

# **INFLUENCE OF MOLECULAR STRUCTURE ON THE LUBRICATION PROPERTIES OF FOUR DIFFERENT ESTERS.**

**R. Tuomas, S. Berg, T. Almqvist, B-O Åhrström**

Division of Machine Elements  
Luleå University of Technology  
971 87 Luleå  
Sweden

## **ABSTRACT**

The lack of published data on the chemical structures of lubricants makes it almost impossible to investigate the influence of structure on lubrication properties. In this investigation, the lubricating properties of three esters with known chemical structure have been investigated and compared with a commercial ester. The lubrication properties that were expected to be dependent on chemical structure such as film thickness and traction, viscosity and friction coefficients were compared by experiment. To measure the film thickness a Ball & Disc Apparatus was used, the traction coefficient was measured in a Jumping Ball Apparatus, the viscosity in a rotational cylindrical viscometer and the friction coefficient in a reciprocating friction and wear test apparatus. The results showed that molecular length has a significant influence on lubrication properties, with longer molecules giving the highest viscosity and greatest film thickness. The length of the molecule did not influence the coefficients of friction, but the traction coefficient,  $\gamma$ , decreased with increasing molecular length.

## **1 INTRODUCTION**

It is an advantage to know what the effect of different designs of ester lubricant molecules have on their lubrication properties. With this knowledge it would be possible to develop esters “tailor-made” for a specific task. However, the poor availability of published information on the chemical structure of esters makes it almost impossible to investigate the influence of structure on lubrication properties. In this investigation, three different esters with known molecular structure were manufactured and then tested to assess their ability to form a lubricating film and determine their viscosity, traction- and friction coefficients. The tested lubricants all had the same basic ester structure, but the length of the molecule differed. An ester with a different branching pattern was used as a reference. The results were then compared with the expected behaviour known from the literature [Briant, J, et al.<sup>1</sup>].

## 2 EXPERIMENTS

Four different experiments were performed to determine viscosity- and traction coefficients and film thickness and friction coefficients. The measurement methods are described briefly below, more details can be found in [Larsson, R, et al<sup>2</sup>

### 2.1 Viscosity measurement

For the viscosity measurements a rotational viscometer was used, consisting of two coaxial cylinders; one stationary and the other rotating. The lubricant was placed between the two cylinders and the frictional torque versus rotational speed measured. Using this technique non-Newtonian behaviour can be detected.

### 2.2 Traction coefficient

An important factor affecting the performance of an oil is how large a shear stress,  $\tau_L$ , it can sustain. This limiting shear stress depends on the applied pressure and is normally approximated to:

$$\tau_L = \tau_0 + \gamma p \quad (1)$$

This experiment measured the limiting shear strength proportionality constant,  $\gamma$ , for the four oils using a, so-called, "Jumping Ball Apparatus" described in detail in [Jacobson, B.O. <sup>3</sup>]. Using this apparatus, the mean friction coefficient during impact and rebound can be determined which gives a rough estimate of the shear strength proportionality constant.

### 2.3 Lubricating film thickness measurements

Lubricant Film thickness was measured with a Ball & Disc Apparatus by using optical interferometry, see [Cameron and Gohar <sup>4</sup>].

The main part of the apparatus is a highly polished steel ball with a radius of 12.7 mm supported by a ball retainer that can be loaded against the chromium-coated underside of a rotating glass disc, in this case with a force of 63N. (See Figure 1).

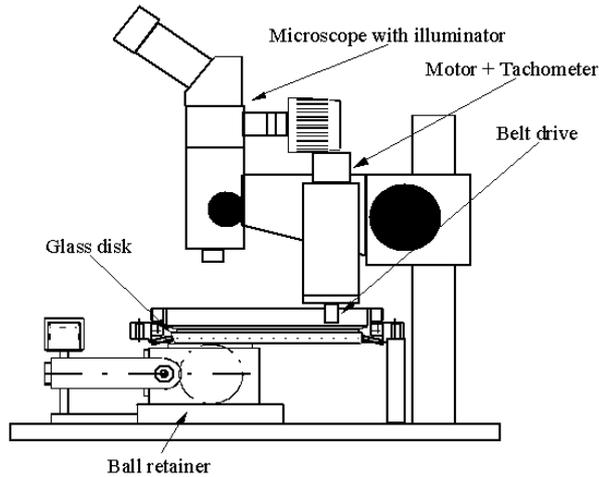


Figure 1. Ball & Disc Apparatus without CCD camera.

A more detailed description of the Ball & Disc Apparatus can be found in [Jonsson U. <sup>5</sup>]. The chrome coating on the disc reflects approximately 25% of the incident light and allows the contact area between the ball and the disc to be viewed through the disc using an optical microscope and a CCD camera. The contact was illuminated by white light, which is reflected from both the chromium layer on the lower side of the glass disc, and from the surface of the ball. The resulting optical interference is observed as fringes in and around the contact area and can be used to determine the topography of the contact using:

$$h = \frac{\lambda_{val}}{2n_{oil}} \left( m - \frac{1.2}{2\pi} \right) \quad (2)$$

Where  $h$  is the central film thickness,  $\lambda_{val}$  the wavelength of the light,  $n_{oil}$  the refractive index and  $m$  the fringe order.

## 2.4 Friction coefficient

To study the coefficient of friction of the esters in boundary lubrication, a high frequency friction apparatus was used, see Figure 2. This equipment produces an oscillating motion between a roller from a rolling element bearing and a steel plate, both with a hardness of 850 HV. The two elements were loaded against each other with a force of 100 N.

A thin lubricating film is formed between the two elements as they oscillates; in this case at a frequency of 12Hz (18.1m/s) and an amplitude of 2.3 mm. The friction force was measured from which the dynamic and static coefficients of friction determined. The temperature during the experiments was  $22 \pm 1^\circ$ . A more comprehensive description of the high-frequency friction apparatus can be found in [6].

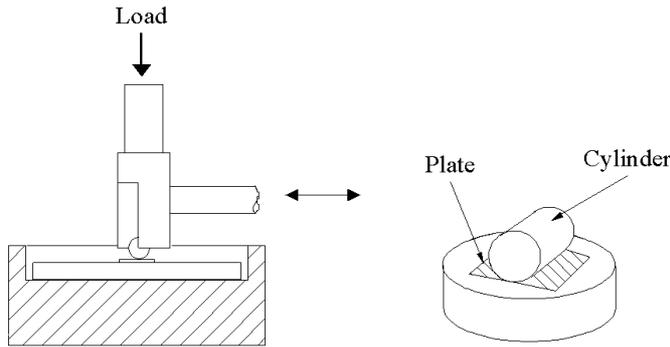


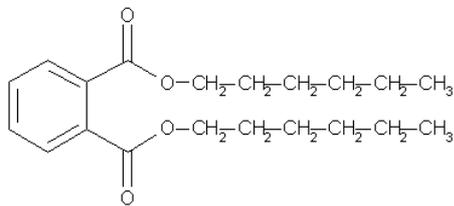
Figure 2 Principal setup of the test pieces in the a high-frequency friction apparatus.

### 3 TESTED LUBRICANTS

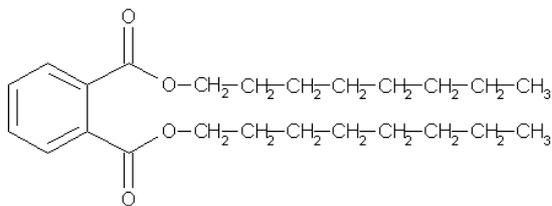
Three different lubricants were developed to allow investigation of the influence of molecular length on lubrication properties. The esters all have the same basic ester structure, but the length of the molecule differs. Bis(2-Ethylhexyl) phthalate was used as a reference for a branched ester with the same basic formula. Table 1 shows the chemical formula of the esters developed and tested. It can be seen that Bis(2-Ethylhexyl) phthalate and Dioctyl phthalate have the same chemical formula, the difference between the two is in how they branch. Bis(2-Ethylhexyl) phthalate is branched and has two ethyl groups attached to the molecule. Figure 3 shows the molecular structure for the four esters tested in this investigation.

Table 1 Chemical Formula for the tested esters.

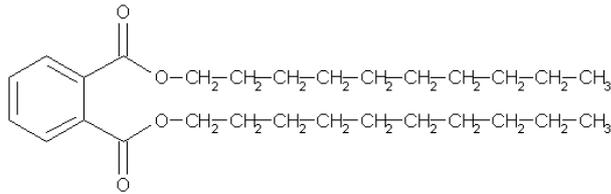
Ester	Chemical formula
Dihexyl phthalate	$C_{20}H_{30}O_4$
Dioctyl phthalate	$C_{24}H_{38}O_4$
Didecyl phthalate	$C_{28}H_{46}O_4$
Bis(2-Ethylhexyl) phthalate	$C_{24}H_{38}O_4$



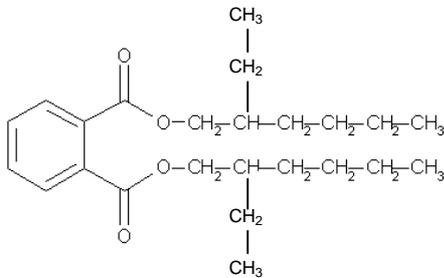
Dihexyl phthalate



Dioctyl phthalate



Didecyl phthalate



Bis(2-Ethylhexyl) phthalate

Figure 3, Molecular structure of the tested esters.

The three different lubricants differ in molecular length and also when compared with the reference oil in how they branch. A lubricant with a long molecule should give a higher viscosity and thus increase the possibility of building proper lubricating films.

The relationship between the different molecular structures and corresponding coefficients of friction is interesting. Long straight molecules like esters, PAO, and polyglycols have relatively low coefficients. The reason for this is that long weak molecule chains find it easier to orient themselves favourably with respect to shear. Due to the small number of branches on the ester molecules, the degree of entanglement is also very low, which also helps reduce the coefficient of friction. The molecules in a refined mineral oil such as naphthenic or paraffinic oils are less able to adopt different kinds of configurations and these oils are therefore expected to have a stiffer behaviour and higher coefficients of friction.

## 4 RESULTS AND DISCUSSION

The results of the investigation are presented below for each of the principle measurements made.

### 4.1 Viscosity measurements

Figure 4 shows the results of the viscosity measurements. All lubricants show the same viscosity / temperature behaviour. The esters have almost the same viscosity at higher temperatures with increasing differences at lower temperatures. Dioctyl phthalate and Didecyl phthalate have the most similar viscosity- temperature relationships. The shortest ester, Dihexyl phthalate, shows a less pronounced viscosity / temperature dependency while the branched ester Bis(2-Ethylhexyl) phthalate shows the greatest variation of viscosity with temperature.

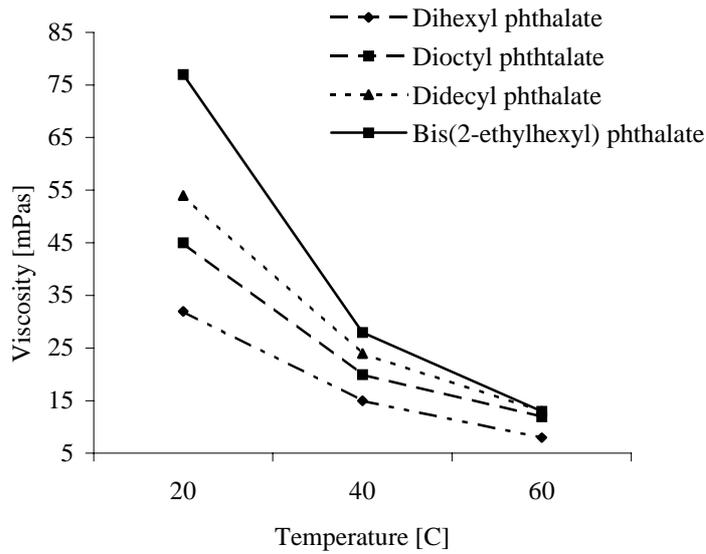


Figure 4 Viscosity vs. on temperature.

## 4.2 Traction coefficient

The traction coefficient versus temperature is shown in Figure 5. Didecyl phthalate with the longest molecule shows the lowest traction coefficient and Bis(2-Ethylhexyl) phthalate has the highest. It can also be seen that the length of the molecule influences the traction coefficient; the shorter molecules having a higher coefficient than the longer ones. The reason for this is that long weak molecule chains find it easier to orient them selves favourably with respect to shear, see also [Höglund, E. <sup>7</sup>].

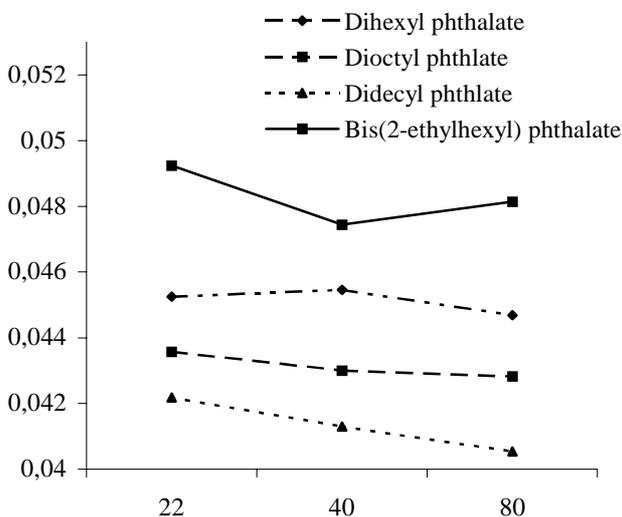


Figure 5 Traction coefficient vs. temperature.

## 4.3 Lubricant film thickness

Figure 6 shows the film thickness results for the three different esters and the reference lubricant. The figure shows that the film thickness increases with increasing length of ester

molecule. The branched Bis(2-Ethylhexyl) phthalate, which is most similar to the Dioctyl phthalate as far as chemical formula is concerned, gave the best film thickness. These results can be compared with those from the viscosity measurements, Figure 4, and it can be seen that the film thickness follows the same pattern as the viscosity, i.e. increasing viscosity leads to thicker films.

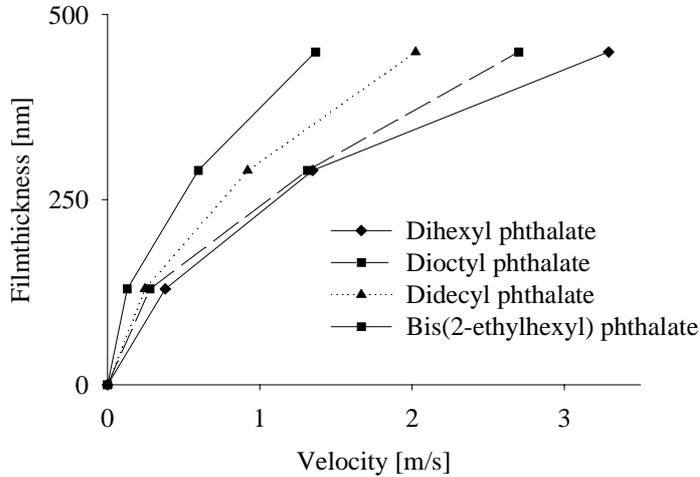


Figure 6. Film thickness vs. velocity.

#### 4.4 Friction coefficients

Table 2 shows static and dynamic coefficients of friction obtained for the esters tested in the high frequency friction apparatus. The static friction is almost the same for all the lubricants but the dynamic friction coefficient results show that the branched ester has the highest coefficient. This confirms the friction measurements made in the Jumping Ball Apparatus.

Table 2. Measured static- and dynamic coefficients of friction.

Ester	Static friction coefficient	Dynamic friction coefficient
Dihexyl phthalate	0,39	0,10
Dioctyl phthalate	0,32	0,10
Didecyl phthalate	0,38	0,10
Bis(2-Ethylhexyl) phthalate	0,35	0,16

## 5 CONCLUSIONS

This investigation shows that it is possible to couple a lubricant's rheological properties to its molecular structure. Such investigations can be used obtain data allowing lubricants with "tailor made" properties to be produced.

## Bilaga 2

The results show that molecular length influences lubrication properties. The longer ester molecules tested giving the highest viscosity and better film thickness than the short esters. The experiments in the Ball & Disc Apparatus confirmed that the Bis(2-Ethylhexyl) phthalate lubricant gave the best film thickness. The length of the molecule did not influence the coefficients of friction, but the traction coefficient,  $\gamma$ , decreased with increasing molecular length. The branched ester differs from the other esters and had the highest traction and friction coefficients. The viscosity is also more temperature sensitive for the branched esters than for the unbranched ones.

### **ACKNOWLEDGEMENT**

The authors wish to thank Mats Lindberg at the department of Inorganic Chemistry, Luleå University of Technology, for providing us the esters for the experiments.

## REFERENCES

---

- <sup>1</sup> Briant, J., Denis, J. and Parc, G., "RHEOLOGICAL PROPERTIES OF LUBRICANTS", Structure/property relationships of viscosity and flow at low temperature, ÉDITIONS THCHNIP, Paris, 1989
- <sup>2</sup> Larsson, R., Larsson, P O., Eriksson, E., Sjödal, and Höglund E., "Lubricant properties for input to hydrodynamic and elastohydrodynamic lubrication analyses". Proc. Instn. Mech. Engrs., vol 214, Part J, 2000.
- <sup>3</sup> Jacobson, B.O., "On the Lubrication of Heavily Loaded Surfaces Considering Surface Deformations and Solidification of the Lubricant", Acta Polytechnica Scandinavica, Mech. Eng. Series.
- <sup>4</sup> Cameron, A. and Gohar, R. 1966. "Theoretical and experimental studies of the oil film in lubricated point contact". Proceedings of the Royal Society, London, Series A. 1966, 291, pp. 520-536.
- <sup>5</sup> Jonsson, U., "Elastohydrodynamic Lubrication and Lubricant Rheology in Refrigeration Compressors", Ph.D. thesis, Luleå University of Technology, Sweden, ISSN: 1402-1544, (1998)
- <sup>6</sup> Anonymous author, "Industrial Lubrication and Tribology", 149 vol 34 nr 4, Jul-Aug 1982, 149p, Paper: 130-132 0036-8792 ILTRA7.
- <sup>7</sup> Höglund, E., "Influence of lubricant properties on elastohydrodynamic lubrication", Wear 232 2 Jun 7-Jun 10 1998 1999 Elsevier Sequoia SA p 176-184 0043-1648.