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TRIBOLOGICAL PROPERTIES IMPROVEMENT OF ZINC INDUCED CANOLA OIL BIO-LUBRICANT WITH ADDITION OF MOLYBDENUM DITHIO PHOSPHATE (MoDTP)

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Engineering Technology (Maintenenace 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 (Department of Mechanical Engineering Technology) (Hons.). The member of the supervisory is as follow:

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ABSTRACT

The long-term pollution of the environment imposed by mineral oil based lubricants, has led to the renewed interest in the needs of finding alternative environmental friendly oil as lubricant. Vegetable oil is seen to be the candidate for the substitution of mineral oil based lubricant because of it properties of biodegradable, environmental friendly and renewable. The purpose of this study is to developnew bio-lubricant using Zinc Dialkyldithiophosphate (ZDDP) induced canola oil added with the addition of secondary additive of Molybdenum Dialkyl Dithiophosphate (MoDTP). The ZDDP induced canola oil was addedwith 0wt%, 0.05wt%, 0.10wt%, 0.15wt%, 0.2 wt% of MoDTP. The newly formulated biolubricantwas tested using American Society for Testing and Materials (ASTM) methods. The oil was tested using ASTM D6595 and heated kinematic viscometer to determine the metal content and the kinematic viscosity. The newly formulated biolubricant was also characterized using using four-ball test and upright laser microscope to determine the coefficient of friction and wear scar diameters. Result found that the 2 wt% ZDDP with 0.05 wt% MoDTP provides the lowest kinematic viscosity value of 38.0 cStwhich was the lowest amongst the other sample. The coefficient of friction of the canola oil with 2 wt% ZDDP and 0.05 wt% MoDTP shows the lowest value which was 0.064. The lowest wear scar diameter obtainedat79.56 μm was also from the introduction of 2 wt% ZDDP and 0.05 wt% MoDTP. Found in this experiment which the composition of canola oil with 2 wt% ZDDP and 0.05 wt% MoDTP gives the most desirable results. In conclusion, the newly formulated bio-lubricant was successfully developed by introducing MoDTP into the ZDDP induced canola oil which further enhanced it anti-wear properties.

ABSTRAK

Pencemaran alam sekitar jangka panjang yang terhasil daripada pelinciryang berasaskan minyak mineral, telah menjurus kepada pembaharuan minat dalam keperluan mencari pelincir alternatif yang mesra alam. Minyak sayuran adalah dilihat menjadi calondalam penggantian pelincir yang berasaskan minyak mineral disebabkan oleh sifatnya yang terbiodegredasi, mesra alam dan boleh diperbaharui. Tujuan kajian ini dijalankan adalah untuk menghasilkan bio-pelincir menggunakan minyak kanola yang diaruh dengan zink diakyldithiophospate (ZDDP) dengan penambahan bahan penambah sekunder iaitu molibdenum diaklyl dithiophosphate (MoDTP). Kepekatan MoDTP yang telah ditambah kedalam minyak kanola teraruh ZDDP adalah sebanyak 0wt%, 0.05wt%, 0.10wt%, 0.15wt%, 0.2wt%. Bio-pelincir yang baru diformulasi ini telah diuji menggunakan kaedah '*American Society for Testingand Materials(ASTM)*'. Minyak ini diuji menggunakan ASTM D6595 dan Meter Kelikatan Terpanasuntuk menentukan kandungan logam and kelikatan kinematik. Bio-pelincir yang baru diformulasi ini juga telah dicirikanmenggunakan Penguji Empat Bola dan Mikroskop Cahaya Sejajaruntuk menentukan pekali geseran dan diameter parut kehausan. Keputusan menemui bahawa 2wt% ZDDP dengan 0.5wt% MoDTP menunjukkan nilai kelikatan kinematik yang paling rendah iaitu 38.0 cSt di mana ia merupakan nilai yang terendah di antara semua sampel. Pekali geseran minyak canola dengan 2wt% ZDDP dan 0.05wt% MoDTP juga menunjukkan nilai yang rendah iaitu sebanyak 0.064. Diameter parut kehausan yang terendah diperolehi pada 79.56 μm juga adalah daripada pencampuran 2wt% ZDDP dan 0.05wt% MoDTP. Ditemui di dalam eksperimen ini dimana komposisi minyak canola dengan 2wt% ZDDP dan 0.05wt% MoDTP memberikan hasil yang paling wajar. Kesimpulannya, bio-pelincir yang baru diformulasi ini telah berjaya dihasilkan dengan pengenalan MoDTP ke dalam minyak canolateraruh ZDDP di mana ia selanjutnya meningkatkan ciri anti-hausanya.

DEDICATION

To my beloved parent, Musli bin Musa and Sareah Binti Jaafar for nursing me with affection and love and their dedicated partnership for succes in my life

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
COF	-	Coefficient of Friction
cSt	-	Centistokes
C_2F_4	-	Tetrafluoroethylene
C_2H_4	-	Ethylene
$C1_5H_{31}COOH$	-	Palmitic Acid
EP	-	Extreme Pressure
g	-	Gram
g/cm^3	-	Relative Density (gram per cubic centimeter)
H	-	Hydrogen
H*	-	Hydrogen ion
Hrs	-	Hours
J/g	-	Specific Heat (Joule per gram)
K	-	Kelvin
Mo	-	Molybdenum
MoDTP	-	Molybdenum Dialkyl Dithiophosphate
MoDTC	-	Molybdenum dithiocarbamate
MoS_2	-	Molybdenum disulfide
mm	-	Millimeter
mm^2/sec	-	Kinematic Viscosity (millimeter square per second)
ml	-	Milliliter
NaOH	-	Sodium hydroxide
No.	-	Number
nm	-	Nanometer
OH	-	Hydroxide
PAOs	-	Polyalphaolefins
PAG	-	Poly Alkylene Glycol
PIB	-	Polyisobutylene

ppm	-	Particles per million
PTFE	-	Polytetrafluoroethylene
R	-	Radical
R*	-	Radical Ion
RDE-AES	-	Rotating Disc Electrode Atomic Emission Spectroscopy
ROO*	-	Peroxide Radical
ROOH	-	Organic Acid
SEM	-	Scanning Electron Microscopy
W	-	Tungsten
W/m.K	-	Thermal Conductivity (Weight per meter Kelvin)
WS_2	-	Tungsten Disulfide
WSD	-	Wear Scar Diameter
wt%	-	Weight Percent
ZnDTP	-	Zinc dithiophosphate
ZDDP	-	Zinc Dialkyldithiophosphate
%	-	Percent
°C	-	Decree Celcius
µ	-	Micron
µm	-	Micro Meter

CHAPTER 1

INTRODUCTION

1.1 History of Lubricant

The significance lubrication development has been exceptionally perceived by our civilization. It has progressed significantly in recent times, however the backgrounds of lubricant stretch out back more distant than we imagine. The lubricant oil is already used by human since ancient times, dates backat least as far as 1400 BC. During this time, grease made of a combination of calcium and fat from animal were used to lubricate chariot axels. After the discovery of petroleum, greases with the blending of potassium, calcium, and sodium soaps were placed on the market in limited quantities (Pirro and Wessol, 2001).

During 1650 BC., natural oil was used as a lubricant from the time of 50 AD until The Industrial Revolution of the late 18th century. This naturallubricant gathered from natural resources such as olive, rapeseed, castor beans, palm oil, and the fats from sperm whale, animal lard, and wool. (Gawrilow, 2004).

In 1769, steam engine automobiles capable of human transport were created. Hence the needs for better lubrication for the various internal moving part of the steam engine become more vital to make sure smoother operation, reducing the risks of undesirable frequent failures and maintaining reliable of the steam engine (Suhane et al., 2012). Lubricant from natural resources was widely used as lubricant due to their availability of other competitive options until 19th century. During the rapid industrialisation in the second half of 19^{th} century, the interests of lubricant turn out to be high putting the weight on the cost and accessibility of lubricant from natural resource.

After the first oil well is successfully drilled in the mid 1950's, the well commercialized oil strike marks the dawn of the petroleum age. With the effective prospecting and extraction of mineral oils, petroleum industry has risen which made accessible vast amounts of substitution of natural oil lubricant with desirable properties (Suhane et al., 2012). In this time, petroleum based lubricants was rapidly ruled the field, thus makes the price for petroleum base lubricant are cheaper than natural oil lubricant as they has better and stable materials properties.

In the 1950s, synthetic lubricant has been develop with with lower volatility, better high- temperature performance, and greater rire résistance after the the development of larger machines used at greater speeds and with tighter specifications (Anderson, 1991).Synthetic lubricants are developed with primarily for use in the aviation and aerospace industries. Multigraade automotive engine oils are introduced.

1.2 Introduction to Lubricants

In a wide range of machines in this world, the surfaces of moving parts that is rubbing against each other produce a resistance are known as friction. These resistances are happened because of the moving contact of one section against another to their movement. It causes a great deal of wear and tear of the surfaces of the moving parts, thus making it number one enemy to machines (Bannister K, 1996). Lubrication is simply an introduction of a substance between these mutual contact surfaces of moving parts to reduce friction and heat. (Holweger, 2013). These substance provide protective film between the two contact surface to separate them and reducing the friction (Suhane et al., 2012). The material which is used in this way is known as a lubricant.

Lubricants have an important role in world of industrial and economic development, mainly by reducing friction and wear in mechanical contacts.In addition to decreasing or controlling friction, lubricants are typically expected that would reduce wear and frequently to avert overheating and erosion(Azhari et al., 2015).The main purpose of lubricating oils is to reduce friction. Friction can reduce the speed of actions and also cause damage. Lubricating oil provides a fluid film between two metal wear surfaces to prevent them from touching. The fluid film formed allowing the friction to occur between the molecular planes of the lubricant instead of the two surfaces (Bannister K, 1996). For example, lubrication added to gears will increase the speed in which the gears operate and reduce wear and tear on the gears.

Typically lubricants are used to separate moving parts in a system. This has the benefit of reducing friction and surface fatigue, together with reduced heat generation, operating noise and vibrations. Lubricants achieve this in several ways. The most common is by forming a thin layer of lubricant separates the moving parts. This is similar to hydroplaning, the loss of friction observed when a car tire is separated from the road surface by moving through standing water. This is termed hydrodynamic lubrication. In cases of high surface pressures or temperatures, the fluid film is much thinner and some of the forces are transmitted between the surfaces through the lubricant (Hamrock and Schmid, 2004).

Lubricating oils can be used as cooling agents. As lubricant moderately moves far from the close metal contact, the heat produced because of locally pressurizing that point stays with the lubricants. Lubricant in ordinary working conditions it gives enough heat exchange to avoid heat runaway. Much of the time, the lubricant must be cooled with an exchanger before being utilized to lubricate again (Bannister K, 1996).

Lubrication keeps the dirt contaminants out. Dirt is evident in all aspect of surface contact. The contaminants may be wear debris, sludge, soot particles, acids, or peroxides. The lubricant job is that to flush these contaminants out of the bearing surface so that they may be wiped away, as in the case of grease, or caught in a filtration medium. The lubrication will also act as a seal against outside dirt ingestion(Nehal and Amal, 2011). Good quality lubricants are typically formulated with additives that form chemical bonds with surfaces, or exclude moisture, to prevent corrosion and rust. It reduces corrosion between two metallic surface and avoids contact between these surfaces to avoid immersed corrosion.(David, 1991).

1.3 Problem Statement

The uses of mineral oil based lubricant in industries nowadays are seen to be one of the contributors to pollution and environmental health. These mineral oil based lubricant is frequently discarded into the environment, causing untold harm to the both aquatic and terrestrial ecosystems (Ssempebwa and Carpenter, 2009). According to Mahipal, et al, (2014) subsequent disposal by activities such as hydraulic, mining, agriculture and petrochemical industries is causing environmental hazard. In addition, one of the major disadvantages of mineral oil based lubricant is its poor biodegradability and thus it's potential for long-term pollution of the environment.

Rapid biodegradation of vegetable oils and originate from a renewable source makes vegetable oils good alternative of finding economic and environmentally safe to substitute mineral oils based lubricant. Vegetable oils can be used as lubricants in their natural forms but they have their several advantages and disadvantages when considered for industrial and machinery lubrication (Honary, 2004). Vegetable oils can have excellent lubricity because the content of erucic acid in it thus makes excellent lubrication oil. Vegetable oils have an advantages deriving from the base stock chemistry such as high viscosity index, high lubricity, high flash point, low evaporative loss, high bio-degradability and low toxicity with regard to their use as base oils for lubricants (Anand, et al., 2014). Nevertheless, it has several disadvantages as a lubricant.

The properties of vegetable oils are determined by their fatty acid composition. Vegetable oils in their natural forms are poor oxidative stability for lubricant use because of its high saturate or polyunsaturated fatty acid content (Liu et al., 2015). It will become thick to plastic like consistency during use if untreated, resulting from its low oxidative stability. Besides that, vegetable oil also known to have poor thermal and poor low temperature characteristic which prevent vegetable oil to be good lubrication oil.

Previous research has found that ZDDP (Zinc Dialkyldithiophosphate) is to be used as anti-oxidation and anti-wear additive in vegetable oil lubricants. It has been proving to be effective antiwear and antioxidant additive to be added into vegetable oils (Azhari, et al.2015). ZDDP added into vegetable oil not only decreases the degradation process, but also act as physical property improver which lowers the kinematic viscosity and reduces coefficient of friction (Azhari, et al.2015). A study conducted by Mahipal et al.(2014) on tribological analysis of lubrication properties of (ZDDP) additive on Karanja oil as green lubricant has showed that karanja oil with 2.0 wt% ZDDP have better coefficient friction, wear scar diameter than the commercial SAE 20W40 oil tested for comparison but the pour point and cloud point were found to be higher than that of the mineral oil. On the other hand, a promising study done by Azhari et al, (2015), has successfully developed and formulates a zinc induced canola which has better performance and improved physical properties with the same addition of 2.0 wt% ZDDP.

With the previous achievements by researcher of developing zinc induced bio-lubricant, researcher are now in search of further enhancing the troboligical properties of this bio-lubricant oil. Molybdenum Dialkyl Dithiophosphate (MoDTP)is good choices of additive to add in zinc induced bio-lubricant as MoDTP are well-known friction modifier and antiwear additives respectively (Kosarieh et, al. 2013).

A study by Yan, et al. (2013), stated that MoDTP has a capability to form tribofilms containing primarily MoS_2 and other molybdenum oxides which can effectively reduce wear and friction thus can promote the fuel economy in engine oils. Also, MoS_2mainlydoes not depend on the presence of absorbed vapours thus make MoS2 an inherent property in low friction and it adheres even more strongly than graphite to metal and other surfaces thus a useful formation of MoS_2 film is focused on the MODTP concentration and rubbing process(Azhari et al, 2015)

According to Xia, et al. (2008), by blending MoDTP additive, into a zinc induce lubricant, the tribofilm cannot be easily sheared because of interface provided by MoDTP and protecting the ZDDP derived phosphate film from high shear stress, thus improves the effectiveness of friction and wears reduction. Therefore in this study, Molybdenum Dialkyl Dithiophosphate (MoDTP)is chosen as friction modifier to be blended with zinc induced canola oil to further enhance it antiwear properties.

1.4 Objectives

Based on the problem statement stated above, the objectives of this study are stated below:

1. To prepare a new bio-lubricant oil with the addition of friction modifier agent.
2. To test and characterize the newly developed bio-lubricantstandard laboratory test methods.

1.5 Scope

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

1. Preparing the new lubricant oil using zinc induced commercialized cooking canola oil with the addition of (MoDTP) as friction modifier.
2. Testing of the newly developed oil using standard laboratory test methods.
3. Characterizing of the newly developed oil by conducting four-ball test.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Lubricant

Lubricant is a substance that provides the boundary of two materials to move well against each other which reduces friction and wears. The lubricant at interface reduces the adhesive friction by lower the shear strength of interface. Tubrication is when the process of reducing friction between moving surfaces, by the introduction of lubricants in between them. Various elements must be considered when selecting lubricant for particular application. Based on the physical states of lubricant or molecular structure, lubricants are classified in three categories. They are solid lubricants, semisolid lubricants or grease and liquid lubricants(Suhane 2012). Each of this lubricant has its own characteristic and different usage in industry.

2.1.1 Solid Lubricant

Lubrication can also be achieved through solid lubricants (Erdemir, 2001).Solid lubrication is simply the lubrication of two surfaces in moving contact by means of solid materials intervened between them. The solids deliver efficient boundary lubrication, improving friction and minimizing wear under extreme operating environments. Depending upon the nature of the two surfaces, a wide variety of solid materials can reduce the friction and prevent wear. For example, dust, sand, or gravel on the surface of a road can cause vehicles to skid because they decrease friction between tires and the road surface(Lansdown, 1982).