UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ADDITION OF MOLYBDENUM DIALKYL DITHIOPHOSPHATE (MoDTP) INTO ZINC DIAMYL DITHIOCARBAMATE (ZDDC) INDUCED CANOLA OIL BIO-LUBRICANT AS TRIBOLOGICAL PROPERTIES IMPROVER.

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

by

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881201-01-5923

FACULTY OF ENGINEERING TECHNOLOGY

2016

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **ADDITION OF MOLYBDENUM DIALKYL DITHIOPHOSPHATE (MoDTP) INTO ZINC DIAMYL DITHIOCARBAMATE (ZDDC) INDUCED CANOLA OIL BIO-LUBRICANT AS TRIBOLOGICAL PROPERTIES IMPROVER.**

SESI PENGAJIAN: **2015/16 Semester 2**

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Signature	:	…………………………………………
Author's Name	:	ALIFF AMIRUDIN BIN MOKHTAZA
Date	:	…………………………………………

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 (Maintenenace Technology) with Honours. The member of the supervisory is as follow:

…………………………………

(Mr Muhamad Azwar bin Azhari)

ABSTRACT

This study reports on the development of a new bio-lubricant with the use of Zinc Diamyl Dithiocarbamate (ZDDC) induced canola oil added with Molybdenum Dialkyl Dithiophosphate (MoDTP). There is an increasing need for the substitution of conventional mineral based lubricants due to increasing environmental concerns as mineral based lubricants are harmful to the environment when improperly disposed. Five samples were prepared with the addition of a constant 2 wt% of ZDDC and varied concentrations of MoDTP at 0 wt%, 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%. The kinematic viscosity of the prepared samples were tested using a heated viscometer and the successfulness of dilution using Rotating Disc Electrode-Atomic Emission Spectroscopy (RDE-AES). Then the samples were characterized using the Four-ball Tester to determine the coefficient of friction and the wear scar diameter is observed and measured with the aid of an Upright Light Microscope. The results demonstrated that the desirable combination of additives were 0.05 wt% MoDTP and 2 wt% ZDDC induced canola oil as it produced the lowest kinematic viscosity at 37.74 cSt, coefficient of friction of 0.080 and wear scar diameter of 115 μm compared to the results for the other samples. The results of the comparison between the newly developed bio-lubricant and conventional SAE 15W-40 shown that the new bio-lubricant have a comparable performance towards SAE 15W-40 lubricants despite of only using the combination of MoDTP and ZDDC. As a conclusion, the newly developed bio-lubricant have the potential to be used as an alternative to conventional mineral based lubricant as observed in the results.

ABSTRAK

Kajian ini melaporkan mengenai pembangunan bio-pelincir baharu dengan penggunaan minyak canola terdorong Zink Diamil Dithiokarbamat (ZDDC) yang ditambah dengan Molibdenum Dialkil Dithiofosfat (MoDTP). Terdapat keperluan yang semakin meningkat terhadap pencarian pengganti pelincir konvensional berasaskan mineral yang disebabkan oleh peningkatan kebimbanagan terhadap alam sekitar kerana pelincir berasaskan mineral adalah berbahaya kepada alam sekitar apabila dilupuskan dengan cara yang tidak wajar. Lima sampel telah disediakan dengan penambahan tetap untuk ZDDC iaitu pada 2 %berat dan kepekatan yang berbeza-beza untuk MoDTP iaitu pada 0% berat, 0.05 %berat, 0.10 %berat, 0.15 %berat, dan 0.20 %berat. Kelikatan kinematic sampel yang telah disediakan diuji menggunakan Meter Kelikatan Terpanas dan kejayaan pencairan menggunakan Elektrod Cakera Berputar Spektroskopi Atom Terpancar. Kemudian sampel telah dicirikan menggunakan Penguji Empat Bola untuk menentukan pekali geseran dan diameter parut kehausan diperharikan menggunakan Mikroskop Cahaya Sejajar. Keputusan menunjukkan bahawa kombinasi yang wajar adalah minyak canola terdorong 0.05 %berat MoDTP dan 2 %berat ZDDC kerana ia menghasilkan kelikatan kinematik yang paling rendah pada 37.74 cSt, pekali geseran pada 0.080 dan diameter parut kehausan pada 115 mikron berbanding dengan sampel-sampel lain. Keputusan perbandingan antara bio-pelincir yang baharu dibangunkan ini dengan minyak pelincir konvensional SAE 15W-40 menunjukkan bahawa bio-pelincir baharu ini mempunyai prestasi yang setanding dengan pelincir SAE 15W-40 walaupun hanya menggunakan gabungan MoDTP dan ZDDC. Kesimpulannya, bio-pelincir baharu ini berpotensi untuk digunakan sebagai alternatif kepada minyak pelincir konvensional berasaskan mineral sebagaimana yang boleh diperhatikan dari keputusan kajian ini.

DEDICATION

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

ACKNOWLEDGEMENT

I would like to express my humble gratitude to Allah S.W.T for his blessings which enable me to finish my thesis. Apart from that, I would also like to thank my supervisor, Mr. Muhamad Azwar bin Azhari for giving me the support and opportunity to do this research under his guidance. I appreciate all the knowledge that he shared on the study and also on writing skills. With his push and encouragements gives me the spirit to finish my thesis. Furthermore, I would also like to thank my family mainly to my parents with their love and support give me the motivation to improve myself in my studies. Other than that, I thank my colleagues who are under the guidance of the same supervisor for their part in sharing the information needed for the research which is a big help towards the completion of this thesis. Last but not least, I would like to thank to all the people who helped and supported me either directly or indirectly during the process of this research. Without everyone's involvement the completion of this thesis will not be possible.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C	-	Degree Celsius
A.D	-	Anno Domini
ADDC	-	Antimony Dialkyl Dithiocarbamate
ASTM	-	American Society for Testing and Materials
AW	-	Anti Wear
B.C	-	Before Christ
cSt	-	Centistoke
EP	-	Extreme Pressure
FeS	-	Iron Sulphide
g	-	Gram
kN	-	Kilo Newton
ml	-	Millilitre
μm	-	Micrometres
mm	-	millimetre
MoDTC	-	Molybdenum Dialkyl Dithiocarbamate
MoDTP	-	Molybdenum Dialkyl Dithiophosphate
MoS_2	-	Molybdenum Disulfide
PAO	-	Poly-alpha-olefin
RH	-	Hydrocarbon Chain
R •	-	Free Radicals
ROOH	-	Hydroperoxide
rpm	-	Revolution per minute
SAE	-	Society of Automotive Engineers
wt%	-	Weight Percentage
ZDDC	-	Zinc Diamylditiocarbamate
ZDDP	-	Zinc Dialkyl Dithiophosphate
μ	-	Coefficient of Friction

CHAPTER 1

INTRODUCTION

1.1 History of Lubricants

Lubricants have been around since ancient time, in fact, there were reports dated as early as 1400 B.C. which shows that animal fat mixed with additives such as lime were used as lubrication for the axles of chariots (Azhari et al., 2015a; Pirro and Wessol, 2001). Gunstone and Hamilton (2001), also had stated that lubricants derived from vegetable or animal origin were widely used before the introduction of mineral based lubricants and that there were evidence of the usage of olive oil as lubrication when handling large stones used to construct the pyramids.

According to Gawrillow (2004), various oils derived from vegetables and animal fats were used from 50 A.D until the Industrial Revolution in late 18^{th} century. During the Industrial Revolution (1750 to 1850 AD), the invention of heavy machineries had reduced the needs for muscle power and this attributed to the transformation and improvement of many sectors including agriculture, manufacturing, mining, transportation etc. (Suhane et al., 2012). Therefore, lubrication is essential during this period in order to maintain and keep the machineries to the appropriate working condition.

The need for lubrications are even more crucial after the introduction of steam engined automobile in year 1769 (Suhane et al., 2012). The engine consists of many moving parts and involves parts which slides against or over one another, hence, the need for effective lubrication in order ensure the smoothness of the operation. Suhane et al. (2012) explained that insufficient lubrication may cause heat build-up and increased in wear between sliding surfaces which often resulted in the welding of parts due to friction (eg. pistons in their cylinders).

According to Azhari et al. (2015a), mineral oil derived from petroleum has been widely used as base stock for lubricants during the Industrial Revolution. The advancements in the improvement of mineral based lubricants had led to the production of new semi- synthetic and fully- synthetic lubricants. Since then, mineral based lubricants have been dominating the lubrication industry.

In recent years, there are increasing concerns of the environmental impacts caused by the disposal of mineral based lubricants. This concern is due to the characteristics of petroleum based produce, whereby, they are non- biodegradable and toxic in nature (Sapawe et al., 2014). The improper disposing of petroleum produce is harmful to the environment. The fact that petroleum produce are non- renewable is also very worrying, due to the depletion of fossil fuel (Habibullah et al., 2014; Sapawe et al., 2014). Therefore, there is a growing need for the development of environmentally friendly lubricants.

1.2 Introduction to Lubricants

When a surface slides against another there will always be resistance of movement which is known as friction (Mann, 2013). Excessive friction will result in the increasing of heat and wear to the sliding surfaces. Lubricants are substance which are used in order to facilitate the movement of two contacting surfaces, whereby, the substance will form a fluid film in between the surfaces and thus reducing wear and friction (Bannister, 1996; Suhane et al., 2012). Other than that, lubricant also keeps the surface of metals clean, assist in heat dissipation and prevents rusting (Ahmed & Nassar, 2013). According to Torbacke et al. (2014), lubricants are capable of reducing wear either directly or by friction reduction.

Lubricants can be classified into three categories which are solid lubricants, semi-solid lubricants and liquid lubricants. Solid lubricants are basically composed of inorganic or organic solid compounds such as graphite, molybdenum disulfide, talcum, etc. Torbacke et al. (2014) stated that, solid lubricants are used in high temperature situations where liquid lubricants are considered in-effective. Semi- solid lubricants consist of liquid which is suspended in a solid matrix consisting of thickener and additives for example grease. Greases are used in situations where liquid lubricants are not suitable, for example, the application involves sealing from contaminant or water (Torbacke et al., 2014). Liquid lubricants are those derived from either mineral based oil, bio-based oil or synthetic based oil (Mobarak et. al., 2014). Mineral oil is produced from the refining process of petroleum, with carbon content varying from C_{24} to C_{50}. Most synthetic oils are petroleum based which are modified through chemical process and bio- based oils are derived from the extraction and purification of fatty oils from plants or animals (Ávila et al., 2005).

Lubrication can be classified into three regimes which are hydrodynamic lubrication, mixed lubrication and boundary lubrication. Hydrodynamic lubrication occurs when the two solid surfaces are completely separated and wear will not take effect because there is no contact between the surfaces (Ahmed & Nassar, 2013). According to Hamrock et al. (2004) the relative motion and the viscosity of the lubricant will create a positive pressure between the hydrodynamic lubricated surfaces. This pressure will then be the support between the surfaces when load is applied. Mixed lubrication can be characterized by the intermediate thickness of lubricating film. The two surfaces are closer together when compared to the hydrodynamic regime and contact between the surfaces occasionally occurs. The applied load is supported by both the lubricant and asperities (Rudnick, 2009). Whereas, Boundary lubrication occurs when the two contacting surfaces are really close to one another and the contact between the surfaces in the asperities region is possible. In this regime the bulk flow of the lubrication will not affect the friction or wear behaviors.

Basically the composition of lubricants are 90% base oil (commonly mineral based) and around 10% additives. Ahmed and Nassar (2009) stated that, additives are the chemical compounds that are mixed into lubricating oils in order to impart certain properties to the oils. There are many types of additives that can be used in lubricant enhancement which includes; friction modifying additive, anti-oxidation additives, detergent, dispersant etc.

Rudnick (2009) stated that friction modifiers are the additives added into lubricating oils in order to manipulate or reduce friction to meet certain specifications for the smoothness of transition from static to dynamic state. Other than that, reducing friction also reduce the noise, heat and starting torque (for rotating shafts). Anti-oxidation additives functions as either radical scavenger or peroxide decomposer in order to increase the oxidation stability of oils and also to prolong the oxidation process (Azhari et al, 2014). Detergents are metal salts consist of organic acids with excess base usually in the form of carbonate which will attack and clean the metal surfaces. Other than that, detergents also suspend the polar- oxygenated components in oil (Shahnazar et al., 2015). According to Shahnazar et al. (2015), dispersants are used in combination with detergents and it was designed to suspend insoluble material or contaminant in oils to ensure that the surfaces are clean.

1.3 Problem Statement

Mineral based oil lubricants are derived from petroleum produce. The main concern for the petroleum based products are that they are non-biodegradable and non-renewable (Sapawe et al., 2014). Habibullah et al. (2014), also stated that the world is facing problems of depletion in fossil fuel and increasing in its prices. Mineral oil is a product of distillation of crude oil, therefore, the production of mineral oils depend on the availability of crude oil. If the world is facing crude oil shortages it will significantly impact the production of mineral oil. Furthermore, disposing of crude oil leads to pollution and has been proven that its combustion is responsible for emission of traces of metals such as calcium, phosphorus, zinc, iron, nanoparticles and magnesium (Habibullah et al., 2014; Mobarak et al., 2014). Due to these reasons researchers have been attracted in producing a new type of lubricant which are environmentally friendly, meaning that it is bio-degradable, renewable, non-toxic and can also perform well as lubricants. Therefore, researchers have turn to the advancements in producing vegetable oil based lubricants or also known as bio-lubricants.

Bio-lubricants are considered as the most likely substitute for mineral based lubricants mainly due to the advantages in terms of the higher flash and fire points, thermal stability and biodegradability compared to mineral based oil (Azhari et al. , 2015a). Despite these advantages, vegetable oil lacks in oxidation stability. In order to counteract this researchers had developed new bio-lubricants with the addition of anti-oxidation additives such as Zinc Dialkyldithiophosphate (ZDDP) or Zinc Diamyldithiocarbamate (ZDDC) into vegetable oil.

According to Azhari et al. (2014), the presence of sulphide in the ZDDP, will decelerate the initiation of new radical chains. Sulfides which are hydroperoxide decomposer react with hydroperoxides producing alcohols and sulfoxides. This sulfoxides may react further and remove additional equivalents of hydroperoxides in a complicated series of reactions. Thus, the oxidation process can be prolonged. Erhan and Sharma (2006) stated in their research that ZDDC functions both as radical scavenger and hydroperoxide decomposer which converts the hydroperoxides formed during the oxidation process into non-radical products, thus preventing chain propagation.

Researchers had conducted test and characterized these zinc induced bio-lubricants of various types of vegetable oil, whereby, Mahipal et al. (2014) had added ZDDP into karanja oil, Azhari et al. (2015a) added ZDDP into canola oil and corn oil, Azhari et al. (2016) added ZDDP into canola oil and Azhari et al. (2015c) added ZDDP into corn oil. Although, these researchers had conducted tests using different types of vegetable oil but they all had arrived to similar conclusion, whereby, the addition of 2 wt% concentration of zinc based additive into vegetable oil provides better results in viscosity, wear scar diameter and coefficient of friction compared to the other concentrations and compared to the commercial SAE 40 lubricant. This shows that the despite being an antioxidant agent the zinc based additive also exhibit anti- friction and anti-wear properties.

With the success of the production of zinc induced bio-lubricants, researchers are now seeking to make further enhancements to the characteristics of these zinc induced bio-lubricants with the addition of Molybdenum containing additives such as Molybdenum Dialkyldithiophosphate (MoDTP) and Molybdenum Dialkyldithiocarbamate (MoDTC). These organomolybdenum compounds acts as friction modifier to achieve energy saving in the systems (Jawale & Jadbav, 2006).

Erdemir and Martin (2007) and Yan et al. (2012), stated that both MoDTC and MoDTP may form a thin film of molybdenum disulfide (MoS_2). The production of MoS_2 occur due to the chemical structure of both additives which contains S-M-S.

MoS_2 will form a thin film (tribofilm) in the surface of the contacting surface and smoothens out the surface. Thus, the friction between the surfaces are reduced significantly. According to Tang and Li (2014) MoDTC and MoDTP can be used independently to reduce friction and wear by the formation of protective films containing MoS_2 and other molybdenum oxides, or used in combination with ZDDP with better anti-wear performance.

Xia et al. (2008) came up with a similar hypothesis, stating that the combination of MODTC and ZDDP additive will form a uniform phosphate film and MoS_2 which is a product formed from the decomposition of MoDTC, that acts as a tribofilm in the wear scar influences in wear performance through friction reduction.

Unnikrishnan et al. (2002) had conducted tests to study the effects of ZDDP addition on the antiwear (AW) and extreme pressure (EP) properties of MoDTC and MoDTP. Whereby it was found that MoDTP possesses better AW properties than MoDTC due to its high reactivity with the metal surface. However, in the presence of ZDDP the AW characteristics of MoDTC could be improved and on the other hand, ZDDP do not have any effect in the frictional properties of MoDTP. Unnikrishnan et al. (2002) explained that ZDDP enhances the decomposition of MoDTC, thus, creating a synergistic action between ZDDP and MoDTC. In the presence of ZDDP, MoDTC form mainly metal sulfides like MoS_2 and FeS under friction whereas, the MoDTP+ZDDP derived surface, produced mainly metal phosphate along with molybdenum oxysulphides and small amount of MoS_2 and FeS (iron sulfide).

Although there are many studies which discusses the effects of molybdenum and zinc compound additives in lubricants but it was found that they mainly convey information theoretically and focuses more on MoDTC and ZDDP in mineral based lubricants. The tests results or research on the combination of molybdenum and zinc compound for MoDTP and ZDDC were scarce. Therefore, this study will seek to determine the best concentration of the combination between MoDTP and ZDDC in canola oil based bio-lubricant so that the newly developed bio-lubricant is comparable with the conventional SAE 15W-40 lubricants.

1.4 Objectives

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

i. To develop a new bio-lubricant with addition of friction modifier.
ii. To test and characterize the new bio-lubricant with standard laboratory testing methods.
iii. To compare the performance of the newly developed bio-lubricants with SAE 15W-40 mineral based lubricant.

1.5 Scope

In order to reach the objectives, a few scopes have been formulated:

i. Developing bio-lubricant using zinc induced canola oil with the addition of Molybdenum Dialkyl Dithiophosphate (MoDTP) as friction modifier.
ii. Testing the dilution of additive for the new bio-lubricant using ASTM D6595 (Rotating Disc Electrode-Atomic Emission Spectroscopy) and kinematic viscosity using kinematic viscometer.
iii. Characterizing the friction and wear of the new bio-lubricant using ASTM D4172 (Four Ball Test).
iv. Comparing the tribological properties of the new bio-lubricant with SAE 15W-40 mineral based lubricant.

CHAPTER 2

LITERATURE REVIEW

2.1 Lubrication

Friction and wear occur when there is two surfaces move in relative to each other. Lubrication is any substance used to alleviate the effects of friction and wear towards the contacting surfaces. Suhane et al., (2012) stated that lubricant reduces the friction between two contacting surfaces by providing a protecting film which separates the surfaces. According to Ahmed and Nassar (2013) the purpose of lubrication includes the reduction of coefficient of friction (will also reduce heat and wear) between the contacting surfaces; reduction of oxidation and thus preventing rust; and provides a seal from any contaminants (i.e water, dust and dirt) which will cause harm to the system. Lubrication has been used in automobile engines for a long time in order to ensure the reliability and smoothness of its operation (Mobarak et al., 2014). In addition Mobarak et al. (2014) stated that, a good lubricant should have high lubricity, high flash and fire point, high viscosity index and high oxidation stability.

Lubrication systems can be divided into three regimes which are hydrodynamic lubrication, mixed lubrication and boundary lubrication. The relation of these three lubrication regimes can be referred using a Stribeck Curve as shown in Figure 2.1. Mang and Dressel (2007) explained that in the case of shaft and bearing, when the initial state is static, the surfaces are only separated by a thin lubricant layer (molecular). As the shafts' rotational speed increases a thicker hydrodynamic lubricant film started to produce. At this stage, initially mixed friction occurs but the coefficient of friction is still lower than before. Then, as the speed continues to increase, a full uninterrupted lubrication film is produced which significantly reduces the coefficient of friction. Finally, if the rotational speed is still increasing the internal friction in the lubrication film will add to the external friction which resulted in the increase of coefficient of friction. Hence, explained the rise of coefficient of friction after a certain point as in Figure 2.1.

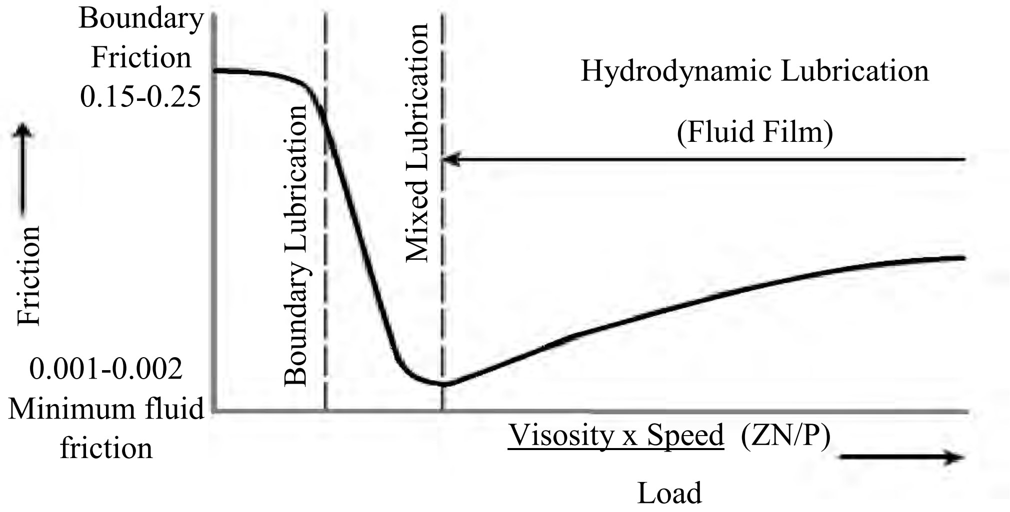

Figure 2.1 Stribeck Curve (Rudnick, 2009)

2.1.1 Hydrodynamic Lubrication

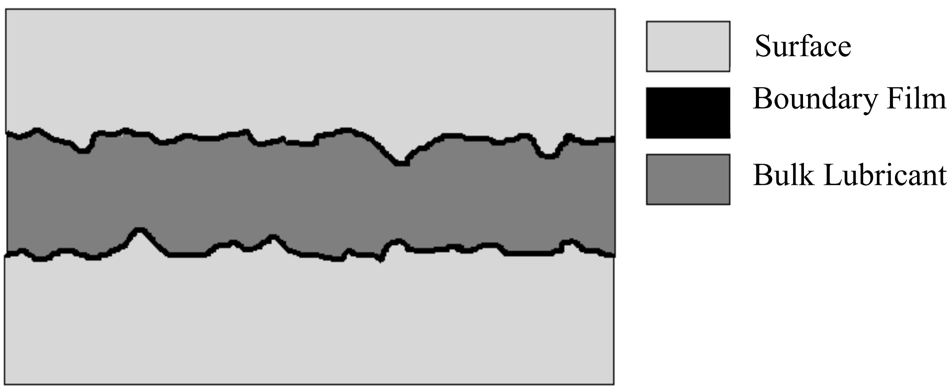

Figure 2.2 Film conditions of lubrication regimes; Hydrodynamic lubrication