Inorganic Metal as Additives in SAE 10W-30 Malaysian Automotive Engine Oils

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**Abstract:** This study presents and discusses the rheological behavior and heat capacity of inorganics metal (Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide, cobalt chloride, copper, cadmium nitrate, arsenic oxide and ferum (II) Nitrate) as additives in Malaysian engine oil (P-1). They are uniformly dispersed in oil P1. Two different samples were prepared including one sample used as reference oil. Rheological test were performed using rotational viscometer under constant shear rate of 600 sec⁻¹ and temperature settings starting from 40-100°C. The performance of samples was determined by measuring area under the curve for each of samples graph. The sample that exhibits the largest area under the curve represented the best performance. Heat capacity was determined using bomb calorimeter in adiabatic mode of operation. The study led to following conclusions; all compounds appended in the samples exhibited shear stress, viscosity-temperature relationships, time and heat capacity enhancement compared to reference oil. The results also found that the dissolution of 0.3-0.4 ppm of copper, 0.1 ppm cadmium nitrate, 0.1 ppm arsenic oxide and 0.04-0.05 ppm of ferum (II) Nitrate (Test 1) had the best viscosity-temperature relationships, exhibiting higher value of area under the curve. Furthermore, P1-T1 also had shown significantly improve in heat capacity of oil P1. An additional of 0.15-0.17 ppm of Nickel (II) hexahydrate, 0.03-0.04 ppm titanium (IV) oxide and 1.3-1.4 ppm of cobalt chloride to the test 1 (test 2), also offering an improvement to the viscosity-temperature relationships and heat capacity for P1. However, results for P1-T1 better than P1-T2 in term of viscosity-temperature relationships and heat capacity.

**Key words:** Malaysian engine oil, shear stress, viscosity-temperature relationships, automotive

**INTRODUCTION**

Lubrication is simply defined as use of a substance that provides an enhancement of smoothness to affect the movement of one surface over another and the material used is called lubricant (Mia, 2010). The utilization of lubricant in engine requires as an intermediary to reduce friction and wear of interacting surfaces and provides smooth running and satisfactory life for engine by forming a protective film. The physical and chemical interactions between lubricants and lubricating surfaces must be understood to provide the engines parts with satisfactory life. Selection of appropriate lubricant that fits specific purposes is of paramount importance. Thus, the common properties of lubricants such as viscosity, viscosity index, density, compressibility, surface tension, cloud point, pour point or low temperature property, flash point, friction coefficient, etc. are necessary to be profiled. The most important property is its viscosity. Nowadays, major attention to viscosity is widely spread as a key parameter to the performance of engine. There are many types of engine oil in lubricant market being sold; designation of the lubricant is based on the viscosity. Different viscosity is designed for different purposes.

Viscosity is defined as measure of oil’s resistance to flow or its readiness to flow at different temperature. As the temperature increases, lubricant viscosity encounters ‘thinning effect’ (reduction in oil viscosity). Viscosity is strongly dependent on temperature, pressure and shear rate (Hoglund, 1999; Taylor, 2002). This phenomenon occur due to molecular distances among molecules in the lubricants. When the temperature of liquid is changed, the molecules vibrate more rapidly at random and in doing so establish a space around them which is proportional to their kinetic energy. This characteristic is called the coefficient of expansion with temperature. The liquid with low coefficient of expansion will generally have lower viscosity-temperature coefficients than those which have high coefficients of expansion. The viscosity must be high enough (for example, at temperatures up to 100°C in the case of an automobile engine) to maintain a lubricating film, but low enough (for example, a cold start in the case

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of an automobile) that the oil can flow around the engine parts under all conditions (McCabe et al., 2001; Haycock et al., 2004). Some researchers reported that with lower viscosity at high-temperature engine operating condition, the lubricant could provide reduction in friction and may lead to the high fuel consumption efficiency (De Carvalho et al., 2010; Taylor, 2002). Measurement of viscosity therefore requires means for evaluating shearing stress and rate of shear, or their equivalents. Many rheology tests are available, such as the use of capillary tube, a rotational viscometer, a falling or rolling ball viscometer and so on.

Another lubricant property that might affect the engine performance is heat capacity. Heat capacity in other term also can be classified as indicator for the effectiveness of lubricant to absorb heat release from combustion process. Heat capacity or thermal capacity is the measurable physical quantity that characterizes the amount of heat required to change a substance's temperature by a given amount. Combustion process that occurs in operating engine usually releases heat significantly at higher temperatures than 100°C. This may lead to the engine overheating; if there is no heat output. Consequently, lubricant is also needed to act as a cooling medium for engine. Most of the heat energy release is absorbed by the lubricant. Clean oil passages, appropriate viscosity and low contamination help provide sufficient flow rate of the engine oil and effective cooling.

Recently, researchers have shown an increased interest in the development of inorganics metal as additives in lubricating oil due to the improvement that it can offers to the tribological properties of the base oil such as displaying good friction and wear reduction characteristics even at low concentrations (Hernandez Battez et al., 2008; Ye et al., 2002; Bao-Sen et al., 2011). Furthermore, the addition of inorganics metal also showed significantly improved the performance of lubricant at elevated temperature (Ye et al., 2002). However, research in inorganics metal based still on-going in the development process.

Recently, the influence of Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide, cobalt chloride, copper, cadmium nitrate, arsenic oxide and ferum (II) nitrate as additives in lubricating oil was studied. This research studies the viscosity-temperature relationship and heat capacity behavior of Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide, Cobalt Chloride, Copper, Cadmium Nitrate, Arsenic Oxide and Ferum (II) Nitrate as additives in a SAE 10W-30 Malaysian engine oil (P1) using rotational viscometer and bomb calorimeter analysis.

MATERIALS AND METHODS

Samples preparation: Samples from SAE 10W-30 mineral engine oils were used in the experimental works which is of Malaysian engine oil brand (P1). Three samples were prepared; two samples with different concentrations of Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide, Cobalt Chloride, Copper, Cadmium Nitrate, Arsenic Oxide and Ferum (II) Nitrate are as listed in Table 1 and one sample acts as reference oil (refer as P1). Samples are then shaken in a shaking incubator for 24h at ambient temperature and 150 rpm setting to uniformly disperse all particles in the samples.

Heat capacity analysis: The test was conducted using bomb calorimeter. All samples were measured with consistent amount and weight of 0.9977 g. The operating condition for bomb calorimeter was set to adiabatic. Three repeated tests for each of samples was performed and average heat capacity was determined.

Viscosity-temperature relationships: Approximately 180 mL of samples were prepared for this experiment. A viscosity-temperature relationship was performed using Grace Instrument M3600 Viscometer, a true Couette, coaxial cylinder, rotational viscometer with rotor radius of 1.7245 cm and bob effective length is 3.8 cm. This is an automated rotational viscometer. All tests were run for a constant shear rate of 600 sec⁻¹ at temperature starting from 40°C (104°F) to 100°C (212°F) with temperature correction of 5°F. The shear stress was recorded throughout each test by means of shear rate to measure the absolute viscosity of samples at different temperature. Time taken for each samples to reach temperature of 100°C also was recorded. The performance of viscosity-temperature relationships were characterized using 1/3 Simpson’s Rule by determining area under the curve.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Nickel (II) nitrate hexahydrate</th>
<th>Titanium (IV) oxide</th>
<th>Cobalt chloride</th>
<th>Copper</th>
<th>Cadmium nitrate</th>
<th>Arsenic oxide</th>
<th>Ferum (II) nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P1-T1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3-0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.04-0.05</td>
</tr>
<tr>
<td>P1-T2</td>
<td>0.15-0.17</td>
<td>0.03-0.04</td>
<td>1.2-1.4</td>
<td>0.3-0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.04-0.05</td>
</tr>
</tbody>
</table>

Table 1: Sample composition
RESULTS AND DISCUSSION

Figure 1 and 2 illustrate how all compound concentrations in P1 (in samples P1-T1 and P1-T2) escalate the shear stress and viscosity in relation to temperature from 40°C (104°F) to 100°C (212°F) compared to reference oil, P1. However, results for each test differed depending on the concentration and types of compound blended in. The lowest shear stress and viscosity-temperature relationship was obtained from sample P1-T2 and the highest was for a sample P1-T1. Both type of tests, therefore, exhibited clearly different shear stress and viscosity to the temperature relationships for diverse compound concentrations combinations. Sample P1-T1 exhibited the best performance in terms of shear stress, viscosity and heat capacity as indicated in Table 2. The performance of all tests was determined by evaluating the area under the curve using 1/3 Simpson’s Rule. The area under the curve is an indicator of the performance measurement in which area that exhibits lower in value is not beneficial to the operating engine that generally perform combustion process releasing temperatures significantly greater than 100°C. The viscosity of lubricant that sustains and drops slowly with incrementing temperature usually exhibit higher value for area under the curve, seems more advantageous and promotes long service life for engine. The area under the curve for samples P1-T1 and P1-T2 for shear stress and viscosity are 58532.94638, 9755.601774 and 57861.28341, 9647.380527, respectively.

Table 2: Test comparison improvement for engine oils

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Time to reach 100°C (min)</th>
<th>Shear stress</th>
<th>Viscosity</th>
<th>Heat capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>36.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P1-T1</td>
<td>38.10</td>
<td>9.73</td>
<td>9.73</td>
<td>0.40</td>
</tr>
<tr>
<td>P1-T2</td>
<td>38.12</td>
<td>8.47</td>
<td>8.51</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Fig. 1(a-b): Shear stress and Viscosity-temperature relationship for P1-T1 at temperature 40 to 100°C

Fig. 2(a-b): Shear stress and Viscosity-temperature relationship for P1-T1 at temperature 40 to 100°C
Time taken for samples to reach a temperature of 100°C add support to the results of enhancement that had been made to P1 (Malaysian engine oil) since it was improved by an average of 1.44 min from the reference sample (P1). This enhancement was likely due to addition of the compounds (Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide, Cobalt Chloride, Copper, Cadmium Nitrate, Arsenic Oxide and Ferum (II) Nitrate) to P1 in which each of them has different specific heat. As temperature increases, the molecule will vibrate more randomly and faster and as a result, the space between the molecules is greater and this space is proportional to their kinetic energy. This clarifies how viscosity changes at higher temperature. The addition of these compounds generally increases the amount of heat that can be absorbed by samples because the thermal distribution amongst molecule and also the compounds themselves lead to the increment of its specific heat. Then, to increase 1°C, it requires more energy than before. Furthermore, the increment of heat capacity will affect the time taken for samples to reach the temperature of 100°C.

Heat capacity or thermal capacity is the measurable physical quantity that characterizes the amount of heat required to change a substance’s temperature by a given amount. Higher value in heat capacity indicates the effectiveness of the lubricant to absorbed heat. The heat capacity results had shown that P1-T1 exhibits higher heat capacity value than P1-T2. Figure 3 indicates the heat capacity comparison for P1, P1-T1 and P1-T2. The heat capacity for P1-T1 and P1-T2 are 45474.66667 J K⁻¹ and 45453.3333 J K⁻¹. The results had shown that for P1-T1 increased the heat capacity by about 0.40% (181.33 J) and P1-T2 is 0.35% (160 J). Values of these difference is taken based on the reference sample, P1. The dissolution of compounds such as Nickel (II) nitrate hexahydrate, Titanium (IV) oxide, Cobalt Chloride, Copper, Cadmium Nitrate, Arsenic Oxide and ferum (II) Nitrate in Malaysian engine oil has been shown improved heat absorption of oil. This increase was aided by the specific heat capacity of each material. Higher specific heat of those compounds increases the amount of energy required to increase 1°C of samples. Addition of Nickel (II) Nitrate Hexahydrate (0.15-0.17 ppm), Titanium (IV) oxide (0.03-0.04 ppm), Cobalt Chloride (1.3-1.4 ppm) not shown a beneficial effect on improving the quality of existing lubricants. This is shown by the amount of compounds used in P1-T1 is similar to P1-T2 for Copper (0.3-0.4 ppm), Cadmium Nitrate (0.1 ppm), Arsenic Oxide (0.1 ppm), Ferum (II) Nitrate (0.04-0.05 ppm) as listed in Table 1 but Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide and Cobalt Chloride in P1-T2 has reduced the heat capacity value indicated by the P1-T1. This is proved by the percent improvement as shown in Table 2, P1-T1 has been shown of increased of 0.4 percent while the P1-T2 decreased by 0.05% from the P1-T1. In addition, this reduction is not confined only to the heat capacity, but also in shear stress and viscosity values. It can be found that these compounds are in the negative direction, in which the addition of these compounds will reduce the quality of lubricating oils.

CONCLUSION

The following conclusions can be drawn from the results presented above:

- A commercially available lubricant blended with metallic oxides and salts, exhibited shear stress, viscosity-temperature relationships, time and heat capacity enhancement compared to Malaysian engine oil (P1)
- The dissolution of 0.3-0.4 ppm of Copper, 0.1 ppm Cadmium Nitrate, 0.1 ppm Arsenic Oxide and 0.04-0.05 ppm Ferum (II) Nitrate (P1-T1) had the best viscosity-temperature relationships, exhibiting higher value of area under the curve. Furthermore, test 1 also had shown significantly improve in heat capacity of Malaysian engine oil (P1)
- An additional of 0.15-0.17 ppm of Nickel (II) Hexahydrate, 0.03-0.04 ppm Titanium (IV) Oxide and 1.3-1.4 ppm of Cobalt Chloride to the P1-T1, also offering an improvement to the viscosity-temperature relationships and heat capacity for P1. However, results for P1-T1 indicate better quality improvement than P1-T2
- Although Nickel (II) Nitrate Hexahydrate, Titanium (IV) oxide and Cobalt Chloride can improve the quality of lubricating oils, but, lubricant blended with these compounds are not recommended since they are in negative direction
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REFERENCES


