6H6N3S2O.
3. TS3 5-p-Chlorophenylamino-2-mercapto-1,3,4-thiadiazole, m.p. 190°C, mol formula C8H6N3S2Cl.

Fig. 1—Preparation of additives
Grease additive blend—The blends were prepared by mixing 0.5, 1.0, 1.5 and 2.0% w/w of the additives in the lithium grease.

Lithium grease—Lithium grease was prepared in situ by reacting 12-hydroxy stearic acid with lithium hydroxide in presence of paraffinic mineral oil (having viscosity at 40°C 64 cSt; at 100°C 8.6 cSt and viscosity index of 95).

Reference grease—The compatibility of the prepared additives in lithium grease was compared with standard lithium base EP grease.

Bearing balls—Alloy steel bearing balls of 12.7 mm diameter having C% 0.71, Cr% 1.72 were used as the test specimen. The hardness of the bearing balls was 720 (average in VHN).

Apparatus

Extreme pressure lubricant test—The tests were conducted on a Four-ball machine (Seta-shell) by following standard procedure (ASTM D 2596). In the Four-ball machine, a vertical spindle rotated a chuck at a speed of ~1800 rpm, in which a steel ball of diameter 12.7 mm was fitted. Below it, three identical balls were clamped together tightly in a cup filled with the grease to be tested. The cup was mounted on a thrust bearing which automatically centred the top ball held in the chuck. Thus, the loads were evenly divided over three stationary balls. The loads were applied on the thrust bearing by suspending a lever arm. The rotation of the driving spindle caused a friction torque which was recorded on a rotating drum. The duration of the test was 60 s. A series of tests were performed with additives until the welding point was reached with various additives and the parameters determined were, initial seizure load (ISL), 2.5 s seizure delay load (SDL), weld load (WL), wear scar diameter (d) at ISL, pressure wear index (PWI) and flash temperature parameter (FTP).

Roll stability test—50 g of the developed grease was worked for 24 h in roll stability test apparatus with a speed of 165±5 rpm. Worked penetrations were measured on the grease before and after rolling.

Dynamic anti-rust test—It was performed by following IP-220 method in SKF Emcor test rig. This method was used to assess the ability of greases to prevent rusting in rolling bearing operated in presence of distilled water. The developed grease was tested in a ball bearing (30 x 72 x 19 mm, SKF 1306 K/236 725) running at 80 rpm under no applied load in the presence of distilled water.

Oxidation stability test—It was carried out using oxidation bomb method (ASTM D 942). In this method the sample of the developed grease was oxidised in a bomb heated to 99±1°C and filled with oxygen at 110 psig. Pressure was observed and recorded at stated intervals. The degree of oxidation after a given period of time was determined by the corresponding decrease in oxygen pressure.

Topography—Topography of the wear-scar surface was studied by scanning electron microscopy (Phillips SEM 515). The loads selected were just before weld load (340 kgf) for the TS2 and TS3 additives. The stains of sludge or varnish found on the ball surface in the vicinity of the wear-scar were removed with cotton and then cleaned with acetone in an ultrasonic bath before taking the micrographs.

Tribochemistry—Tribochemistry was performed to study the film formed on the bearing ball surface using EDAX (Phillips PV 9900) technique. The presence of sulphur in the film, formed during lubrication, was detected. The loads selected for the investigation were just before weld load, 340 kgf (for TS2 additive). The tested ball was cleaned with acetone in an ultrasonic bath before EDAX analysis.

Results and Discussion

The blends of 5-arylamino-2-mercapto-1,3,4-thiadiazoles additive with lithium grease were evaluated as extreme pressure additives. The results are recorded in Tables 1 and 2 and compared with base lubricant (lithium grease) and lithium base EP grease, as reference.

Wear properties—Fig. 2 shows the relationship between log load and log wear scar diameter for lithium grease and its blends with (2% w/w) additives. The wear-scar diameter first increases slowly until initial seizure load (ISL) and then shows a sudden increase to SDL, which corresponds to the second discontinuity of the wear-load diagrams

Table 1—Lithium grease + 5-arylamino-2-mercapto-1,3,4-thiadiazoles

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Additive + Grease</th>
<th>Weld load (kgf)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>0.5%</td>
</tr>
<tr>
<td>1</td>
<td>TS1</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>TS2</td>
<td>260</td>
</tr>
<tr>
<td>3</td>
<td>TS3</td>
<td>260</td>
</tr>
<tr>
<td>4</td>
<td>Reference grease</td>
<td>260</td>
</tr>
<tr>
<td>5</td>
<td>Lithium grease without additive</td>
<td>160</td>
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</table>
(Fig. 2) and again increases slowly until welding load is reached.

The slow increase in the wear scar diameter is because of the physisorbed/chemisorbed thin layer of the additive/lubricant on the rubbing surfaces. The sudden increase in the values of the wear-scar diameter and the friction coefficient in the load range between ISL and SDL is attributed to the rise in temperature and consequent partial desorption of the adsorbed thin layer of lubricant and additive. Beyond the SDL, a further rise in temperature causes decomposition of the additives and leads to the formation of the chemisorbed/or chemical film by the interaction of lubricant-additive/decomposed additive. This chemisorbed/or chemical film prevents the metallic contact between the rotating specimens and lowers the friction coefficient and wear-scar diameter values, even at much higher loads.

As an illustration, the wear-load diagram for 5-p-methoxyphenylamino-2-mercapto-1,3,4-thiadiazole shows that the curve deviates from the Hertz-line at a load of 120 kgf and it (TS2) shows higher weld load (360 kgf) with lower values of wear-scar diameter as compared to lithium grease without additive and reference grease. It can be seen from Table 1, that all the tested additives are found to improve EP properties of the base lithium grease by functioning well upto higher loads. Whereas, the reference EP grease and base lithium grease show comparatively lower weld loads at 160 and 260 kgf, respectively.

5-p-Methoxyphenylamino-2-mercapto-1,3,4-thiadiazole’s (TS2) (2% w/w) admixture with lithium grease.

### Table 2—Summary of the experimental results obtained with different 5-arylamino-2-mercapto-1,3,4-thiadiazoles additives (2% w/w) in lithium grease

<table>
<thead>
<tr>
<th>SL No.</th>
<th>L*</th>
<th>ISL*</th>
<th>ISL</th>
<th>SDL*</th>
<th>JBWL*</th>
<th>JBWL</th>
<th>WL*</th>
<th>FTP*</th>
<th>PWI*</th>
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<tr>
<td>1</td>
<td>BL*</td>
<td>80</td>
<td>0.70</td>
<td>100</td>
<td>140</td>
<td>1.90</td>
<td>160</td>
<td>132</td>
<td>9</td>
</tr>
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<td>2</td>
<td>TS1</td>
<td>100</td>
<td>0.60</td>
<td>120</td>
<td>300</td>
<td>2.10</td>
<td>320</td>
<td>205</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>TS2</td>
<td>120</td>
<td>0.52</td>
<td>140</td>
<td>340</td>
<td>2.00</td>
<td>360</td>
<td>306</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>TS3</td>
<td>120</td>
<td>0.56</td>
<td>140</td>
<td>340</td>
<td>2.20</td>
<td>360</td>
<td>270</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>RG*</td>
<td>100</td>
<td>0.65</td>
<td>120</td>
<td>240</td>
<td>1.95</td>
<td>260</td>
<td>183</td>
<td>18</td>
</tr>
</tbody>
</table>

$d^*$ = water-scar diameter, ISL* = initial seizure load, SDL* = 2.5 second seizure delay load, JBWL* = just before weld load, WL* = weld load, BL* = base lubricant, L* = lubricant, RG* = reference grease, FTP* = flash temperature parameter, PWI* = pressure wear index.

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**Fig. 2—Log load versus log wear scar diameter**
grease affords higher values of FTP (306) and PWI (19) and thus appears to be an effective EP agent.

Out of all the additives, 5-p-methoxyphenylamino-2-mercapto-1,3,4-thiadiazole's admixture (2% w/w) blend with lithium grease pass oxidation stability, roll stability as well as dynamic anti-rust tests.

Surface topography—To reveal the topography and shape of the scars produced, the technique of scanning electron microscopy (SEM) was used. The wear-scar obtained with TS₂ and TS₁ additives at just before weld load (340 kgf) were selected for the study. The micrographs are shown in Figs 3 and 4. It is obvious that regions of smooth and rough surfaces are present. In the smooth surface region reaction films are present, as black lines and prevent metallic contact,
whereas, in the rough surface region this reaction film is broken and it seems that adhesive wear occurs. The TS$_2$ additive appears to produce smoother surfaces as compared to the TS$_3$ additive. This surface smoothness is retained almost up to weld load.

*Tribochemistry*—Energy dispersive X-ray analytical facilities for electron probe analysis were used to investigate the films formed during lubrication in the wear tracks$^{11}$. Fig. 5 shows the presence of sulphur and it appears to be responsible for higher weld load. This may probably be due to the formation of iron sulphide at high temperature, which diffuses into the first atomic layer of the metal and forms a new alloy, which then provides effective lubrication to the bearing ball surface.

**Conclusions**

The blends of additives in lithium grease were found to be more effective in reducing friction and wear at sliding surfaces and increasing the load carrying capacities as compared to lithium grease without additives. The additive, TS$_2$ showed higher weld load value of 360 kgf as compared to reference lithium base EP grease, weld load 260 kgf. The surface analysis shows the presence of sulphur in the wear tracks of the used balls. The TS$_2$ additive passes oxidation stability, roll stability as well as dynamic anti-rust tests and it acts as multifunctional additive.

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**References**