



UNIVERSITI TEKNIKAL MALAYSIA MELAKA

**TRIBOLOGICAL PROPERTY MODIFICATION PROFILING OF PALM
OIL THROUGH ADDITION OF ZINC DIALKYLDITHIOPHOSPHATE
(ZDDP)**

This report submitted in accordance with requirement of the Universiti Teknikal
Malaysia Melaka (UTeM) for the Bachelor Degree of Engineering Technology
(Maintenance Technology) (Hons.)

by

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ABSTRACT

Mineral oil lubricant was harmful towards the environment due to its difficulty in disposal process and non renewable. Vegetable oil was chosen as a candidate to replace mineral oil lubricant because it has properties such as bio-degradable, non-toxic and renewable. This study is conducted in order to develop a new formulated lubricant using palm oil induced with Zinc Dialkyldithiophosphate (ZDDP). This ZDDP and palm oil were blended and was inserted into bottle to be immersed in a water bath at 50 °C for 20 minutes. The palm oil was added with 0wt%, 0.5wt%, 1.0wt%, 1.5wt%, 2.0wt% and 2.5wt% of ZDDP. This new formulated lubricant was tested and characterized using standard laboratory test method in order to determine metal content, kinematic viscosity, coefficient of friction and wear scar diameter. After testing and characterization, it was found that 2 wt% amount concentration of ZDDP that was added into palm oil gives the best results. For the kinematic viscosity, 2 wt% gives the lowest kinematic viscosity result which is 42.50 cSt. Meanwhile, the coefficient of friction and wear scar diameter obtained from the 2 wt% was the lowest result which is 0.069 and 80.28 μm respectively. Furthermore, this new lubricant with 2 wt% of ZDDP possesses 0.069 of coefficient of friction and 80.28 μm of wear scar diameter which are lower compared to SAE 15W-40 which possess 0.075 of coefficient of friction and 91.44 μm of wear scar diameter. To conclude, this had proved that 2 wt% amount concentration of ZDDP is to be the most desirable concentration of additive to be added into palm oil and highly potential to replace mineral based lubricant.

ABSTRAK

Minyak pelincir mineral adalah berbahaya terhadap alam sekitar kerana kesukaran dalam proses pelupusan dan tidak boleh diperbaharui. Minyak sayuran telah dipilih sebagai calon untuk menggantikan minyak pelincir mineral kerana ia mempunyai ciri-ciri seperti mudah terurai, tidak toksik dan boleh diperbaharui. Kajian ini dijalankan untuk membangunkan rumusan baru bagi pelincir menggunakan Zinc Dialkyldithiophosphate (ZDDP) dicampur dengan minyak sawit. ZDDP dan minyak sawit ini telah dicampur dan dimasukkan ke dalam botol untuk direndam didalam rendaman air pada 50 °C selama 20 minit. Minyak sawit telah ditambah dengan 0% berat, 0.5% berat, 1.0% berat, 1.5% berat, 2.0% berat dan 2.5 berat% ZDDP. Rumusan baru pelincir ini telah diuji dan dicirikan menggunakan kaedah ujian makmal standard bagi menentukan, kandungan logam, kelikatan kinematik, pekali geseran dan diameter kehausan parut. Selepas melakukan ujian dan pencirian, ianya didapati bahawa 2% berat kepekatan ZDDP yang telah ditambah kedalam minyak sawit memberikan hasil yang terbaik. Untuk kelikatan kinematik, pelincir dengan 2% berat ZDDP telah memberikan hasil kelikatan kinematik yang paling rendah iaitu 42.50 cSt. Sementara itu, pekali geseran dan diameter parut kehausan yang diperolehi daripada 2% berat ZDDP adalah hasil yang paling rendah iaitu 0.069 μ dan 80.28 μ m. Tambahan pula, minyak pelincir baru dengan 2% berat ZDDP ini mempunyai 0.069 pekali geseran dan 80.28 mikron diameter kehausan parut yang mana ianya lebih rendah berbanding dengan SAE 15W-40 yang mempunyai 0.075 pekali geseran dan 91.44 mikron diameter kehausan parut. Kesimpulannya, ini telah membuktikan bahawa 2% berat ZDDP adalah menjadi kepekatan yang paling wajar untuk bahan tambahan yang akan ditambah kedalam minyak sawit dan ianya sangat berpotensi untuk menggantikan pelincir berasaskan mineral.

DEDICATIONS

To my beloved parent, Rodwan Bin Abdullah and MashitahBinti Hassan.

To my respected supervisor, Muhamad Azwar Bin Azhari.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	-	Percent
AD	-	Anno Domini
ASTM	-	American Society for Testing and Materials
BC	-	Before Christ
C	-	Carbon
°C	-	Degree Celcius
cSt	-	Centistokes
DBP	-	DibutylPhosphite
G	-	Gram
HO•	-	Hydroxy Radical
HP	-	Hindered Phenolic
kg/m ³	-	Kilogram per Cubic Metre
Mm	-	Millimetre
MoDTC	-	Molybdenum Dithiocarbamate
MoDTP	-	Molybdenum Dithiophosphate
MoS ₂	-	Molybdenum Disulfide
N	-	Newton

PAO	-	Polyalphaolefin
PKO	-	Palm Kernel Oil
PTFE	-	Polytetrafluoroethylene
R•	-	Free Radical
RDE-AES	-	Rotating Disc Electrode Atomic Emission Spectroscopy
RO•	-	Alkoxy Radical
ROO•	-	Peroxy Radical
ROOH	-	Hydroperoxides
RPO	-	Red Palm Oil
SAE	-	Society of Automotive Engineers
SEM	-	Scanning Electron Microscopy
TCP	-	Tricresyl Phosphate
UV	-	Ultraviolet
WSD	-	Wear Scar Diameter
Wt	-	Weight
ZDDP	-	Zinc Dialkyldithiophosphate
A	-	Alpha
Mm	-	Micrometre

CHAPTER 1

INTRODUCTION

1.1 History of lubricants

Lubricant is essential in civilization that depends so much on a machinery application. Any substance that placed in between 2 surfaced in order to reduce wear and friction is called lubricant and the process is called lubrication. Many years ago, lubricant made from vegetable and animal was widely used (Gunstone, et al., 2002). According to Azhari et al (2015), since 1400 B.C, animal based oil mixed with additive already had been used. This shows that, lubricant already has been used by people thousand years ago and upgrading in order to fulfil their needs. Lubricant had been used for a very long time and it is still used until nowadays. Animal fat was mixed with lime in order to lubricate chariot axle. They also, used beeswax, animal tallow and water to lubricated wooden wheels and bearing. Furthermore, olive oil was used since 1650 B.C as a lubricant. Oil obtained from olive, rapessed, castor beans, palm oil and the fats from sperm whale were used from A.D 50 to 19th century (Gawrilow, 2004). It also stated by Anderson, (1991) that lubricant was used from vegetable, animal or mixture of two during 16th century.

The 19th century is also known as Industrial Revolution, where technology had improved economic and culture at this time by changed every industrial machine (Suhane, et al., 2012). The development in industrial was so enormous because of the findings of the new technology at that time. In this era, synthetic lubricant over wide range was developed because of the serious effort were initiated. After that, in order to enhance grease oil properties, petroleum were combined with calcium, potassium

and sodium soap. Thus, the price is increase because of it widely used (Pirro, et., 2001).

Demands on the lubricant were really excruciate and that is why it price were increase heavily. However, current lubricant at that time was not that good, because it cannot provide a good viscosity and retaining their viscosity over wide temperature range. Therefore, according to Anderson, (1991), synthetic lubricant was developed in 1930s. This is because synthetic lubricant able provides excellent viscosity and retaining their viscosity over wide temperature range. Besides that, silicone polymer which has superior viscosity temperature properties and its used for lubrication at high temperature is one of the good example.

1.2 Function of lubricant

In today's world, with advance machinery and technology, lubricant is essential. Modern equipment must be lubricated in order to prolong its lifetime, protect the system and make it more efficient (Azhari, et al., 2015). Lubricant is a substance used between contact surface of moving parts that reduce friction, wear and heat. Whereby, the process of reducing friction between moving or sliding surfaces is called lubrication. According to Bannister, (1996), lubricant used for two moving part contacting and form a boundary layer between contacting surface to reduce wear. Based on a study by Azhari and Bannister (2015, 1996), the main function of lubricant is to reducing friction and wear in the system. Existence of lubricant will provide lubricant to surface friction instead of surface to surface friction. Thus, the use of lubricant reduces overall friction of the system. Besides that, lubricant also keeps moving parts apart so it can prevent wear due to metal-to-metal contact. Metal to metal surfaces that contacting each others, will produce a large amount of heat. Therefore, lubricant reacts as coolant agent to reduce equipment temperature and cool down the system (Caines, 2004).The liquid lubricants like engine oil constantly circulate inside the engines. This circulating process flow of oil will result the heat is carry away from the hot surface and also

warms cold surface. It will help the engine to cool that cause by fluid friction and combustion of fuel.

Moreover, sufficient use of lubricant can lead to energy reduction. This is because the friction has been reduced and will result of the energy reduction. Oxidation and corrosion is likely to happen in the engine system because of the existence of moisture in it. Thus, lubricant can provide a coat for surface in order to protect it from moisture that can cause oxidation and corrosion (Bannister, 1996). Furthermore, a study by Nehal, et al, (2011) stated that, lubricant also can keep the system from contaminant, dirt and dust. Circulation systems of lubricant will carry dirt and contaminants to get to the filter system which where they can be removed. It is also can provide a sealing between pistons and cylinders. Therefore, to reduce friction and wear, the correct lubricant need to be select in order it to perform at its most optimum. However, inappropriate in selecting a lubricant will cause a bad friction and wear which will eventually result to the equipment failure.

1.3 Classification of lubricant

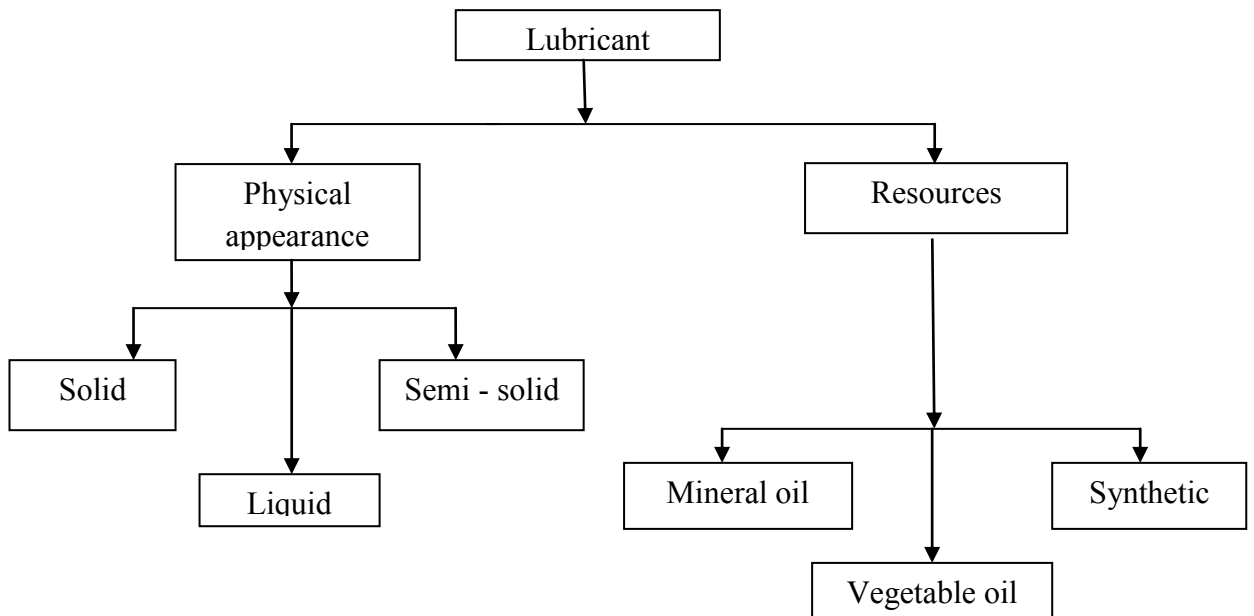


Figure 1.1 Classification of lubricant

Generally, for physical appearance, lubricant can be classified by 3 classes which is solid, semi-solid and liquid lubricant. Besides that, for resources of base oil which are, mineral oil, vegetable oil and synthetic oil. Solid lubricant character is either dry powder or with binder to make them stick such as graphite and cadmium disulphate (Erdemir, 2003). They can withstand temperature up to 650° C and can be applied in continuously operating situations. Moreover, it come in solid state and posses low coefficient of friction and have lamellar shape to preventing direct contact between sliding surface even at high loads. It capability are to improve equipment life to make it last longer, prevent from contamination and use in extreme environment that liquid lubricant not capable (Filip, et al., 2007). Next is semi-solid lubricant. Based on a study by Srivastava (2013), semi solid lubricant is used as anti friction for roller bearing and other. Develop by emulsifying oil or fat with metallic soap and water. Furthermore, when thick lubricant is required or when liquid lubricant can't be use, semi-solid lubricant is the best solution. Examples of application are roller bearing, steam turbine and spindle.

Liquid lubricants or grease are made from viscous of crude oil that go through distillation process (Pawlak, 2003). Petroleum, vegetable oil and synthetic oil are the example of liquid lubricants. Synthetic oil is developed by the modification of the mineral oil. Mineral oil capability is not so good for high performance. Therefore, synthetic oil is developing in order to replace mineral oil. According to Sharma, et al., (2001), U.S military has doing so much research and development of new synthetic oil because military required a high performance lubricant. Vegetable oil or bio-lubricant, can be obtain from containing seeds, fruits or nuts by different method such as pressing or solvent method (Bennion, 1995). A study by Azhari et al, (2015), vegetable oil is biodegradable and comes from renewable source. Vegetable oil also has high viscosity index, high lubricity, and low toxicity.

1.4 Problem statement

The depletion of the world mineral oil reserve has results the mineral oil price increase. It also has caused an immense pollution towards environment because of its non biodegradable (Erhan et al, 2006 & Srivastava, 2013). A part from that, mineral oil is also a non renewable (Srivastava, 2013). According to Gawrilow (2004), 5 to 10 million tons of wasted oil is entering the environment every year. Moreover, 40% of that amount of wasted oil is contributed by industrial waste, refinery process and urban waste. Nowadays, a rising concerns on environment pollution has force industrial to search an alternative way instead of using mineral oil. These studies involve to replaced mineral oil as lubricant by using vegetable oil as an alternative way to overcome these issues but at the same time possess the same lubricity effect that is essential for a good lubricant.

Vegetable oil properties are biodegradable and it is also a renewable source, which make it a good replacement of mineral oil as a lubricant (Azhari, et al, 2015). Furthermore, vegetable oil has good technical properties that make it a reasonable replacement of mineral oil such as have high viscosity index, high lubricity, high flashpoint, biodegradability and low toxicity (Anand, et al, 2014). However, the biggest drawback of using vegetable oil as lubricant is it lack in oxidation stability. Through oxidation vegetable oil based lubricant may cause increase in oil acidity, kinematic viscosity, corrosion and volatility (Liu, et al, 2015). A study by Azhari et al., (2014) explained that high content of unsaturated fatty acids causing the oil to be less supportive in stabilizing oxidation process is one of the main problem that prevent vegetable oil to be using as a lubricant. The rate of oxidation increases with the increment number of double bond. This will result to the increasing on the level of unsaturation. Oxidation may result in degradation of oil which can harm the moving contacting surfaces of metal. Therefore, in order to overcome these issues, an additive should be added to the vegetable based oil to enhance the properties that vegetable lack to make it a good lubricant.

A researched had found that, zinc dialkyldithiophosphate (ZDDP) can be the additives that might overcome these issues (Azhari et al., 2015). Besides that, widespread use of ZDDP is because of its good antioxidant, radical scavenger, anti wear and hydroperoxide decomposer (Erhan, et al., 2006). Moreover, ZDDP also provide wear protection of key metal to metal (Mahdi, 2012). Anti oxidant of ZDDP is act by the radical scavenger that decelerates the radical peroxide from further the propagation of free radical chain (Azhari et al., 2015). After that, according to Chang et al., (2011), ZDDP is providing a solid protective film when it reacts with the metal surface which makes it an excellent anti wear. Hence, with these findings, an improvement can be made towards vegetable oil to become alternative oil.

Upon addition of ZDDP, the coefficient of friction and wear reduces. This is proven through studies by Azhari, et al., (2015) where in their studies added ZDDP into corn and canola oil. From the studies, it can be found that the coefficient of friction and wear scar diameter of pure corn and canola oil was reduced with the addition of ZDDP. It was also found out by Mahipal, et al.,(2014) through their studies added ZDDP into karanja oil. It reviewed that the coefficient of friction and wear scar diameter of pure karanja oil was also reduced. Most of the stated studies revealed that the desirable concentration of ZDDP to be added is at 2wt%. However, the concentration tested in the sample by these researchers comes from a comparably big range. Therefore, a smaller range should be tested to see which concentration give the most desirably effect on wear scar diameter and coefficient of friction. Henceforth, this study will focus on profiling with a smaller range in order to determine the most desirable concentration of ZDDP to be added.

1.5 Objective of research

Based on the introduction and problem statement above, the objective of this study are as follows:

- i. To develop a new formulated bio-lubricant with addition of friction modifier agent.
- ii. Test and characterize newly develop bio-lubricant using standard laboratory test and method.
- iii. To compare newly develop bio-lubricant with SAE 40.

1.6 Scope of research

A few scopes have been made, in order to achieve the objective:

- i. Prepare the new lubricant oil using palm oil with addition of Zinc dialkyldithiophosphate (ZDDP).
- ii. Testing the newly develop bio-lubricant oil using RDE – AES (ASTM D6595).
- iii. Characterizing of newly develop bio-lubricant using four ball tester (ASTM D4271)
- iv. Comparing of newly develop bio-lubricant with mineral oil SAE 40.