



UNIVERSITI TEKNIKAL MALAYSIA MELAKA

**ADDITION OF ZDDP IN CANOLA OIL AS PHYSICAL
PROPERTY IMPROVER VS SAE 40 MINERAL OIL**

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

by

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APPROVAL

This report is submitted to the Faculty of Engineering Technology of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Engineering Technology (Bachelor's Degree of Mechanical Engineering Technology (Maintenance Technology)) (Hons.). The member of the supervisory is as follow:

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ABSTRACT

Mineral based oil is non-biodegradable and due to complex disposal procedure making it non-environmental friendly. As such, this study will be focused on developing new bio-lubricant as alternative to mineral based oil lubricant. In this study, differences of the newly developed bio-lubricants compared to normal SAE 40 mineral oil were investigated. The bio-lubricants were developed using commercialized cooking canola oil with addition of ZDDP as physical property improving agent. The introduction of ZDDP into the oil was prepared by direct introduction method. The samples were tested for its kinematic viscosity and metal content determination by using standardized ASTM test methods. It was then characterized for their coefficient of friction and wear scar diameter properties by using four ball test and the wear scar image was observed under light microscope. The result from test and characterization of the newly developed bio-lubricant showed canola oil with 2 wt% of ZDDP exhibit the desirable result from the selected samples which give the lowest kinematic viscosity at 40°C at 37.96 cSt and coefficient of friction of 0.081. The smallest wear scar diameter also was observed at 34.72 μm . As a conclusion, the positive performance of this newly developed bio-lubricant resulted in producing an alternative lubricant which can be applied to industry today as substitution of using mineral based oil lubricant.

ABSTRAK

Minyak berasaskan mineral adalah tidak terbiodegradasi dan oleh kerana prosedur pelupusan yang kompleks menjadikannya tidak mesra alam. Oleh itu, kajian ini akan menumpukan kepada pembangunan bio-pelincir baru sebagai alternatif kepada minyak pelincir berasaskan mineral. Dalam kajian ini, bio-pelincir yang baru dibangunkan ini akan dibandingkan dengan minyak mineral biasa SAE 40. Bio-pelincir ini akan dihasilkan dengan menggunakan minyak masak komersial kanola dan ditambah ZDDP sebagai ejen peningkat sifat fizikal. Pengenalan ZDDP ke dalam minyak kanola akan menggunakan kaedah pengenalan secara langsung. Sampel akan diuji kelikatan kinematik dan penentuan kandungan logam dengan menggunakan ujian yang akan mengikut piawaian ASTM. Kemudian, sampel akan dicirikan sifat pekali geseran dan diameter parut terhakis dengan menggunakan ujian empat bola. Diameter parut terhakis akan diimbis dibawah mikroskop bercahaya. Hasil dari ujian dan pencirian bio-pelincir yang baru dibangunkan menunjukkan minyak kanola dengan 2 wt% ZDDP memberikan keputusan yang diinginkan daripada sampel terpilih dimana ia memberi nilai paling rendah terhadap kelikatan kinematik pada 37.96 cSt dan pekali geseran pada 0.081. Nilai paling kecil diameter parut terhakis dilihat pada 34.72 μm . Kesimpulannya, prestasi yang lebih baik daripada bio-pelincir yang baru dibangunkan ini akan mendorong penghasilan pelincir alternatif yang boleh digunakan untuk industri hari ini seterusnya menukarkan penggunaan minyak pelincir berasaskan mineral.

DEDICATION

I would like to dedicate my thesis to my beloved parents and my siblings.

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I would like to give my full gratitude to Allah S.W.T because with his grace and kindness I can carry out this study. Apart of that, I would like to dedicate my thanks to my supervisor, Mr. Muhamad Azwar bin Azhari for give me the opportunity to do this study under his guidance. I have learn a lot from him and a lot of knowledge has he shared with me. I am gratefully to have him as my supervisor since he always teach us how to write a good thesis, give a lot of briefing about this study and give full guidance until I can produce this thesis. Besides that, my thanks also for my family that always give me full encouragement and morale support throughout this study. Their supports really give me the strength to continue and completely this study. My thanks also to all of my friend that have always give me help and support either directly or indirectly during this study. They have shared some journal and time in order for me to do this study. They also always have besides me in any condition I have during this study. Last but not least, my thanks also to anyone that give me help directly or indirectly during this study. I believe this thesis would not have been possibly done without all of these support and help.

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
BC	-	Before Christ
BSD	-	Benzothiazole derivative containing dialkyldithiocarbamate
CO	-	Carbon monoxide
FEP	-	Fluorinated ethylene propylene
IPZ	-	Intake protection zone
MCT	-	Medium chain triglycerides
MoDTC	-	Molybdenum dithiocarbamate
MoDTP	-	Molybdenum dithiophosphate
MoS ₂	-	Molybdenum disulphide
PAO	-	Polyalphaolefin
PIB	-	Polyisobutylene
PIO	-	Polyinternalolefin
PKO	-	Palm kernel oil
PCTFE	-	Polychlorotrifluoroethene
PTFE	-	Polytetrafluoroethylene
PV	-	Present value
PVF	-	Polyvinyl fluoride
RDE-AES	-	Rotating disc electrode atomic emission spectroscopy
SAE	-	Society of automotive engineer
SEM	-	Scanning electron microscopy
SI	-	International system of unit (Systeme internationale)
SiO ₂	-	Silicon dioxide
UHV	-	Ultra high vacuum
VI	-	Viscosity index
ZDDC	-	Zinc Dialkyldithiocarbamate
ZDDP	-	Zinc Dialkyldithiophosphate

cm	-	centimeter
cSt	-	Centistokes
ft	-	Feet
Kg	-	Kilogram
kN	-	Kilo newton
min	-	minute
ml	-	milliliter
nm	-	Nanometer
Psi	-	Pounds per square inch
rpm	-	Rotation per minutes
mm	-	Millimeter

CHAPTER 1

INTRODUCTION

1.1 History of Lubricant

Lubricant is a substance that is used to reduce friction and wear between surfaces that are in mutual contact. According to Mang and Dresel (2007), there will be some cases in which if lubricant is present, the relative movement of two bearing surfaces is possibly to occur. This is because the surface of the bearing will be sticking each other and with present of impurities will make the surface cannot move. So with present of lubricant, this impurities can be move and the relative movement of two bearing surface can happen. Caines et al., (2004) has stated in their book that lubricant is already been used in the Middle East several thousands of years B.C. This is proven with the founding of various forms of primitive bearing on that year. It is reasonable to accept that if the concept of a bearing had been developed, then the use of a lubricant must have happened, even if only by using water as lubricant. Besides that, there are also traces of a bituminous substances adhering on a primitive bearing that contain in Mesopotamian potter's wheel dating from 4000 B.C. (Caines et al., 2004). Therefore, it can be accepted that lubricant already has been used by people from thousands of year ago.

The early lubricant use from vegetable oil and animal fat started since 1650 B.C. According to Caines et al., (2004), before the discovery of petroleum oil, Egyptian chariot wheels were lubricated by animal tallow while whale fat was extensively used as a lubricant for certain equipment and machinery. These lubricants are then replaced during late 1800s with mineral oils since it became the primary base stock for many lubricants due to price and overall performance. Furthermore, the use of mineral based oil was also caused by the industrial

development during the 19th century. This is because the need for lubricant has increase which surpassed supply of natural oils (Koushik et al., 2012). With high exploitation of petroleum as a fuel source has increase the availability of mineral oil in large quantities and at reasonable prices. Thus it make the use of mineral oil as lubricant more reasonable since mineral oils are found to be more stable than natural oil and also they are cheaper and available in a wide range of viscosities.

1.2 Function of Lubricant and Lubrication

The main purposes of lubricant are to reduce wear and heat loss from the contact of surfaces in motion (Mobarak et al., 2014). This will result in reducing of the coefficient of friction between contacting region. Other than that, lubricant can prevent rust and act as a seal against dirt, dust and water (Caines et al., 2004). It will form a protective film on the surface of an engine part thus water and air cannot react with the engine part. Besides that, the oil should avoid fouling of mechanical parts from combustion contamination or from its own degradation products. This will make the lubricant act as cleaning agent in the systems. Caines et al., (2004) also stated that lubricant is a preliminary heat transfer agent between certain parts heated by combustion and the heat dissipating systems in an engine. Obviously, liquid lubricant is constantly circulated to and from a cooler part of the system; this lubricant may be used to warm as well as cool when a needed temperature is required (Gupta, 2013). Moreover, the system also determines the amount of heat that is carried away in certain time. The high flow system could carry a lot of heat thus the thermal stress on the lubricant can be reduced.

Lubrication is a method or technique employed to reduce wear of one or both surfaces in close proximity and moving relative to each other (Googelberg, 2012). According to Salih et al., (2013) there will be a substance that called lubricant which will intervene between surfaces to carry or support load between the opposing surfaces. This phenomenon then makes reducing in the occurrence of wear between the surfaces. The intervened lubricant film can be a solid, liquid or semi-solid substance which will be determined based on the application or working method of

the machines (Srivastava, 2014). In the industrial area, lubrication is very important to make sure the machines and tools can be operated in good condition. A good lubrication system must have the proper lubricant used since different methods of lubrication will use different types of lubricants at the different parts of a machine (Lansdown, 1982). This is because each of the lubricant must have differed in certain properties and availability in certain condition. Therefore, selection of lubricant must properly decide so that a good lubrication system can be achieved.

1.3 Classification of Lubricant

Lubricant can be classified into several medium. These can be solid, semi-solid and liquid (Srivastava, 2014). Solid lubricant is in the form of film of a solid material that composed of inorganic or organic compound such as graphite, molybdenum disulphide and cadmium disulphide (Mobarak et al., 2014). This solid lubricant can be used depending on the nature and condition of the surface. Semi-solid lubricant is liquid that is suspended in a solid matrix of thickener and additives such as grease. Semi-solid greases are used in some applications where liquid lubricant cannot be used conveniently. As example of this grease used is as anti-friction of roller bearings of automotive wheels and other industrial machinery (Srivastava, 2014). Liquid lubricant typically is oil. Oils consist of severe resources which come from natural, mineral and synthetic (Mobarak et al., 2014). Natural oil usually is oil that is derived from animal fats and vegetable oils. Most of the oil from vegetable usually is extracted from its seed or fruit. Example of vegetable oil that is popular as lubricants are palm oil, soybean oil and corn oil. Meanwhile, mineral oils are oil that is derived from crude or petroleum reserve. The mineral oils used for lubrication were originally portions obtained by distilling petroleum which has a suitable viscosity for lubrication (Lansdown, 1982). Lastly, synthetic oil which oil that is synthesized as final products of reactions that is personalized according to necessity. Generally, synthetic oil is from mineral oil, but it is advanced than mineral oil since several modifications and personalization has been done to enhance the properties and performance of the oil according to function and the used.

1.4 Problem Statement

Most of the lubricant oil today is based on mineral oil derived from petroleum. This mineral oil generally is not adaptable with the environment because of its toxicity and non-biodegradability (Shahabuddin et al., 2013). Besides that, petroleum is also a non-renewable resource which has potential to run out in a foreseeable future. According to Musa (2009), it has been reported that about ten major oil fields from the 20 largest world oil producers are already face decreasing in oil reserves. With the notion that we live on a planet with finite resources, thus finding renewable resources base oil has been a necessity to lubrication industry today (Ahmed et al., 2014). The depletion of the world's crude oil reserve, increasing of oil prices and the demand to protect the environment against pollution cause by lubricating oils and their uncontrolled spillage have brought renewed interest in the development and use of alternative lubricants (Suhane et al., 2012). Therefore, this study will concentrate on the use of vegetable oil to replace mineral oil as alternative lubricant to overcome these issues.

Vegetable oils are said to be alternatives to mineral oils for lubricant formulations because of their capability towards biodegradability and several inherent technical properties (Suhane et al., 2012). A study by Chauhan and Chhiber (2013), has found that conventional mineral based lubricating oils and synthetic esters can be replaced with vegetable oils because of its high oleic content. Besides that, Chauhan and Chhiber, (2013) also stated that vegetable oils are ideal over synthetic fluids because they are renewable resources, cheaper and eco-friendly. Vegetable oils also have excellent qualities like greater flash and fire points, higher viscosity and viscosity index (Azhari et al., 2014). Other than that, it also has high lubricity and very less toxicity. So this can assure the safety of workers in handling the lubricant (Srivastava and Sahai, 2013).

However, there are some disadvantages in replacing mineral oil with vegetable oil as lubricant. The properties of vegetable oil which are poor thermal and oxidation stability make the use of this oil is limited in industry. According to Azhari et al., (2014) the oil is less cooperative in stabilizing the oxidation because of the high content of unsaturated fatty acids in the vegetable oils. In other hand, vegetable oil

also has shorter shelf life, storage time, low cold flow behavior and poor seal compatibility (Srivastava and Sahai, 2013). As such to overcome these disadvantages, certain additive shall be blended with the vegetable oil. The introduction of Zinc Dialkyldithiophosphate (ZDDP) as anti-oxidant additive in the vegetable oil can solve these problem (Azhari et al., 2014). Besides as anti-oxidant, ZDDP also can act as anti-wear function. Thus it plays an important role in providing wear protection of key metal-to-metal contact points in engines and transmissions (Mahdi et al., 2012). A few sample tests will be carried out to test the effectiveness of the ZDDP in the vegetable oil, than the results will then be compared to an SAE 40 mineral oil. The hypothesis have been made by a researcher that a small addition of ZDDP can improve the performance to a number of lubricants demonstrated by 15% to 60% reductions in coefficient of friction versus the unmodified lubricant (Chang et al., 2011).

1.5 Objective of Research

From the problem statement stated above, the objectives for this study are stated below:

1. To prepare an alternative bio-lubricant oil with the addition of physical property improver.
2. To test and characterize the newly developed bio-lubricant oil.
3. To compare the effectiveness of the newly developed bio-lubricant oil with SAE 40 mineral oil as lubricant.

1.6 Scope of Research

In order to achieve the objectives, some scopes for this study have been constructed as below:

1. Preparing alternative bio-lubricant oil using commercialized cooking canola oil with the addition of ZDDP as physical property improver.
2. Testing the newly developed bio-lubricant oil by using ASTM physical property laboratory test.
3. Characterizing of newly developed bio-lubricant oil by the properties of wear scar diameter and coefficient of friction of the oil.
4. Comparing the effectiveness between the newly developed bio-lubricant oil and SAE 40 mineral oil as lubricant by results from testing and characterizing of the oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Lubricant Physical Appearances

Physically, lubricant can be divided into three appearances. It can be a solid, semi-solid or liquid state. Each state has difference properties and application to the industry. Further description about these lubricants will be discussed in next sections.

2.1.1 Solid Lubricant

The lubrication of two surfaces in moving contact which a solid material is interposed between them is known as solid lubrication (Lansdown, 1982). The wide variety of solid materials that can reduce friction and prevent seizure is depending on the nature of the two surfaces. As example, in real life condition, dust, sand or gravel on the surface of a road can be lubrication to the vehicle since they decrease the friction between tyres and the road surface. However, according to Lansdown (1982), no one would normally recommend them as solid lubricants. This is because there are several properties that a solid lubricant is needed as following:

- Provide low but constant and controlled friction between two bearing surfaces.
- Chemically stable over the required temperature range and not attack or damage the bearing materials.
- Preferably adhere strongly to one or both bearing surfaces. So that it is not rapidly lost from the bearing.
- Have sufficient resistance to wear to deliver a useful life.

- Easy to put on a controlled manner.
- Non-toxic
- Economical.

Therefore as to fulfil these properties, Lansdown (1982) has stated that the vast majority of solid lubrication involves only three substances which are graphite, molybdenum disulphide or polytetrafluoroethylene (PTFE). However, many others different solids nowadays have been tested for use as solid lubricant. And, these compounds are actually have been used in practical service applications. Most of these compounds used are either polymers, inorganic powders or metals and others as listed in Table 2.1.

A useful property for assessing the lubricating capacity of a solid lubricant is the PV factor (Lansdown, 1982). It is the highest product of pressure and velocity which the lubricant can be used satisfactorily. It is usually quoted as

$$(\text{Psi} \times \text{ft}/\text{min})$$

or in SI unit

$$(\text{kN}/\text{m}^2 \times \text{m}/\text{s} \text{ or } \text{kN}/\text{ms})$$

The PV factor is in fact an over-simplification. This is because it is suggested that no matter how high the pressure or the velocity is as long as the product of the two is below the limiting PV. This is definitely not true since it would be beneficial if the maximum pressure, maximum PV and maximum sliding speed were all quoted (Lansdown, 1982).

Table 2.1: Other Materials Used As Solid Lubricant (Lansdown, 1982)

Type of compound	Material	
Layer-lattice	Graphite fluoride	Molybdenum disulphide
	Tungsten diselenide	Tungsten disulphide
	Graphite	Calcium fluoride

Polymers	Nylon	PTFE
	Acetal	PTFCE
	Polyimide	PVF
	Polyphenylene sulphide	FEP ²
Metals	Lead	Indium
	Gold	Tin
	Silver	
Other organics	Molybdcic oxide	Boron trioxide
	Lead monoxide	Boron nitride

2.1.2 Semi-Solid Lubricant

A semi-solid lubricant is usually defined as grease. Grease classically defines as a solid-to-semifluid product of a thickening agent in a liquid lubricant. Other than that, grease also can be thought as a sponge of oil (Rudnick, 2006). Grease is most regularly used as lubricant instead of fluids lubricant at places where a lubricant is required to maintain its original position in a mechanism, especially where chances for frequent relubrication may be limited or economically unjustifiable (Pirro and Wessol, 2001). This requirement may be due to the physical configuration of the mechanism. Other than that, the type of sealing, the type of motion or to the need for the lubricant to perform all or certain part of any sealing function in the prevention of lubricant loss or the entrance of contaminants also the requirement in order to use grease as lubricant. This is because the nature of grease which do not perform the cooling and cleaning function like as the function of a fluid lubricant (Pirro and Wessol, 2001).

Grease is lubricating oils in which thickeners have been detached to produce a steady colloidal structure or gel which is alike in numerous ways to an emulsion (Lansdown, 1982). According to Rudnick (2006), all lubricating greases consist of