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# The Effect of Gas Turbine Lubricant Base Oil Molecular Structure on Friction

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# **1** ABSTRACT

The tribological behaviour of lubricant base oils used in aviation gas turbine engines wasere evaluated on their tribological behaviour to further understanding of how the molecular structure of the group V polyol ester base oils influence friction. The frictional properties of the oils were investigated using a Mini-Traction Machine (MTM) to produce Stribeck curves over the range of to evaluate their performance across the range of lubrication regimes relevant to seen throughout a gas turbine oil system. Whilst the viscosity of the lubricant plays an important role in governing the tribological characteristics, the base oils were also examined independent of viscosity to reveal the impact of the base oil molecular structure on friction. The effect of two molecular variables on the measured traction coefficient were explored; the effect of chain length of the protruding alkyl chains and the number of ester groups in the polyol ester. It was shown that friction decreases as the chain length increases and as the number of ester groups increases (from neopentyl glycol (NPG) based ester to trimethylol propane (TMP) based ester to mono-pentaerythritol (MONOPE) based esters). The decrease in traction coefficient as the chain lengthsize increases was attributed to improved packing efficiency and that larger chains can separate surfaces better since they take up more space thus providing improved support. In addition, These findingsthis testing wereas further explored by testing obtaining Stribeck curves for fully formulated gas turbine lubricants with different base oils, but the same additive package. The results showed a reversal in the trend showing friction increased as the number of ester groups in the polyol ester increased. The variable responsible was the increased the amount of molecular branching giving rise to increased friction due to more bulkier molecules hindering packing efficiency by interfering with neighbouring molecular layers.

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# **2** INTRODUCTION

The formulation of a lubricant requires a careful balance of different chemistries to tailor the lubricant to a specific environment thus ensuring optimal performance. The oil system of an aerospace gas turbine engine presents highly challenging conditions for a lubricant, which requires a sufficiently low pour point that it is still able to flow on start up in a cold climate at -40 °C, and also possess the chemical stability to resist degradation during take-off when the engine is at full thrust with bulk oil temperatures over 200 °C (1). There are many other requirements in which additives are needed to boost capability in other areas and these additives include anti-wear additives, antifoamants, corrosion inhibitors, metal deactivators and anti-oxidants (2). However, the largest proportion of the formulation of a gas turbine lubricant is the base oil; approximately 95% of the total. Hence the base oil governs most of the <del>lubricant's</del> physical characteristics <u>of the lubricant</u> and is the focus of this study.

In most mechanical systems, low friction is desired to improve machine efficiency and limit component wear. It has been highlighted in many industries that frictional losses are a major source of energy loss and <u>understanding of</u> tribology can be implemented to conserve energy and therefore efficiency (3). This is especially relevant within a gas turbine oil system where it is vital that the oil lubricates the many different components such as bearings and gears to prolong the component life and ensure the safe operation of the engine. Advances in gas turbine technology has resulted in an increase in engine oil temperature as gas turbines run hotter to increase power and efficiency. This is due to the Brayton cycle which shows thermodynamically that the power and gas turbine efficiency is proportional pressure ratio, therefore by increasing the compression ratio, this increases engine temperatures as expected from the ideal gas law (1).

Consequently, aviation lubricant technology has evolved to cope with the rise in oil system temperatures. Specifically, the type of base oil has moved away from crude oil derived mineral oils that were unstable at high temperatures resulting in excessive volatility and degradation and onto entirely synthetic polyol esters (2,4). Base oils are categorized by the American Petroleum institute (API) and are used in many lubricant specifications worldwide (5). The base oil categories are:

- Group I − Mineral oil-based containing <90 % saturates and/ or >0.03 % sulphur with a viscosity index ≥80 and <120.</li>
- Group II Mineral oil-based containing ≥90 % saturates and/ or ≤0.03 % sulphur with a viscosity index ≥80 and <120.</li>

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- Group III Mineral oil-based containing ≥90 % saturates and/ or ≤0.03 % sulphur with a viscosity index ≥80 and ≥120.
- Group IV Polyalphaolefin (PAO) base oils.
- Group V All other synthetic base stocks not included in the other groups. Therefore, aviation polyol esters are part of this group.

Research on how the molecular structure of the latest generation of aviation base oils influences friction is limited and inconclusive due to difficulty in acquiring base oils with a specific molecular chemistry. This is because standard production produces base oils containing mixture of chain lengths which would require a costly separation process. However, a mixture of chain lengths is beneficial as it lowers the pour point giving enhanced lower temperature capabilities <u>as</u>. A <u>a</u> mixture of molecule sizes hinders the close packing necessary for freezing to occur at low temperatures. Previous research in this area has mostly been done with base oils containing a mixture of molecules therefore resulting in generally assumed conclusions, especially as it is not always possible to reproduce a base oil mixture exactly. Conversely, base oils with a mixture of chain lengths are more relevant to lubricants used in real applications and hence, trends drawn from simplified single molecule compounds have to be balanced with understanding how mixtures of different size base oil molecules synergistically affect friction (6).

Previous trends in the effect of base oil types on friction have been reviewed. It is well known that a higher kinematic viscosity results in higher elastohydrodynamic (EHD) friction due to the higher viscosity fluid having more resistance to shear (2,7). However, this research focuses on the effect of molecular chemistry on friction when the effect of viscosity is removed by testing the oils at the same viscosity by varying the test temperature for each oil.

Most papers evaluating base oils relate the molecular characteristics to EHD friction as this is the regime where additives have little influence and the properties of the base oil dominate. It is also useful to understand how various fluids behave in high speed conditions (6,8–16). Conversely, there has also been extensive work looking at how the molecular structure of fatty acid friction modifier (FAFM) additives affect friction too, but this is mostly for the boundary regime as they are added as boundary additives to reduce boundary and mixed friction beyond the capabilities of low viscosity grade oils (3,17). Consequently, by considering the effect of base oil propertiess in the EHD regime and FAFM in the boundary regime, these trends provide a useful insight into the expected behaviour of polyol base oils across a range of lubrication regimes.

FAFM are believed to readily adsorb on to a surface either via dipole interactions (Frewing 1942 and 1944) or via hydrogen bonding interaction (Beltzer *et al* 1986 and 1988)(18–23). Friction trends for

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FAFM are well documented and it has been shown that friction decreases as chain length increases (24,25), in unsaturated chains, trans isomers give rise to lower friction than cis isomer due to straighter chains (26) and that polarity is <u>also</u> a dominant facto<u>r</u> too (18,19). It has also been demonstrated that branching leads to higher friction due to creating an irregular profile of molecular repulsion and deep interaction zone that gives rise to high friction and has weak cohesive forces between adjacent chains in the monolayer resulting in increased vulnerability to shear (18–22,26).

Consequently, some of the trends seen with friction modifiers may be synonymous to polyol ester base oils, however due to the difference in structure, location of the polar functional group in the molecule and the difference in reactivity between a carboxylic acid and an ester group, care needs to be taken in how transferrable these trends are. Polyol esters associate with metal surfaces due to their polarity as well and increasing chain length and decreasing branching also decreases boundary friction. However, the shielding from attached carbon chains around the ester group will result in a decrease in their surface activity and could hinder monolayer formation leading to a decrease in the applicability of the branching trend seen with FAFMs (27).

Contrariwise, there has been a wide range of research investigating base oils, but this mostly related to EHD performance. Tsubouchi proposed five molecular properties that are likely to increase friction in traction fluids (28). The first is high molecular stiffness caused by structures with restricted molecular mobility, due to a high proportion of unsaturated bonds, or complex ring structures as this hinders molecular slip as molecules cannot deform and rotate easily, which can also give rise to molecular entanglement. Through various studies, it is believed that EHD friction is influenced mostly by the flexibility and structure of individual molecules as this will affect how molecular layers shear over one another under high pressure. This was seen by Zhang *et al* 2017-[number]where it was shown that flexible groups and linear molecules favoured low friction which allowed more free movement and prevented molecular entanglement. Synthetic esters are an example of a flexible molecule as the ester bond allows free rotation of substituents (6). Hentschel *et al* 1985 (9) also discovered that bulkier and more irregular shaped cyclic structures gave rise to more steric hindrance hindering fluidity due to neighbouring molecule interlocking resulting in higher friction in comparison to regular spherical and ellipsoidal rings (9).

The second was large molecule size as it was believed this produces more steric hinderance. More specifically, this is referring to the degree of branching and linearity of molecule, how much free space a molecule occupies and how it interacts with neighbouring layers. Zhang et al <u>[number]</u> showed that bulky cyclo-hexyl rings and methyl branches gave higher EHD friction due to hindering movement against neighbouring layers. While linear chains favour low friction as they interact less

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with neighbouring layers. An NPG based polyol ester with a branched substituent gave higher friction than a linear one containing a double bond. It was also found that the friction of polyglycols was strongly influenced by the amount of branching, with more propylene instead of ethylene units resulting in more branching and therefore higher friction (6). This was confirmed by Hentschel who suggested the low friction of polyglycols was caused by the low degree of branching resulting in a thread-like structure which allowed the polyglycols chains to align which minimal interaction with other layers (10). These results were backed up againconfirmed by Hirst and Moore-1979 (11). Further confirming that bulkier molecules give a higher EHD friction, Hammann et al 1970 showed that molecules with one or two cyclohexyl rings gave high EHD friction (29). Cecil et al 1973 backed this upconfirmed this result -by -finding that paraffinic mineral oils gave a lower EHD friction than naphthenic, the latter having more saturated rings substituents. The paper also showed that glycol compounds produced a lower friction than the mineral oils tested (30). A similar study was also performed by Hirst and Moore 1979 where EHD friction was higher for molecules containing multiple side chains and saturated rings, but it was found to be lower for polyglycols. It was also found that friction was found to be lower for benzene ring containing base oils where the substituents were located para to one another as opposed to ortho and meta due to the molecule being more linear (11). Another study discovered that EHD friction increased with increased degree of branching. Friction data was analysed using a viscoelastic Eyring model and it was noted that the Eyring stress decreased with the degree of branching and with molecular volume (31). LaFountain et al 2001 measured observed the EHD friction properties of three base oils a found that the EHD friction increased from PAO (polyalphaolefins) to diesters to alkylated aromatic base\_oils. This again confirmed that bulkier molecules can give rise to higher friction (14). Zhang et al reported a general trend with base oil group with group 1 having the highest friction, then group 2 and then groups 3 and 4 which also follows the trend of decreasing proportion of cyclic and branched components (6).

However, an increase in the size of the molecule can also decrease friction if the larger molecule can pack more efficiently than the smaller molecule. With regards to base oils seen in aviation lubricants, Chang utilized an in-contact temperature rise mapping method to measure the shear stress properties of a range of ester base oils and it was found that pentaerythritol esters had a lower shear stress than trimethylolpropane (TMP) based esters. The paper also noted that more branching lead to an increase in shear stress (16).

The third molecular characteristic was short alkyl chains resultings in <u>a poor</u> molecular packing efficiency. Zhang et al showed an increase in chain length from adipic to azelaic to sebacic acid results in decreasing friction (6,28).

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The fourth factor was a high melting point, but this may just be due to larger molecules and molecules with more polar atoms resulting in stronger intermolecular bonding as they inherently have a higher melting point (28).

The fifth molecular characteristic is low molecular polarity as high polarity gives rise to repulsion between neighbouring molecules preventing close packing and aiding the molecules sliding over one another (28). It was found that solvent treated mineral base oils gave a higher friction than hydrotreated oils and that the lowest friction was produced by group III and group IV base oils therefore showing the introduction of polar water resulted in lower friction than those treated with organic non-polar solvents (15).

There have also be other studies that observed the loss of torque and efficiency of real bearings and gears and found that the synthetic base oils tested; PAOs, polyglycols and esters produced a reduction in torque in comparison to other mineral oils. This could be due to a few characteristics such as molecular packing efficiency, polarity or bulky substituents, but it is difficult to make further deductions without more detail on the molecular chemistry of the mineral oils, but is likely to be due to a higher proportion of cyclic and branched substituents (32–36). When compared the synthetic base oils to each other, the literature sources found opposing results in that Yoshizaki et al found PAO to give a lower friction than polyglycols whereas the opposite was found by Höhn et al. This may be due to differences in the PAOs and polyglycols tested hence the reason for the difficulty in understanding trend with base oils and the necessity for control of base oil production for research purposes (32,33).

<u>The above literature shows that Hence the trends for the effect of molecular structure on base oils</u> in the EHD regime and FAFM in the boundary regime <u>haveindicate</u> similar trends but differ the mechanism behind the frictional effects. The <u>literature suggests that y both suggest</u> low friction is favoured by longer chain lengths, linear molecules, less branching and therefore less bulky molecules.

Therefore, the <u>The</u> -aim of this current paper is to deduce whether the molecular structure of the aviation derived base oils influences friction following the trends previously outlined in the literature independent of viscosity. Specifically, the effect of varying the alkyl chain length on the end groups on the polyol esters, the number of ester groups in the polyol ester and the introduction of branching to these structures on friction <u>iswere</u> explored. This was done by producing Stribeck curves to compare the different molecular structure of base oils <u>over</u>at a range of temperatures. Also, <u>T</u>to deduce whether the molecular structure still influences friction when independent of

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viscosity, the different base oils were compared at the same kinematic viscosity by testing each base oil at a specific temperature to attain the same specific kinematic viscosity.

### **3** EXPERIMENTAL

#### **3.1 MINI TRACTION MACHINE**

A Mini Traction Machine (MTM2, developed by PCS instruments) was used to evaluate the tribological performance of the oils. The MTM uses a ball on a disc configuration, each component with a specific rotational speed and to achieve the defined slide-roll ratio (SRR).

The contact between the ball and the disc is submerged in a reservoir of lubricant (approximately 35 mL) and the ball rotates against the disc at an inclined axis to eliminate spin in the contact. The speed of both ball and disc are controlled independently and driven by separate motors, which allows different combinations of surface speeds and SRR to be set by the operator. The load and lubricant temperature can also be controlled and the traction coefficient (friction) is measured.

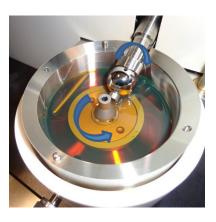


Figure 1 - Configuration of the MTM showing the rotational directions of the ball and disc.

Specifications of the test specimens are shown in Table 1, both of which showed minimal wear throughout the Stribeck tests.

Table 1– Specification of test specimens.

Property	MTM Standard Disc	MTM Drilled Ball
Dimensions (diameter)	46 mm	¾″ (19.05 mm)
Material	AISI 52100	AISI 52100
Surface Finish, R <sub>a</sub>	<0.01 µm	<0.02 μm
Hardness, $H_v$	720-780	800-920

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**Comment [MS18]:** Schematic showing key parameters needed.

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#### **3.2 TEST CONDITIONS**

The MTM was used to produce Stribeck curves at a range of temperatures. Each of these tests was completed three times to confirm repeatability and all Stribeck curves have been plotted with error bars of one standard deviation for each data point. Representative gas turbine oil system contact conditions were used for Stribeck analysis are shown in Table 2.

Table 2- Conditions used for Stribeck analysis.

Parameter	Value
Applied Load	40 N
Contact Pressure	1.01
Contact Pressure	GPa
Slide-to-Roll Ratio (SRR)	50 %
Entrainment Speed	0 – 3 m/s

It should be noted in these tests, the type of EHD lubrication seen at high entrainment speeds was hard viscous EHD lubrication as the steel specimens used have a high elastic modulus, the viscosity changes in the contact due to the high contact pressures and the contact is elastically deform<u>eds</u> due to the high contact pressure in the non-conformal contact (37,38).

The entrainment speed U and the SRR are defined by equations (1) and (2) where  $u_1$  and  $u_2$  are the surface velocities of surface 1 and 2 respectively.

$$U = \frac{|u_1 - u_2|}{2}$$
(1)

$$SRR = \frac{|u_1 - u_2|}{U} \tag{2}$$

Two different methods of normalising for viscosity were applied to the tests to isolate the effect of the molecular structure on friction. One method involved plotting the measured traction coefficient against\_ a dimensionless number called the Hersey number (3) where  $\mu$  is the dynamic viscosity, N the entrainment speed in revolutions per second and  $p_0$  is the maximum contact pressure.

Hersey Number = 
$$\frac{\mu \times N}{p_0}$$
 (3)

The dynamic viscosities were calculated using the supplied densities and can be seen in the Appendix 8.1.

The second method involved testing each lubricant by carrying out experiments at different temperatures for each oil so that they all had the same kinematic viscosity. This was done using data from measurements of kinematic viscosity and ASTM D341 (39). The viscosities <u>selected</u>chosen were

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7.3 cSt, 5.0 cSt and 2.9 cSt, these values - These viscosities were chosen as the calculated test temperature required for each oil was within the temperature range capability of the MTM. The calculated temperatures for each base oil can be seen in Table 10.

Another consideration worth noting is shear stability of the base oil molecules. Walker *et al* (40) showed by sampling the base oil through a small hole, that polymeric base oils can break down into smaller molecules in EHD contacts. (40). <u>TheyAn equation was</u> suggested that polymeric scission will begin to occur in linear hydrocarbon polymers if shear stress x molecular weight<sup>2</sup> >1 x  $10^{14}$  dyne/ cm<sup>2</sup>, but this is generally only a concern for much larger base oil molecules and hence, the shear stability of the base oils tested in this study was assumed not to be an issue (41).

Also, due to the low roughness of the superfinished specimens ( $R_a < 0.01 \mu m$  for the disc and  $R_a < 0.02 \mu m$  for the ball), very minimal wear was produced for all tests and therefore the wear was not investigated.

#### 3.2.1 Test Lubrication Regimes

Using the supplied pressure-viscosity coefficients, the fluid film thickness and therefore lambda ratio, the lubrication regimes can be estimated for each oil over the range of speeds seen in the Stribeck test. The <u>formulas equations</u> used to calculate the contact pressure, film thickness and the lambda ratio can be seen in Appendix 8.1. These calculations utilized the data provided by the manufacturer to calculate the dynamic viscosity at each test temperature to give a more accurate estimate of the film thickness and therefore the lambda ratio.

Hence from Figure 2, it can be seen from the plot of lambda ratio against the entrainment speed <u>that</u> the NPG C7 base oil does not reach the EHD regime with the conditions used. Therefore, whilst previous studies have only compared the effect of base oil structure on EHD friction, the results presented in this paper observe the effect of the molecular structure across a range of lubrication regimes as not all the oils will reach the EHD regime at higher entrainment speeds due to specific lubricant properties and limitations of the test rig. However, the results across the range of conditions seen in this study <u>have-given an-</u>insight into the behaviour of different base oils on friction.

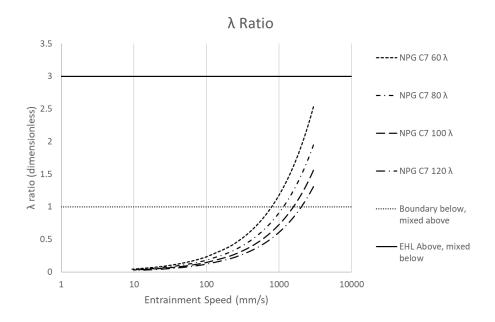


Figure 2 – Lambda ratio against the entrainment speed for the NPG C7 base oil showing that it does not reach the EHD at any test temperature for the test conditions used.

#### 3.3 TEST FLUIDS

#### 3.3.1 Pure base oil blends

A variety of group V base oils were acquired of known chemical composition and molecular structure with no additives. The five pure base oils can be seen in Figure 3.

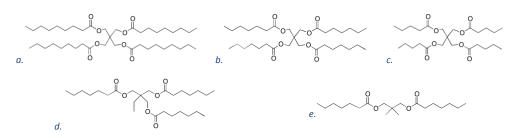


Figure 3 - Molecular structure of the base oils tested. a. polyol ester made from pentaerythritol with chains of n-C9, b. polyol ester made from pentaerythritol with chains of n-C7, c. polyol ester made from pentaerythritol with chains of n-C7, d. polyol made from trimethylol propyl with chains of n-C7 and e. polyol ester made neopentyl glycol with chains of n-C7.

The base oils represent esters typically seen in aerospace lubricants and <u>havewith</u> representative chain lengths. The <u>two parameters considered are</u> re are two variables being observed; the chain length of the substituent end groups on the esters and the amount of ester groups on the molecule. The chain lengths of the pentaerythritol base oils vary by increments of two carbons. These variations were selected as they were readily available from the supplier.

Extra data for these base oils both measured and calculated can be seen in <u>Extra Data for the Pure</u> <u>Base oil blends</u>Extra Data for the Pure Base oil blends in Appendix 8.1. Tests have shown that the base oils tested are Newtonian up to shear rates of 200 s<sup>-1</sup> due to the <u>Imeasurement</u> imitation of the cone <u>andon</u> plate rheometer centrifugally forcing out low viscosity fluids at high shear rates. But it is assumed that these base oils are all Newtonian in the EHD regime as well as shown by *Moore 1997* (Appendix Base Oil Rheology)(8).

#### 3.3.2 Fully formulated pure base oil blends

Fully formulated lubricants based on a commercially available aviation lubricants were acquired which all contain the same additive package but have different amounts and types of group V base oils (A, B, C and D) to alter their viscosity.

The base oils used contain varying amounts of different polyol esters to vary the viscosity; they differ in the proportion of base oils with a different number of ester groups (Figure 4). Typically, the alkyl chain branching is 2-ethylhexyl but there may be some low level of iso C9 branching.

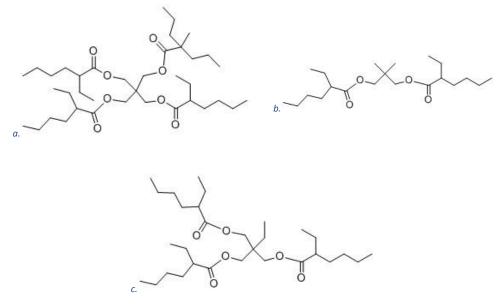


Figure 4 – Molecular structure of the base oils used in the formulated oils tested. a. polyol ester made from pentaerythritol with chains of 2-ethylhexyl and some iso C9, b. polyol ester derived from neopentyl glycol with side chains of 2-ethylhexyl and c. polyol ester derived from trimethylol propane with side chains of 2-ethylhexyl.

<u>The composition of each formulated lubricant tested in terms of additives and base oil can be seen</u> <u>in Table 3Table 3.</u> The High viscosity oil (made from base oil D) are predominantly pentaerythritol based (4a) and the Low viscosity oils (from base oil A) are mostly neopentyl glycol (4b) based but <u>also</u> contain<del>s</del> some trimethylol-propane-based ester (4c). Formatted: Font color: Text 1

Both Medium viscosity oils (made from base oils B, C and D) are a blend of polyol esters (pentaerythritol and neopentyl glycol) with the Medium High containing more pentaerythritol esters and less neopentyl glycol ester esters than Medium Low. Exact formulation details of oils are unavailable. The composition of each formulated lubricant tested in terms of additives and base oil can be seen in Table 3-Table 3-

Field Code Changed

Table 3 – Table showing oil compositions.

	Oil A (v/v %)	Oil B (v/v %)	Oil C (v/v %)	Oil D (v/v (%)	Additives (v/v %)	Kinematic Viscosity @ 100°C (cSt)
High	-	-	-	94.8	5.2	8.0
Medium High	-	-	28.0	66.8	5.2	6.9
Medium Low	-	10.0	84.8	-	5.2	5.0
Low	94.8	-	-	-	5.2	3.1

## **4 RESULTS & DISCUSSION**

#### 4.1 PURE BASE OIL ANALYSIS

This section will interpret the tribological properties of the base oils containing no additives with specific molecular structures.

#### 4.1.1 Effect of Temperature

The normalised Stribeck curves solely showing the MONOPE C7 base oil are shown in Figure 5. The other base oils displayed similar trends.

Generally, it is known that a higher viscosity results a lower traction coefficient in the boundary regime due to the fluid forming a thicker oil film to protect asperities, but a lower viscosity will result in a lower traction coefficient at high speeds as a thinner fluid is sheared more easily (42). As the temperature is varied, this results in a viscosity change, which alters the performance in the boundary and EHD regimes and the general trend is the friction decreases from low to high temperature due to the difference in viscosity and temperature effects. The calculated kinematic viscosities of these oils can be seen in Table 9.

Normalisation of the Stribeck curves would lead to a single master curve if viscosity was the sole parameter governing frictional characteristics, but the fact that there is still separation of results in Figure 5 shows that another variable as well as viscosity is contributing to the underlying tribological behaviour.

Figure 5 shows a decrease in traction coefficient as the temperature is increased which is due to the increased temperature resulting in a decrease in viscosity and hence the fluids are sheared more easily. Prior to normalisation of the Stribeck curves, higher viscosities would favour a lower traction coefficient in the boundary regime however, normalisation results in shifting <u>of</u> the curves as the tests have been normalised for viscosity. The separation in <u>the</u> curves is also larger for the test fluids that have a larger difference in viscosity across the range of test temperatures.

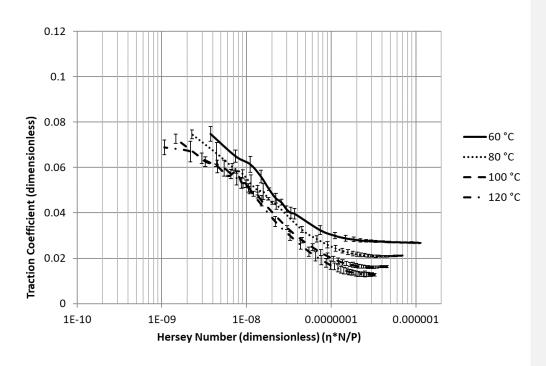


Figure 5 – Normalised Stribeck curves of the MONOPE C7 base oil at a range of temperatures.

#### 4.1.2 Effect of Base Oil Structure at Constant Temperature

Figure 6 shows that when the base oils are compared at a constant temperature, separation of the Stribeck curves only emerges at <u>the</u> higher temperatures (120°C). At the lower test temperature of 60°C s there is no significant trend. <u>But at higher test temperatures</u>, the prominence of this separation becomes more apparent. By considering the viscosities of each of these oils at each test temperature, there is a larger difference in kinematic viscosity at the lower test temperatures. Hence it can be seen that at the highest test temperature of 120 °C, this has the smallest range of viscosities of 2.83 cSt whereas at 60 °C the range is 12.04 cSt. Consequently, at low temperatures, viscosity dominates the behaviour leading to similar curves due to normalising for viscosity in minimised, a difference in friction emerges due to other underlying variables in the system, <u>namely</u>; the difference in molecular structure.

The order of the friction decreased from NPG C7 to TMP C7 to MONOPE C5 to MONOPE C7 and then to MONOPE C9. Hence, this indicates an effect of molecular structure on friction. <u>The results shown</u> that friction decreases with an increase in both As-the number of ester groups increases the friction decreases and as the the \_-chain length increases the friction decreases too. It is likely this is due to the larger molecules being able to pack more efficiently and separate the surfaces <u>due to with their</u> larger <u>size</u>. <u>LEssentially larger</u> chains can <u>better</u> separate surfaces <u>better</u> since they take up more space thus providing improved support, but this can often come with increased friction if larger bulkier molecules have more difficulty moving which can mask this effect.

However, at high test temperatures at high entrainment speeds, the pentaerythritol base oils converge, and the neopentyl and trimethylol base oils remain separated from them. This suggests that the pentaerythritol base oils behave similarly at higher entrainment speeds regardless of their difference in chain length as they reach the EHD regime and that the neopentyl and trimethylol base oils require higher speeds to reach the same traction coefficient. Hence this shows that the effect of the number of ester groups potentially has a larger impact on the molecular packing than differences in substituent chain length.

**Comment [TM23]:** The section is a bit confusing – if you are not careful you imply smaller difference in viscosity means larger difference in friction, but what you should mean is that the viscosity dominates behaviour leading to not much difference but where you minimise that factor the effect of molecule on its own becomes apparent.

**Comment [TM24]:** Something like this as an extra? Essentially bigger chains can separate surfaces better since they support and separate more – they take up more space in between – often this comes with increased friction due to larger molecules having more difficulty moving which can mask the effect. (chain length effect is limited though sometimes just general size is important which fits your pattern nicely.

**Comment [TM25]:** If I am reading the graph right those 2 haven't reached the end of the mixed regime, once viscosity corrected I would expect them to line up when they get there – I would remove this part if I were you or test those 2 at higher speed to prove they are different or say they appear not to collapse because they haven't reached the EHD yet?

**Comment [MS26]:** But WHY???! Is there nothing in the literature to help you?

**Comment [AJ(27]:** I can't find anything in the literature but think it should still be pointed out as an observation

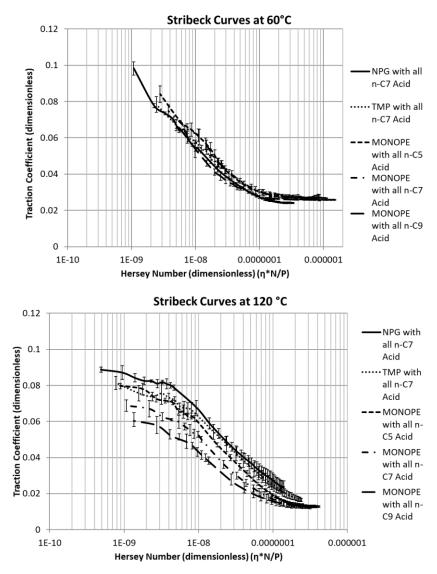


Figure 6 – Normalised Stribeck curves comparing the different base oils at 60 °C and 120 °C.

#### 4.1.3 Effect of Base Oil Structure at Constant Viscosity

When tested at a constant viscosity, there is a clear separation of Stribeck curves across each of the different test viscosities, but there appears to be a slightly larger separation on the lowest viscosity graph; Figure 7. The order from high to low friction is marginally different to the same temperature Stribeck curves as the trend now goes NPG C7, PE C5, TMP C7, PE C7 and then PE C9. Therefore, the PE C5 and TMP C7 have swapped. However, this is <u>due to the fact that</u>likely as they have very similar molecular weights and therefore viscosity (as shown in Table 5) and have performed very similarly throughout all the tests.

Despite this marginal change in frictional order, the same trend <u>can clearly be observed</u>, showing that as <u>both</u> chain length increases, and the number of ester groups increases, the friction decreases <del>can clearly be seen</del>. This reinforces the theory that viscosity is not the only factor influencing friction and that the molecular structure has a substantial effect <del>too</del>-which is revealed after viscosity has been eliminated as a variable. It is likely this is due to the larger molecules being able to pack more efficiently, which results in less frictional resistance and be able to separate the rubbing surfaces more effectively because of their increasing size.

Another observation is that the pentaerythritol base oils do not completely converge at high entrainment speeds as they did when all compared at the same test temperature. This could be due to increasing chain length effect being more apparent at the same viscosity and potentially requires higher entrainment speeds to converge. Again, the effect of the number of ester groups potentially has a larger impact on the molecular packing than differences in substituent chain length as there is a larger separation between the NPG C7, TMP C7 and MONOPE C7 than each of the MONOPE curves.

**Comment [TM28]:** This element needs to come in again I think but not what I wrote necessarily

**Comment [MS29]:** But WHY???! Is there nothing in the literature to help you?

**Comment [AJ(30]:** I can't find anything in the literature but think it should still be pointed out as an observation

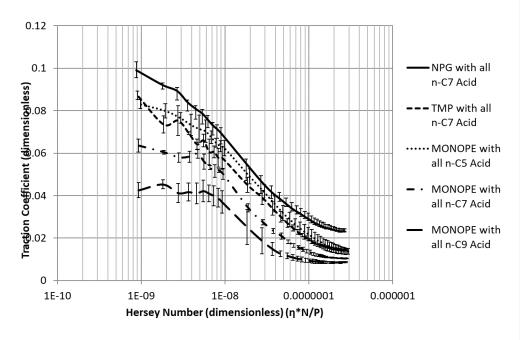


Figure 7 – Normalised Stribeck curves comparing the different base oils at a kinematic viscosity of 2.9 cSt by varying the test temperature for each base oil.

#### 4.2 FULLY FORMULATED BASE OIL ANALYSIS

The section <u>describes the results obtained for</u> will show the results of the the fully formulated lubricants each with the same additive package and all have a controlled mixture of different structure base oils to vary viscosity.

#### 4.2.1 Effect of Temperature

The Stribeck curves for the high viscosity formulation are shown in Figure 8 (the other formulations are not shown as they show a similar trend). There is a trend showing that traction coefficient decreases with increasing temperature as shown with the pure base oils.

The difference in traction coefficient in the boundary regime is smaller than the difference in traction coefficient in the EHD regime. This is because the boundary region is affected much more by additive performance and as all the oils contain the same additive package, similar performance is expected. As it is the base oil which is being varied and not the additives, it is expected that the main differences will be seen in the EHD regime and this is confirmed <u>byin</u> the<u>se</u>-presented results. <u>T</u>-But the differences that are seen in the boundary regime must be due to higher viscosity oils forming thicker films and therefore they can separate the surface asperities more than lower viscosity blends (7). It is likely that the additives will introduce some surface chemistry effects that could interact with the base\_oils creating a different frictional response in comparison to the unadditised oils. However, it is not expected these effects will be significantly different between each of the fully formulated lubricants.

Figure 8 shows that the Stribeck curves for the higher viscosity oils do not flatten off. This could be a possible effect of shear heating. Shear heating occurs when shearing of high viscosity fluids results in friction which generates heat as the molecules shear over one another and as a result causes a decrease in viscosity. Higher entrainment speeds may cause more shearing resulting in a thinner film and therefore lower friction. But it is also possible that a higher entrainment is needed for the more viscous oils to reach a minimum traction and hence these may not have reached the EHD regime yet.

**Comment [MS31]:** Could this explain earlier results?

**Comment [AJ(32]:** I'm not sure, can't think of an explanation that would fit

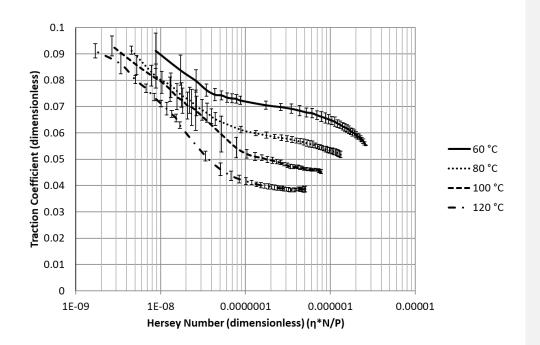


Figure 8 – Stribeck curves of the High Formulation at a range of temperatures.

#### 4.2.2 Effect of Base Oil Structure at Constant Temperature

Figure 9 shows the Stribeck curves comparing the fully formulated oils at the 120 °C (the other test temperatures show a similar trend). There is a clear trend of decreasing friction from the high to the low viscosity blend most likely due to differences in base oil molecular structure as the graph has been normalised for viscosity.

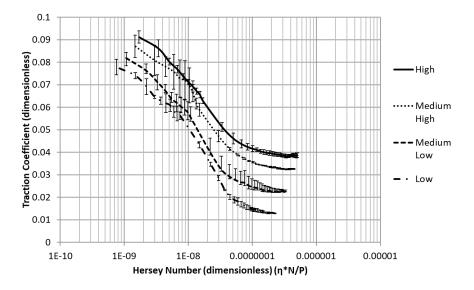


Figure 9 – Normalised Stribeck curves of the fully formulated blends with different base oils at 120 °C.

#### 4.2.3 Effect of Base Oil Structure at Constant Viscosity

The Stribeck curves at 5 cSt and results shown are in Figure 10. There is a clear trend showing that friction decreases moving from the high viscosity to the low viscosity formulations even when all of them have the same kinematic viscosity. Therefore, if the viscosity is not the main influence behind the tribological effects, the only other difference between the oils is difference in base oil chemistry. This graph demonstrates the opposite to Figure 7 as the oils with a larger size now result in higher friction.

As mentioned earlier, the low viscosity oil is mainly composed of polyol esters from NPG and TMP and the high viscosity oil is predominantly polyol esters from pentaerythritol, but these esters are now branched too. Therefore, from the low to the high viscosity formulations, there is an increase in the number of esters with more branching. Consequently, this increase in branching, has led to more interference with molecular packing giving rise to higher friction.

Hence this shows that the inclusion of branching may inverse the trends seen with the previous oils where increasing chain length and increasing the number of ester groups decreased friction potentially due to larger molecules being able to pack more efficiently. It may be that the inclusion of branched side chain prevents the larger molecule packing as efficiently giving rise to more steric hinderance as the molecules get larger with more branching. However, this effect of branching needs to be further confirmed with branched base oils of a known molecular structure without the added variable of additives.

**Comment [MS33]:** It's a bit unsatisfactory as you don't know presumably the base oil structure in the fully formulated oils? If I was a reviewer I would criticise this as you can't really explain your results...

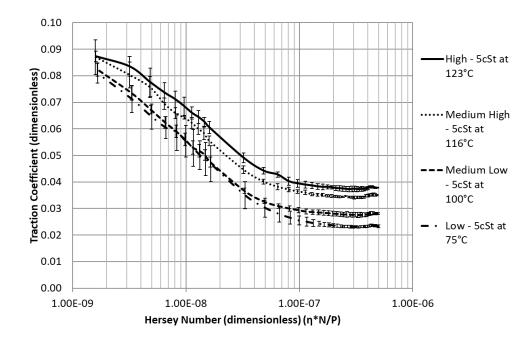


Figure 10 – Normalised Stribeck curves comparing fully formulated lubricants with different base oils at the same kinematic viscosity of 5 cSt by varying the test temperature for each base oil.

# **5** CONCLUSIONS

In conclusion, Stribeck curves <u>have been produced</u> were produced for a range of base\_oils of specific molecular structures<u>and fully formulated oils</u>-to understand the effect of molecular structure on friction. Whilst changes to molecular structure influence the viscosity of the fluid, the base\_oils were also tested at the same viscosity by varying the temperature of each test.

The results showed the molecular structure has a substantial impact on the measured friction across all lubrication regimes. It was shown from the results that Twhilst the viscosity behaviour is as affects as expected with an increase in viscosity leading to an increase in friction as a higher viscosity fluid incurs more resistance to shear. After viscosity was eliminated as a variable through plotting Stribeck curves against the Hersey number and by conducting wears tests at the same viscosity, two molecular variables were explored; the effect of chain length and the influence of the number of ester groups on friction. It was shown that the friction decreases across all lubrication regimes as the chain length increases and by increasing the number of ester groups which is most likely due to larger molecules being able to pack more efficiently and separate the contacting surfaces. Essentially Liarger chains can separate surfaces better since they take up more space thus providing improved support, but this can often come with increased friction if larger bulkier molecules have more difficulty moving which can mask this effect. It was also seen that the number of ester groups potentially has more of an effect on friction that the substituent chain length as the pentaerythritol base oils converge when compared at the same temperature, but the TMP and NPG oils remain separated. This suggested that the pentaerythritol base oils behave very similarly at high entrainment speeds regardless of their difference in chain length.

Thein addition, fully formulated lubricants showed a reversal the friction trend such that the friction was seen to increase as the number of ester groups was increased. This was attributed to the increase in proportion of branching on the ester substituents. Consequently, the results show an increase in friction as the amount of branching increases creating more interference with molecular packing.

Overall, these results are in <del>clear</del>-agreement with the literature in that low friction is favoured by longer chain lengths, increasing the number of ester groups (within a polyol ester) and maintaining a linear molecule. Branching leads to producing a bulkier molecule which gives rise to high friction whereas, whilst increasing the chain length and the number of ester groups increases the size of the molecule, the molecule remains linear and flexible giving rise to improved load carrying capacity and packing efficiency which reduces friction.

**Comment [MS34]:** Need to start with a sentence or two summary of what was done. Some people will read conclusions without reading the rest of the paper.

**Comment [TM35]:** Maybe something here?

**Comment [MS36]:** But can you prove that?

# **<u>6</u>** ACKNOWLEDGMENTS

JA was funded by the EPSRC Centre for Doctoral Training in Formulation Engineering (EP/L015153/1) at the University of Birmingham and <u>The authors express their gratitude to the University of</u> <u>Birmingham</u>, Rolls-Royce Plc. The authors would like to acknowledge Dr Thomas Mills of Chemical Engineering at the University of Birmingham for his helpful comments on the manuscript. <u>-and the</u> <u>EPSRC (Engineering and Physical Sciences Research Council) for their funding and support toward</u> <u>this research</u>. Formatted: Heading 1, Indent: Left: 0 cm, First line: 0 cm, Widow/Orphan control, Adjust space between Latin and Asian text, Adjust space between Asian text and numbers

## **67R**EFERENCES

- Rolls-Royce. The Jet Engine. Fifth edit. Rolls-Royce plc, editor. Chichester, West Sussex: John Wiley, 2015.; 2015. p. 288.
- Mortier RM, Fox MF, Orszulik S. Chemistry and Technology of Lubricants [Internet]. Dordrecht: Springer Netherlands; 2011. (SpringerLink: Springer e-Books). Available from: https://books.google.co.uk/books?id=YTa5TsL0KnIC
- Tung SC, McMillan ML. Automotive tribology overview of current advances and challenges for the future. Tribol Int. 2004;37(7):517–36.
- 4. Shell Aviation Limited. The AeroShell Book. Aviation. 2003;196.
- American Petroleum Institute. Engine Oil Licensing and Certification System, Annex E API base oil interchangeability guidelines for passenger car motor oils and diesel engine oils. Washington; 2017.
- Zhang J, Tan A, Spikes H. Effect of Base Oil Structure on Elastohydrodynamic Friction. Tribol Lett. 2017;
- 7. Williams JA. Engineering tribology. Cambridge: Cambridge University Press; 2005.
- Moore AJ. The behaviour of lubricants in elastohydrodynamic contacts. Proc Inst Mech Eng Part J J Eng Tribol. 1997;
- Hentschel KH. The influence of molecular structure on the frictional behaviour of lubricating fluids. J Synth Lubr. 1985;2:143–74.
- Hentschel KH. The influence of molecular structure on the frictional behaviour of lubricating fluids 2: low coefficients of traction. J Synth Lubr. 1985;2:238–60.
- 11. Hirst W, Moore AJ. Elastohydrodynamic lubrication at high pressures. II. Non-Newtonian behaviour. Proc R Soc A. 1979;365:537–65.
- 12. Gentle CR, Cameron A. An investigation of traction in elastohydrodynamic point contacts using optical interferometry. ASLE Trans. 1975;
- Biresaw G, Bantchev GB. Elastohydrodynamic (EHD) Traction Properties of Seed Oils. Tribol Lubr Technol [Internet]. 2013;12. Available from: WWW.STLE.ORG
- 14. LaFountain AR, Johnston GJ, Spikes HA. The elastohydrodynamic traction of synthetic base oil

blends. Tribol Trans. 2001;

- 15. Gunsel S, Korcek S, Smeeth M, Spikes HA. The elastohydrodynamic friction and film forming properties of lubricant base oils. Tribol Trans. 1999;
- 16. Chang H-S, Spikes HA, Bunemann TF. The shear stress properties of ester lubricants in elastohydrodynamic contacts. J Synth Lubr. 1992;
- Beeck O, Givens JW, Smith AE. On the Mechanism of Boundary Lubrication. I. The Action of Long-Chain Polar Compounds. Vol. 177, Source: Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences. 1940.
- Frewing JJ. The Influence of Temperature on Boundary Lubrication. Proc R Soc London. 1942;181:23–42.
- Frewing JJ. The Heat of Adsorption of Long Chain Compounds and their Effect on Boundary Lubrication. Proc R Soc London. 1944;182:270–85.
- Beltzer M, Jahanmir S. Role of Dispersion Interactions Between Hydrocarbon Chains in Boundary Lubrication. ASLE Trans. 1986;30(1):47–54.
- 21. Jahanmir S, Beltzer M. Effect of Additive Molecular Structure on Friction Coefficient and Adsorption. J Tribol. 1986;108:550–74.
- Beltzer M, Jahanmir S. Effect of Additive Molcular Structure on Friction. Lubr Sci. 1988;1(1):3–
   26.
- Davidson JE, Hinchley SL, Harris SG, Parkin A, Parsons S, Tasker PA. Molecular Dynamics Simulation to Aid the Rational Design of Organic Friction Modifiers. J Mol Graph Model. 2006;25:495–506.
- 24. Hardy WB, Doubleday I. Boundary Lubrication The Paraffin Series. In: Proceedings of the Royal Society London. 1922. p. 49–68.
- Okabe H, Masuko M, Sakurai K. Dynamic Behaviour of Surface Adsorbed Molecules Under Boundary Lubrication. ASLE Trans. 1980;24(4):476–473.
- Askwith TC, Cameron A, Crouch RF. Chain Length of Additives in Relation to Lubricants in Thin Film and Boundary Lubrication. In: Proceedings of the Royal Society of London Series A, Mathematical and Physical. London: Royal Society; 1966. p. 500–19.
- 27. Housel T. Synthetic Esters: Engineered to Perform [Internet]. Machinery Lubrication, Noria

Corporation.2019.p.1.Availablefrom:https://www.machinerylubrication.com/Read/29703/synthetic-esters-perform

- Tsubouchi T, Hata H, Yoshida Y. Optimisation of molecular structure for traction fluids. Lubr Sci. 2004;16:393–403.
- 29. Hammann WC, Schisla RM, Groenweghe L. C. D., Gash VW. Synthetic Fluids for High-capacity Traction Drives. ASLE Trans. 1970;13(2):105–16.
- Cecil R, Pike WC, Raje NR. Development of methods for evaluating traction fluids. Wear. 1973;
- 31. Muraki M. Molecular structure of synthetic hydrocarbon oils and their rheological properties governing traction characteristics. Tribol Int. 1987;
- Yoshizaki M, Naruse C, Nemoto R, Haizuka S. Study on frictional loss of spur gears (Concerning the influence of tooth form, load, tooth surface roughness, and lubricating oil). Tribol Trans. 1991;
- Höhn B-R, Michaelis K, Doleschel A. Frictional Behaviour of Synthetic Gear Lubricants. Tribol Res. 2001;10.
- 34. Martins R, Seabra J, Brito A, Seyfert C, Luther R, Igartua A. Friction coefficient in FZG gears lubricated with industrial gear oils: Biodegradable ester vs. mineral oil. Tribol Int. 2006;
- Michaelis K, Höhn B-R, Hinterstoißer M. Influence factors on gearbox power loss. Ind Lubr Tribol. 2011;63(1):46–55.
- 36. Fernandes CMCG, Amaro PMP, Martins RC, Seabra JHO. Torque loss in cylindrical roller thrust bearings lubricated with wind turbine gear oils at constant temperature. Tribol Int. 2013;
- Hamrock BJ, Schmid SR, Jacobson BO. Elastohydrodynamic Lubrication of Elliptical Conjunctions. In: Fundamentals of Fluid Film Lubrication. 2nd ed. CRC Press; 2004. p. 35.
- Hamrock BJ, Schmid SR, Jacobson BO. Film Thicknesses for Different Regimes of Fluid Film Lubrication. In: Fundamentals of Fluid Film Lubrication. 2nd ed. CRC Press; 2004. p. 23.
- ASTM D341-09. Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum. ASTM Int West Conshohocken, PA. 2009;
- Walker DL, Student G, Sanborn ; D M, Winer AO. Molecular Degradation of Lubricants in Sliding Elastohydrodynamic Contacts [Internet]. 1975. Available from:

https://asmedigitalcollection.asme.org

- 41. Mackenzie K, Jemmett AE. Polymer shear stability. Wear. 1971;
- 42. Hutchings IM. Tribology : Friction and Wear of Engineering Materials. Oxford: Butterworth-Heinemann; 1992.

#### <u>Acknowledgments</u>

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# **7<u>8</u>**Appendix

# 7.18.1 EXTRA DATA FOR THE PURE BASE OIL BLENDS

#### 7.1.1 <u>8.1.1</u> Kinematic Viscosities of the base oils

Table 4 shows some of the measured properties of the base oils provided. Viscosity increases with the molecular weight as expected and the pour point increases with viscosity and therefore molecular weight also.

Table 4 – Table I	listina some d	of the measured	properties of	f the pure base oils.
	insting some c	j the measured	properties of	the pare base ons.

	Kinematic	Kinematic
Ester description	Viscosity at 40	Viscosity at 100
	°C (cSt)	°C (cSt)
PE with all n-C5 acid	15.4	3.6
PE with all <i>n</i> -C7 acid	21.3	4.6
PE with all <i>n</i> -C9 acid	30.3	5.9
TMP with all <i>n</i> -C7 acid	14.0	3.4
NGP with all <i>n</i> -C7 acid	5.6	1.9

Table 5 – Table displaying the number of each element in the compound and hence the molecular weights of the base oils.

Ester description	Carbon	Hydrogen	Oxygen	Molecular Weight g/mol
PE with all n-C5 acid	41	76	8	472.619
PE with all <i>n</i> -C7 acid	33	60	8	584.835
PE with all <i>n</i> -C9 acid	25	44	8	697.051
TMP with all <i>n</i> -C7 acid	27	50	6	470.691
NGP with all <i>n</i> -C7 acid	19	36	4	328.493

The kinematic viscosities for the formulated oils provided are shown in Table 6 with their

corresponding viscosities at 40 and 100  $^{\circ}\mathrm{C}.$ 

Table 6- Table of the fully formulated blends viscosities at 40 and 100°C.

	Kinematic Viscosity at 40 °C	Kinematic Viscosity at 100 °C
	(cSt)/ (mm²/ s)	(cSt))/ (mm²/ s)
High	66.1	8.04
Medium High	52.4	6.93
Medium Low	31.5	4.99
Low	12.6	3.08

7.1.28.1.2 Temperature and viscosity prediction using ASTM D341

The ASTM method D341 was used to calculate the temperature at which each oil has certain viscosity (1). The example shown here is for the fully formulated blends, but the same method was done for the pure baseoil blends. To predict the temperature at which the oils are 5 cSt, at least two measured viscosities are needed for each oil at known temperatures. Using equations (4), (5) and (6), the kinematic viscosities can be calculated by plotting a line of LogT against LogLogZ as shown in Figure 11.

$$LogLogZ = A - BLogT \tag{4}$$

$$Z = v + e^{(-1.47 - 1.84v - 0.51v^2)}$$
(5)

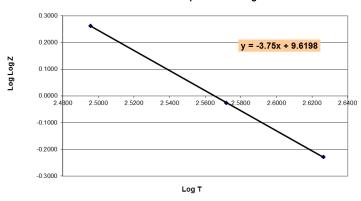
$$v = (Z - 0.7) + e^{(0.7487 - 3.295(Z - 0.7) + 0.6119(Z - 0.7)^2 - 0.3193(Z - 0.7)^3)}$$
(6)

_	Temperature (°C)	LogT (T converted	Kinematic Viscosity	LogLogZ	
		into K)	(cSt)		
_	40	2.4958	66.1	0.2612	
	100	2.5719	8.04	-0.0262	
	150	2.6265	3.19	-0.2289	

 Table 7 - Table showing the measured kinematic viscosities and at measured temperatures and the calculated values for

 LogT and LogLogZ.

The kinematic viscosities at 40 and 100°C were provided by the supplier and the viscosity at 150°C was measured using ASTM D445.



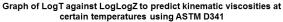


Figure 11 - Graph of LogT against LogLogZ to predict kinematic viscosities at certain temperatures using ASTM D341.

From the graph the values of A and B in equation (4) are the intercept and gradient of the line created respectively. Using this, the temperatures at which each oil is 5 cSt were calculated and are shown in Table 8.

Table 8 - Table showing the temperatures at which each oil has a kinematic viscosity of 5 cSt and the measured viscosity at that temperature to confirm the viscosity (measured by Intertek West Thurrock using method IP 71 REF).

	Temperature at which the	Measured viscosity at	
Oil	oil has a kinematic viscosity of 5	the corresponding	
	cSt (°C)	temperature (cSt)	
High	122.8	5.036	
Medium High	115.9	5.021	
Medium Low	100.6	5.130	
Low	74.9	5.187	

From the provided kinematic viscosities, the kinematic viscosity can be estimated at the test temperatures using ASTM D341 and these can be seen in Table 9.

Cator description	Kinematic Viscosity cSt				
Ester description	60 °C	80 °C	100 °C	120 °C	
PE with all n-C5 acid	8.48	5.29	3.92	2.65	
PE with all <i>n</i> -C7 acid	11.40	6.95	4.66	3.36	
PE with all <i>n</i> -C9 acid	15.65	9.33	6.14	4.35	
TMP with all <i>n</i> -C7 acid	7.82	4.94	3.41	2.51	
NGP with all <i>n</i> -C7 acid	3.61	2.54	1.91	1.52	

Table 9 – The estimated kinematic viscosities using ASTM D341 of the base oils at the temperatures tested.

The lubricants were also tested at the same viscosity by varying the test temperature for each base oil. These temperatures were also calculated using ASTM D341 and can be seen in Table 10.

Table 10 – Table showing the calculated temperatures at which the base oils have the following viscosities.

Ester	Temperature at which the lubricant has a kinematic viscosity of (°C)				
description	2.9 cSt	5 cSt	7.3 cSt		
PE with all n- C5 acid	113.8	82.5	65.9		
PE with all <i>n</i> - C7 acid	130.2	96.2	77.8		

PE with all <i>n</i> - C9 acid	149	111.5	91.3
TMP with all <i>n</i> -C7 acid	110.1	79.4	62.7
NGP with all <i>n</i> -C7 acid	71.9	44.8	30

#### 7.1.38.1.3 Calculation of the dynamic viscosities required for the Hersey Number

The density of these fluids was also required such that their dynamic viscosity could be calculated which was needed to calculate the Hersey number.

Table 11 – Densities pure base oils.

	NPG, all	TMP, all C7	PE, all C5	PE, all C7	PE, all C9
	C7 acids	acids	acids	acids	acids
Density of Liquids, 15.6 °C	0.9291	0.9628	1.022	0.9809	0.9569

The dynamic viscosity has been calculated from the density multiplied by the kinematic viscosities in Table 9 and then converted from cP to Pa. s by multiplying by  $10^{-3}$ . These dynamic viscosities can be seen in Table 12. The density will change with temperature, but only the density at 15.6 °C could be acquired and hence the dynamic viscosities have been estimated using this.

Table 12 – Dynamic viscosities at of the pure base oils at a range of temperatures.

Pa. s	Dynamic Viscosity Pa. s					
Pd. 5	60 °C	80 °C	100 °C	120 °C		
NPG, all C7 acids	0.003354	0.00236	0.001775	0.001412		
TMP, all C7 acids	0.007529	0.004756	0.003283	0.002417		
PE, all C5 acids	0.008667	0.005406	0.004006	0.002708		
PE, all C7 acids	0.011182	0.006817	0.004571	0.003296		
PE, all C9 acids	0.014975	0.008928	0.005875	0.004163		

Hence the dynamic viscosities can also be calculated for when they were all tested at different temperature to achieve the same kinematic viscosity, these can be seen in Table 13.

Table 13 - Dynamic viscosities calculated from the kinematic viscosity.

Ester description	Dynamic viscosities calculated from the kinematic viscosity (Pa. s)				
	2.9 cSt	5 cSt	7.3 cSt		
NPG, all C7 acids	0.00269439	0.0046455	0.0074606		
TMP, all C7 acids	0.00279212	0.004814	0.00702844		

PE, all C5 acids	0.0029638	0.00511	0.0074606
PE, all C7 acids	0.00284461	0.0049045	0.00716057
PE, all C9 acids	0.00277501	0.0047845	0.00698537

# 7.1.48.1.4 Estimation of the pressure viscosity coefficient at different test temperatures

The pressure viscosity coefficients (PVC) have also been supplied for these oils (Table 14) and have been used to calculate the film thickness and the therefore the lambda ratio. This parameter also varies with temperature and the PVC at different temperatures has been estimated by plotting the known PVC against temperature and using the equation of the line to calculate the other temperatures. These can be seen in Table 15 and the graph of the plotted pressure viscosity coefficients can be seen in Figure 12. For most of the base oils, the PVC increases as temperature decreases except for TMP n-C7, this is not currently understood.

Table 14 – Supplied PVC of the pure base oils.

Pressure-Viscosity	NPG, all	TMP, all	PE, all C5	PE, all C7	PE, all C9
Coefficient, x 10 <sup>-8</sup> m <sup>2</sup> /N	C7 acids	C7 acids	acids	acids	acids
at 40°C	0.67	1.07	2.28	2.18	0.92
at 70°C	0.63	1.13	1.57	1.49	0.72
at 100°C	0.6	1.18	1.21	1.13	0.6
at 130°C	0.58	1.22	0.99	0.92	0.52

PVC estimation (based on line	NPG, all C7 acids	TMP, all C7 acids	PE, all C5 acids	PE, all C7 acids	PE, all C9 acids
equations) x 10-8 m <sup>2</sup> /N	y = - 0.001x+0.705	y = 0.0017x+1.0083	y = 31.087x	y = 32.713x	y = 1.1531e
60	0.65	1.11	1.53	1.44	0.77
80	0.63	1.14	1.15	1.08	0.68
100	0.60	1.18	1.21	1.13	0.60
120	0.58	1.21	0.77	0.72	0.54
30	0.68				
44.8	0.66				
71.92	0.63				
62.7		1.11			
79.4		1.14			
110.1		1.19			
65.9			1.39		

82.8		1.11		
113.79		0.81		
77.8			1.11	
96.2			0.90	
130.2			0.66	
91.25				0.63
111.5				0.56
149				0.46

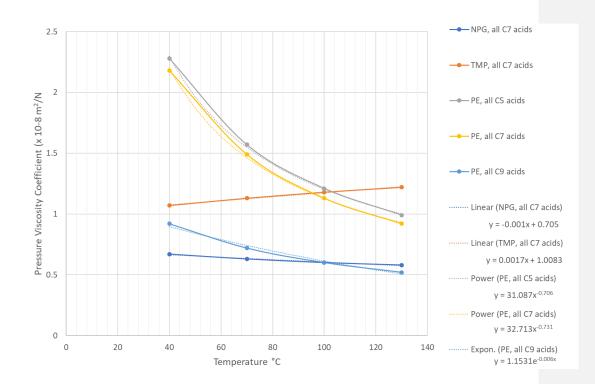


Figure 12 – Graph showing the pressure viscosity coefficients for the pure base oils plotted against the temperature. These were fit to line equations that allowed the estimation of the PVC at other temperatures.

# 7.28.2 HERTZIAN CONTACT PRESSURE CALCULATION

As the configuration of the MTM is a ball on disc, this rig has a point contact geometry as the ball will contact the disc at a single circular point. However, the calculation for an elliptical contact can be used and as both radii on the contact patch are equal, it should give the same contact pressure (2).

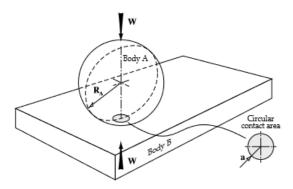


Figure 13 – Diagram illustrating how a ball would contact a flat surface (2).

Firstly, the reduced radius (R') of the contact was calculated from the reduced radii for the x and y planes ( $R_x$  and  $R_y$ ).

$$R_x = \left(\frac{1}{R_{1x}} + \frac{1}{R_{2x}}\right)^{-1}$$
$$R_y = \left(\frac{1}{R_{1y}} + \frac{1}{R_{2y}}\right)^{-1}$$
$$R' = \left(\frac{1}{R_x} + \frac{1}{R_y}\right)^{-1}$$

Then the reduced elastic modulus (E\*) was calculated from using the Poisson's ratio (v) and Young's modulus (E) for both the ball and the disc.

$$E^* = \left(\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}\right)^{-1}$$

The contact area dimensions (a and b) were then calculated.

$$a = \sqrt[3]{\frac{3k^2 EPR'}{\pi E^*}}$$

$$b = \sqrt[3]{\frac{3EPR'}{\pi kE^*}}$$

Where P is the normal load, k is the ellipticity parameter and  $\mathbf{E}$  is the elliptic integral of the second kind.

$$k = 1.0339 \left(\frac{R_y}{R_x}\right)^{0.6360}$$
$$E = 1.0003 + \frac{0.5968R_x}{R_y}$$

Then finally the maximum contact pressure  $(p_0)$  can be calculated.

$$p_0 = \frac{3P}{2\pi ab}$$

# 7.3<u>8.3</u> Dowson & Higginson Film Thickness and Lambda Ratio Calculation

The lubrication regimes defined by the lambda ratio are derived from film thickness calculations, these equations were derived empirically by Dowson and Higginson in 1977 (3; 2; 4).

The minimum film thickness  $(h_{min})$  was calculated from the individually calculated material parameter (G), speed parameter (U) and the parameter (W).

$$\frac{h_{min}}{R'} = 2.65G^{0.54}U^{0.7}W^{-0.13}$$
$$W = \frac{P}{2E^*R'L}$$
$$U = \frac{\eta_0 u}{2E^*R'}$$
$$G = 2\alpha E^*$$

The length of the contact area (L) is the diameter of the contact area (2 times a),  $\eta_0$  is the dynamic viscosity of the lubricant at ambient pressure, u is the entrainment speed and  $\alpha$  is the pressure - viscosity coefficient.

After the film thickness was calculated, the lambda ratio can be deduced using the roughnesses both the ball and the disc.

$$\lambda = \frac{h}{\sqrt{\sigma_1^2 + \sigma_2^2}}$$

The lambda ratio gives an indication of the lubrication regime that a contact is operating in and can be simplified into the following.

Table 16 – Table showing what lubrication regime the lambda ratios correspond to (4).

λ	Full fluid film separation (the EHL or hydrodynamic			
>3	regime)			
1	Partial or Mixed FHL (come accority contact)			
<λ<3	Partial or Mixed EHL (some asperity contact)			
λ	Aspority contact (Poundary Pogimo)			
<1	Asperity contact (Boundary Regime)			

#### 7.48.4 BASE OIL RHEOLOGY

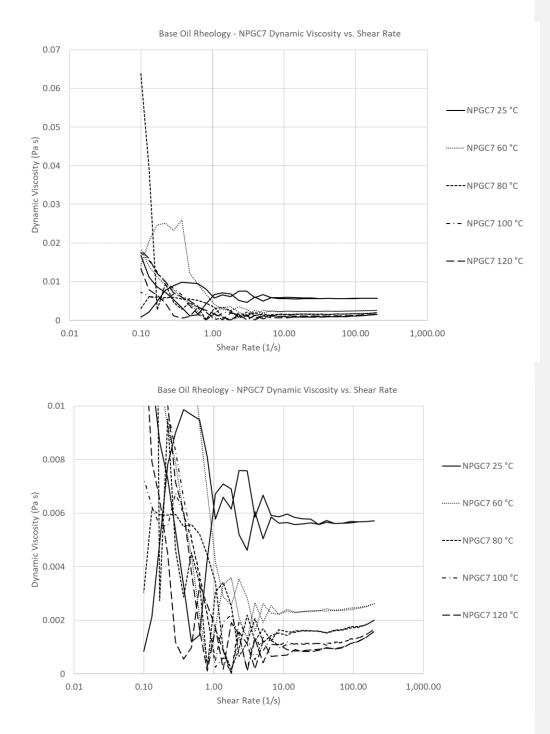
The bases oils were tested using a Bohlin Gemini HR Nano Rotonetic Drive 2 rheometer with a cone on plate configuration. The parameters for the rheometer can be seen in Table 17. The cone attachment was a 40 mm stainless steel cone with a 4 ° angle. The tested conducted used a controlled shear stress ramp up to a shear rate of 200 s<sup>-1</sup> and then back down to check for hysteresis. Temperature was controlled using the Peltier plate attachment.

All the base oils were tested at 25 °C but only 2 of the base oils were tested at a range of temperatures to show no effect with temperature and viscosity influencing non-Newtonian behaviour. The lowest and highest viscosity base oils were selected to show under the rationale that if these were Newtonian, the base oils in between are also Newtonian.

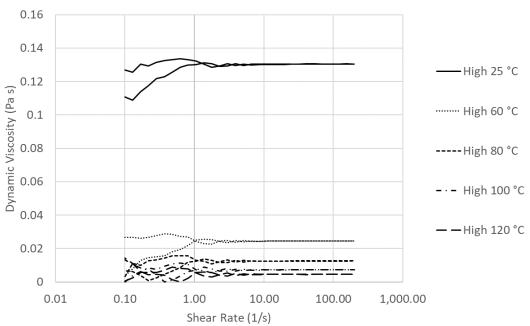
Parameter	Value		
Torque Range in controlled stress & rate viscometry:	10nNm to 200mNm		
Torque Range in controlled stress & strain oscillation:	3nNm to 200mNm		
Torque resolution:	Better than 1nNm		
Position resolution:	50nrad		
Frequency range:	1µHz to 150Hz		
Controlled speed range (CR mode):	0.01mrad s-1 to 600rad s-1		
Measurable speed range (CS mode):	10nrad s-1 to 600rad s-1		
Normal force N1 measurement range:	0.001N to 20N (50N optional)		
Step change in strain:	<10ms		
Temperature controls: Peltier Plate:	-30ºC to 200ºC		
Nominal operating voltage	110 or 220V		
Size (with Peltier plate)	52cm (H) x 33cm (W) x 37cm (D)		
Weight (with Peltier plate)	28kg		

Table 17 – Table showing the parameters for the Bohlin Gemini HR Nano Rotonetic Drive 2 rheometer.

It can be seen from Figure 14 and Figure 15 that the lowest and highest viscosity lubricants in this study are Newtonian and therefore all the baseoils used in this study can be assumed to be Newtonian. The graphs are expected to be noisier at lower speeds and more so with less viscous fluids however it can be seen at higher shear rates, the viscosity remains relatively constant with shear thus suggesting Newtonian behaviour.







Base Oil Rheology - High Lubricant Blend - Dynamic Viscosity vs. Shear Rate

Figure 15 – Graph showing the measured dynamic viscosity against shear rate for the High lubricant blend showing Newtonian behaviour.