Rheological Properties and Behavior of Modified Coal Tar Pitch in Soderberg Use

R. K. Rawat & L. R. Duara
India Carbon Limited
Calcutta 700 001
India

Introduction
Pitch is regarded as newtonian fluid. Most workers agree that a good pitch for soderberg use, should have low temperature susceptibility of viscosity as well as flowability which are relative properties attributable to high \( \rho \)-resin content.\(^{(1-5)} \) Modifications with different additives is also a common practice from different point of industrial applications.\(^{(8,9,11,12)} \) We report that, pitches examined by us are non-newtonian and a shift to newtonian behaviour can be obtained by variations in compositions. Temperature susceptibility of viscosity and flowability are two unrelated behaviours not attributable to any typical properties of the pitch. Baked properties of electrodes with modified pitches will be discussed.

Experimental
The investigations were performed with four commercial coal tar pitches (A,B,C,D,) and a modified coal tar (E). They are characterized by the following data:

<table>
<thead>
<tr>
<th>Pitch</th>
<th>SP°C</th>
<th>CV%</th>
<th>BI%</th>
<th>OI%</th>
<th>A - R%</th>
<th>Y - R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110</td>
<td>34.2</td>
<td>33.3</td>
<td>12.0</td>
<td>21.5</td>
<td>20.7</td>
</tr>
<tr>
<td>B</td>
<td>107</td>
<td>58.7</td>
<td>28.2</td>
<td>12.6</td>
<td>15.6</td>
<td>30.5</td>
</tr>
<tr>
<td>C</td>
<td>108</td>
<td>62.2</td>
<td>27.0</td>
<td>14.0</td>
<td>13.0</td>
<td>35.2</td>
</tr>
<tr>
<td>D</td>
<td>107</td>
<td>53.6</td>
<td>28.4</td>
<td>7.0</td>
<td>21.4</td>
<td>25.2</td>
</tr>
<tr>
<td>E</td>
<td>Liquid</td>
<td>21.1</td>
<td>4.9</td>
<td>2.2</td>
<td>2.7</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Viscosities were determined under different shear rate at different temperature between 110 and 175°C by Brookfield Viscometer, and temperature co-efficient of viscosity (\( \eta \)) obtained from the following expression:

\[
\eta = \frac{\log n_1 - \log n_2}{\log t_2 - \log t_1}
\]

where \( n_1 \) and \( n_2 \) are viscosities at temperature \( t_1 \) and \( t_2 \).

Flowability or elongation tests were carried out by mixing pitch and calcined petroleum coke fines (-200 Tyler mesh) at 150°C for 30 min. in 50:50 ratio and moulding into test cylinder (9mm x 35mm), heated on a slopping board (15°C) at 140 and 180°C for 1 hr. From the per cent increase in length of the cylinders, co-efficient of flowability (\( T_f \)) obtained from the following expression:

\[
T_f = \frac{\log E1^n 180°C - \log E1^n 140°C}{\log 180 - \log 140}
\]

Plasticity tests were carried out as reported earlier.\(^{(14)} \)

Baking of the paste was carried out in a programmed controlled furnace at 1000°C in 48 hrs.

Results and Discussion

a. Viscosities of all the four pitches at 150°C under different shear rate are plotted on semi-log scale (Fig-1) and are shear dependent, as has been reported by Bhatia et al.\(^{(6)} \). The view of some workers regarding newtonian flow of all coal tar pitches probably needs to be revised.

b. The variations of apparent viscosity with temperature between 120 and 175°C at one of the shear rate (0.675 sec\(^{-1}\)) are plotted in Fig 2. All the pitches are highly susceptible and upto equiviscous temperature nearly uniform. Difference however, set in beyond 140°C and pitch C and D have low temperature susceptibility than A & B in high temperature region as shown by the value of \( \eta \) in Table 1. Since a pitch with low value of \( \eta \) is preferred,\(^{(2)} \) pitch C&D is superior, but both the pitches differ in their typical properties.
Similarly pitch A&D having nearly equal properties differ in their behaviour. Thus the view held in certain quarter(2) that high $\beta$-resin reduces the value of $\gamma$ does not substantiate.

c. Alteration in properties of pitch A on addition of modified coal tar and sulfur are given in Table 2. As expected coal tar reduces SP, CV, RD, $\beta$ - $\gamma$-resin with increase in BS fraction. Increase in SP, RD, CV and BI with increasing amount of S is due to condensation of low mol. wt. compounds to relatively high mol. wt. constituents(10-12). Reference to Fig.3 indicate viscosities of less shear dependence with gradual increasing amount of coal tar, while shear dependence of viscosity with increasing amount of S increase with increase in apparent viscosity. This could be due to shift in molecular weight constitution(7) as mixture of sulfur yield a more complex liquid of less newtonian character. Similarly temp. dependence of viscosity decreases due to coal tar and increase with sulfur (Fig. 4) correspondingly changing the value of $\gamma$ in opposite way.

d. Reference to Table 3 indicate that coal tar and sulfur reduce the value of $T_f$ identically. The value of $\gamma$ thus may not reflect the behaviour of pitch when mixed with carbon fines and a significantly reduced value of $T_f$ in modified pitch-sulfur mixture is obtained due to increased plasticity at low temperature. It was found that a 0.5% (w/w) S can reduce binder requirement by 4% for a given plastic property.

e. Properties of baked electrode with modified binder are given in Table 3. Improvement in compressive strength, density and electrical conductivity with low amount of S is caused by carbon yield of the binder (8-9) and loss of macroporosity(11), while high amount of S increase porosity and reduce mechanical properties of the electrode(13). Coal tar had no effect.

Table 2. Changes in Properties of Pitch A.

<table>
<thead>
<tr>
<th>Modifier</th>
<th>SP</th>
<th>BI</th>
<th>$\beta$-resin</th>
<th>SP</th>
<th>CV</th>
<th>RD</th>
<th>BI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Coal tar</td>
<td>1015</td>
<td>33.2</td>
<td>11.5</td>
<td>21.7</td>
<td>51.3</td>
<td>18.1</td>
<td>1.30</td>
</tr>
<tr>
<td>2. Sulfur</td>
<td>1005</td>
<td>32.5</td>
<td>11.0</td>
<td>21.5</td>
<td>50.8</td>
<td>18.3</td>
<td>1.30</td>
</tr>
<tr>
<td>3. Coal tar</td>
<td>985</td>
<td>31.8</td>
<td>11.0</td>
<td>20.8</td>
<td>49.4</td>
<td>17.6</td>
<td>1.21</td>
</tr>
<tr>
<td>4. Sulfur</td>
<td>930</td>
<td>30.8</td>
<td>10.6</td>
<td>20.2</td>
<td>48.5</td>
<td>17.7</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Fig. 3. Viscosity vs. shear rate of modified pitch A at 175°C.

Table 3. Value of $T_f$ and Baked Properties with Modified Pitch A.

<table>
<thead>
<tr>
<th>BLANK</th>
<th>COAL TARP (%)</th>
<th>SULFUR (%)</th>
<th>$T_f$</th>
<th>$C_s$ (kg/cm²)</th>
<th>$A_d$ (g/cc)</th>
<th>RD</th>
<th>Resistivity (oh-m)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>8</td>
<td>0.5</td>
<td>1.93</td>
<td>1.42</td>
<td>1.14</td>
<td>0.60</td>
<td>0.044 0.035 0.024</td>
<td>31.8</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>2.02</td>
<td>1.73</td>
<td>1.33</td>
<td>1.36</td>
<td>1.50</td>
<td>1.52 1.45 1.40</td>
<td>31.8</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>2.02</td>
<td>2.01</td>
<td>2.01</td>
<td>2.02</td>
<td>2.01</td>
<td>2.02 2.02 2.02</td>
<td>31.8</td>
</tr>
</tbody>
</table>

Fig. 4. Viscosity vs. temperature of modified pitch A at 0.675 sec⁻¹.

Conclusion

1. All pitches are not newtonian
2. Temperature co-efficient of viscosity ($\gamma$) does not reflect the behaviour of pitch when mixed with carbon fines.
3. High $\beta$-resin does not reduce the value of $T_f$.
4. Value of $\gamma$ can be changed with change in chemical constituents of pitch.
5. Reduce value of $T_f$ depend on low SP and high $\gamma$ value.

Reference