Mannich bases and Phosphosulphurized Mannich bases: Synthesis, characterization and performance evaluation as potential lube oil additives

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With increasing demands being placed on lubricants for automotive engines and transmissions, it has become necessary to improve the function of lubricants. Modern lubricants are formulated from a range of base fluids and chemical additives to improve their function or to add some new performance properties in them. In this study, some Mannich bases were prepared by using p-cresol, formaldehyde and different polyethylene polyamines. Phosphosulphurized Mannich bases were also prepared by the using $P_2S_5$. Structure of the prepared compounds has been confirmed by infrared spectroscopy, NMR and molecular weight determination. The performance of the prepared Mannich bases as well as their Phosphosulphurized derivatives was investigated as antioxidants and detergents/dispersants. It was found that the efficiency of additive performance increases with increasing the number of -NH groups in the amines used.

Keywords: Mannich base, antioxidants, detergents/dispersants, additives.

Introduction

Modern engine oil contains a wide range of additives, which are blended with base oil to form a complete package capable of meeting demanding performance. The functions of lubrication additives include improvement of the viscosity index, pour point, oxidative or thermal stability, anti wear performance of the base oil, to minimize rust and corrosion, to lessen the deposition of harmful chemicals on lubricated parts and so on. Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal surfaces clean by preventing deposition of oxidation products of internal combustion engines. The main functions of detergents in engine oils are acid neutralisation, oxidation inhibition and rust prevention. These functions provide engine cleanliness and extended trouble free operation. The most important mode of lubricant degradation is oxidation. Additives that reduce the oil oxidation are called antioxidants, which act to retard oxidation of lubricating oil, thus preventing the formation of corrosive products. Antioxidants act in two different ways, by inhibition of peroxides or as radical scavengers, which react with peroxy radicals, thus preventing further propagation of the free radical chain. In the present work, some Mannich bases were prepared by using p-cresol, formaldehyde and different amines, and finally the Mannich bases were treated with $P_2S_5$ to synthesize phosphosulphurized Mannich bases. The efficiency of the prepared compound was investigated as antioxidant and detergents/dispersants additive for lube oil.

Materials and Methods

Preparation of Mannich bases

In a 5 necked round bottom flask, fitted with a mechanical stirrer, a ground joint thermometer, a condenser and a dropping funnel, the appropriate amount of p-cresol in methanol and aqueous solution of polyethylene polyamines were added. A formaldehyde (37%) solution was added drop wise during 1 hour at room temperature under nitrogen atmosphere. When the addition of formaldehyde is completed, the temperature of the mixture was raised to reflux temperature for 3 hour. The mixture was then cooled to room temperature. The upper layer was separated from the lower viscous layer (product). The product was dissolved in benzene and washed three times with distilled water to remove the excess of amine and formaldehyde. The molar ratio of p-cresol, formaldehyde and amines were taken as 1:1:1 ratio. The prepared three Mannich bases with ethylenediamine, diethylenetriamine and triethylenetetramine have been designated by $A_1$, $A_2$ and $A_3$ respectively.

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Preparation of Phosphosulphurization Mannich Bases

A four necked round bottom flask, fitted with a mechanical stirrer, thermometer, condenser and inlet for passing nitrogen gas was used for the reaction. The reactions were carried out with four moles of prepared Mannich bases and one mole of \( \text{P}_2\text{S}_5 \) in methanol. The reaction mixture was maintained at 185-190 °C with continuous stirring for 4 hour. Three products of phosphosulphurized Mannich bases have been prepared using three Mannich bases to give \( \text{B}_1 \), \( \text{B}_2 \) and \( \text{B}_3 \) respectively.
Measurements
Spectroscopic Measurements
IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range (400 to 4000) cm$^{-1}$. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl$_3$ was used as solvent and tetramethylsilane (TMS) as reference material.

Determination of the molecular weight
The mean molecular weight of the prepared six additives was determined by using Gel Permeation Chromatography (GPC, Model number-water 2414). In this method the samples were dissolved in tetrahydrofuran (0.4%, w/v) (used as mobile phase) in the Water GPC system (polystyrene calibration) at 40 °C.

Performance evaluation of the prepared compounds as lube oil additives
As Antioxidant
The lube oil sample and its blends containing 2% additive (w/w) of each of the prepared additives were subjected to severe oxidation condition in presence of copper and iron strips at 165.5 °C for 72 hours using Indiana test method of oxidation $^8$. The oxidation stabilities of the lube oil blends is expressed in terms of variation of viscosity ratio and change in total acid number and it was determined by taking samples at intervals of 24 hour and up to 72 hour of oxidation and the samples were tested for:

Variation of viscosity ratio V/V$_0$

The variation of viscosity ratio was determined using Ubbelohde OB Viscometer using ASTM D-2270 method, where V = Kinematic viscosity at 40°C of sample after oxidation, V$_0$ = Kinematic viscosity at 40°C of sample before oxidation.

Change in total acid number (ΔT.A.N)

The change in total acid number was calculated according to ASTM D 664-95 standard test method where ΔT.A.N = total acid number of sample after oxidation – total acid number of sample before oxidation.

As Dispersant
Spot method was applied to determine dispersancy $^9$. Drops of oxidized 2% additive (w/w) and lube oil mixture were taken from the Indiana oxidation apparatus after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper (Durieux 122) and dispersancy of the sample were measured as follows:

\[ \% \text{Dispersancy} = \frac{\text{Diameter of black spot}}{\text{Diameter of the total spot}} \times 100 \]

The efficiency of dispersants has been classified as follows:
Values up to 30%, no dispersancy; 30-50%, medium; 50-60%, good; 60-70%, very good and above 70% excellent dispersancy performance.

Results and Discussion
Determination of molecular weight
The molecular weight of the prepared Mannich bases and Phosphosulphurized Mannich bases were determined by GPC and values are given in table 1.

Spectroscopic Analysis
IR spectrum of prepared Mannich bases: The –NH and –OH group regions are overlapping in the range of 3600-3200 cm$^{-1}$. Peak for the presence of C-N linkage appeared at 1250 and 1103cm$^{-1}$.
In case of $^1$H-NMR, the disappearance of –CHO proton peak at δ 9.92 ppm and appearance of benzylic –CH$_2$ peak at δ 3.8 ppm supports the IR observation. C$^{13}$NMR also confirms the formation of benzylic –CH$_2$ proton, (appearance of peak at δ 47 ppm). The IR peaks at 2400 cm$^{-1}$ (-SH group), 1018 cm$^{-1}$ (P-O bond), 686,624 and at 463 cm$^{-1}$ (P=S bond) and in the range 1100 – 1050 cm$^{-1}$ (Ar-O bonds) indicates the formation of phosphosulphurized Mannich base.

Performance Analysis of Mannich Bases
The prepared compounds $A_1$, $A_2$, and $A_3$ were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

<table>
<thead>
<tr>
<th>Prepared compounds</th>
<th>Theoretical</th>
<th>Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>180</td>
<td>189</td>
</tr>
<tr>
<td>$A_2$</td>
<td>223</td>
<td>228</td>
</tr>
<tr>
<td>$A_3$</td>
<td>266</td>
<td>276</td>
</tr>
<tr>
<td>$B_1$</td>
<td>454</td>
<td>462</td>
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<tr>
<td>$B_2$</td>
<td>540</td>
<td>546</td>
</tr>
<tr>
<td>$B_3$</td>
<td>626</td>
<td>635</td>
</tr>
</tbody>
</table>

Table 1—Theoretical and determined mean molecular weights of compounds $A_1$, $A_2$, $A_3$, $B_1$, $B_2$ and $B_3$.
As antioxidants

The prepared Mannich bases A₁, A₂ and A₃ were added to the lube oil samples in 2% concentration by weight and the blends were subjected to severe oxidation condition as described in experimental section. The oxidation stability is expressed in terms of increase in kinematic viscosity ratio (V/V₀), and change in total acid number (ΔT.A.N), compared with lube oil samples free from additives. Results are given in figures 1 and figure 2, which indicate the followings: The additives A₁, A₂ and A₃ exert better oxidation resistance properties to the additive doped lube oil than the additive free oil. It may be due to the presence of phenolic or amino groups in their structures, which act as chain breaking inhibitors (antioxidants) by donation of labile hydrogen from groups (–OH or –NH) to stabilize the chain radicals; i.e., these inhibitors destroy the peroxide radicals and thus, the oxidation chain is broken. The presence of amine part present in the prepared Mannich bases neutralizes some of the acidic products formed during oxidation. The kinematic viscosity ratio (V/V₀) and total acid number change (ΔT.A.N) decrease with increasing the number of –NH groups present in the amines used. The performances of the additives follow the order A₃ > A₂ > A₁. figure 1 and figure 2

As Dispersants/ Detergents

The base oil with 2% (w/w) additives were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which the efficiency of the dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the –NH groups form hydrogen bonds with the polar end of alcohol, aldehyde, ketone, acids etc which are formed during oxidation. The values of dispersants are given in table 2. From the data, it is clear that dispersancy increases with increasing the number of –NH groups present in the prepared additive. The highest dispersancy was found in case of A₃ due to presence of higher number of –NH groups.

Performance analysis of phosphosulphurized Mannich bases

The prepared compounds B₁, B₂ and B₃ were added to the lube oil samples and the oxidation stability as well as detergency/dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

As antioxidants

Mannich bases were treated with P₂S₅ to produce the additives B₁, B₂ and B₃. The prepared additives were added to the base oil and subjected to severe oxidation conditions using the Indiana test method discussed in experimental section. The oxidation stability is expressed in terms of change in total acid number and increase in kinematic viscosity ratio and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersancy time,(in hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil only</td>
<td>24 48 72</td>
</tr>
<tr>
<td>Base oil + additive A₁</td>
<td>42 40 35</td>
</tr>
<tr>
<td>Base oil + additive A₂</td>
<td>45 53 55.5</td>
</tr>
<tr>
<td>Base oil + additive A₃</td>
<td>63.6 66 68</td>
</tr>
<tr>
<td>Base oil + additive A₃</td>
<td>66.6 71 75.75</td>
</tr>
<tr>
<td>Base oil + additive B₁</td>
<td>60 62 66</td>
</tr>
<tr>
<td>Base oil + additive B₂</td>
<td>63 71 74</td>
</tr>
<tr>
<td>Base oil + additive B₃</td>
<td>64 71 77</td>
</tr>
</tbody>
</table>

Table 2—Dispersancy of the base oil and its blends containing additives A₁, A₂, A₃, B₁, B₂ and B₃ after different oxidation period
compared with the additive free lube oil. Results are given in figure 3 and figure 4 which indicate the followings. With increasing the number of –NH groups, the oxidation stability increases and therefore B3 gave better results than others. In comparison to Mannich bases, phosphosulphurized Mannich bases gave somewhat better results. It is due to presence of phosphorus and Sulphur. The sulphur and phosphorous compounds combine with metal to form sulphide and phosphide films that prevent the contact between metal surfaces and lube oil, and hence interfere with the catalytic action of metal on lube oil oxidation process\textsuperscript{11}. figure 3 and figure 4

As dispersants/detergents

The dispersancy values of phosphosulphurized Mannich bases are not very much different from those of dispersancy of Mannich bases. The values are given in table 2. The dispersancy capability mainly depends on the number of –NH groups present on the prepared additives. That is why B3 has highest dispersancy capacity than B2 and B1.

Conclusions

This comparative study indicated that addition of very small amount of prepared additives to lube oil enhances the efficiency as antioxidant and dispersant. It is also found that phosphosulphurized Mannich bases are more efficient as antioxidant than Mannich bases only. The performance of all the prepared additives increases with increasing number of –NH groups present in the additives.

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References