UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BLENDING OF ZDDP AND MoDTP INTO CORN OIL AS TRIBOLOGICAL PROPERTIES IMPROVERS

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

by

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ABSTRAK

Mesin-mesin yang terdapat di industri pada masakini menggunakan bahan pelincir yang terhasil dari perlombongan petroleum. Namun begitu petroleum tidak mampu bertahan kerana, bahan ini diketahui sebagai bahan tidak boleh diperbaharui dan tidak boleh terurai secara semula jadi. Kajian ini adalah bertujuan untuk mencampurkan minyak masak komersial diperbuat dari minyak jagung bersama dua bahan tambah yang dikenali sebagai ZDDP dan MoDTP yang bertindak sebagai penambahbaik terhadap ciri tribologi. Enam sampel akan disediakan bersama campuran bahan tambah ZDDP pada kepekatan yang tetap iaitu 1.5wt% dan kepekatan yang berbeza menggunakan MoDTP, dimana sampel-sampel ini akan direndam di dalam takungan air dengan suhu terkawal. Semua sampel akan diuji menggunakan kaedah ASTM D6595 RDE-AES bagi mengenalpasti kelarutan bahan tambah dalam minyak asas. Selepas itu, semua sampel akan diuji dengan menggunakan kaedah ASTM D4172 terhadap pekali geseran dan diameter parut kehausan. Keputusan menunjukkan, sampel mengandungi campuran 1.5wt% ZDDP dan 0.1wt% MoDTP terbukti sebagai campuran yang diingini sejurus sahaja memperlihatkan pekali geseran dan diameter parut kehausan yang lebih rendah. Kesimpulannya, nilai campuran bahan tambah yang diingini kedalam bio-pelincir jelas menunjukkan prestasi pelinciran yang hampir baik berbanding campuran bahan tambah yang optimum seterusnya mencadangkan untuk mesra alam sekitar membawa ke arah masa hadapan yang lestari.

ABSTRACT

Machineries in the industry nowadays are lubricated with a lubricant which derived from petroleum mining product. However it would not sustain as it is known to be non-renewable source with highly non-biodegradable in nature. This study is aim to blend a commercial cooking oil made up from corn oils with addition of two types of additives known as ZDDP and MoDTP as a tribological improvers. There are 6 samples will be prepared with fixed concentration of Zinc dialkyldithiophosphate at 1.5wt% and varies concentration of Molybdenum dialkyldithiophosphate (MoDTP) by immersing those sample in water bath. These samples will then test to ensure dilution of additives with the base oil using Rotating Disc Electrode according to ASTM D6595. Next all samples will be characterize based on friction and wear scar diameter by a method in accordance to ASTM D4172. Results shown, sample blend contains 1.5wt% ZDDP and 0.1wt% MoDTP exhibited desirable performances with lower coefficient of friction and lower wear scar diameter. Thus it is worth to note that, the desirable concentration of additives into the bio lubricant expressed marginal lubricity performances compared to optimum concentration of additives with suggestion to be environmentally friendly leading to sustainable future.

DEDICATION

To my beloved parents En. Rosly Bin Hj. Mat Nor and Pn. Aspalela Binti Puasa, and my siblings and fellow colleagues.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

μ	-	Coefficient of friction
ADDC	-	Antimony dialkyldithiocarbamate
Ag	-	Silver
ASTM	-	American society for Testing and Materials
Au	-	Aurum (Gold)
B_2O_3	-	Boron trioxide
CaF_2	-	Calcium fluoride
CAS	-	Chemical Abstract Series
CO_2	-	Carbon dioxide
cSt	-	Centistoke
CuO	-	Copper (II) oxide
DLC	-	Diamond like Carbon
DPDA	-	Dialkylphosphorodithioc acids
EHL	-	Elasto-hydrodynamic Lubrication
EPA	-	Environmental Protection Agency
EU	-	European Union
g	-	Grams
HBN	-	Hexagonal Boron Nitride
IENICA	-	Interactive Network for Industrial Crops and Applications
KOH	-	Potassium Hydroxide
M	-	Mega (10^6)
mgKOH	-	milligram Potassium Hydroxide
MoDTC	-	Molybdenum dialkyldithiocarbamate
MoDTP	-	Molybdenum dialkyldithiophosphate
MoO_3	-	Molybdenum trioxide
MoS_2	-	Molybdenum disulphide (Molybdenite)
OECD	-	Organisation for Economic Co-operation and Development
Pb	-	Lead

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

PTPE	-	Perfluoropolyether
P_2S_5	-	Phosphorus pentasulphide
r	-	Radius
RBD	-	Refined Bleached Deodorised
RDE AES	-	Rotating Disc Electrode Atomic Emission Spectrometry
SAE	-	Society of Automotive Engineers
Sn	-	Tin
T	-	Torque
TBP	-	tri-butyl phosphate
TCP	-	tri-cresyl phosphate
VI	-	Viscosity index
W	-	Load
WS_2	-	Diamond disulphide
Wt%	-	Weight percent
ZDDC	-	Zinc diamyldithiocarbamate
ZDDP	-	Zinc dialkyldithiophosphate
α	-	Pressure-viscosity coefficient
γ	-	Stress-pressure coefficient
HBN	-	Hexagonal Boron Nitride

CHAPTER 1

INTRODUCTION

1. Introduction to lubricant

Lubricant can be defined as thin layer of film introduced between surfaces to prevent them from contacting. In late 1699, Guillaume Amontons had published three law of friction and those laws originally developed to explain dry friction. Based on Webster's Dictionary, lubricant can be any substance such as grease, oil, soap that when introduced between solid surfaces which move over one another, reduce resistance to movement, heat production and wear by forming a fluid film between the surfaces. Anderson, (1991), stated that, lubricant is any substance that placed between surfaces to minimize friction and wear. Lubricant can also function as coolants, cleansing agent, electrical insulator and rust prevention agent. Another sources by Kenneth, (1996), mentioned that, lubricant can perform several functions which are reducing friction, reducing wear, absorbing shock, reducing temperature, minimizing corrosion, and seal out contaminants.

In 19^{th} century, petroleum base oil is used since the Egyptian and American Indian used it as for lighting and medical purposed and the earliest crude oil being used was found in Pittsburgh, Pennsylvania in 1845 from cotton seed spinning mill (Anderson, 1991).

Friction affects the performance of mechanical systems due to wear (Holmberg et al., 2012). According to Kunc et al., (1952), friction and abrasion between rubbing surfaces are the main factors that affect the wear in engine. Wear can be grouped into adhesive and abrasive wear. An example of adhesive wear is galling. Inadequate lubrication can cause galling. A remedy to those complications is to use suitable lubricant for suitable application. A good lubricant must have an excellent physical and chemical property. A lubricant should pose good viscosity-temperature behaviour and cryogenic flow behaviour, high thermical, chemical stability, high boiling point and solidifying point. Lubricant layer can be in form of solid, liquid, or gas. Wear dependent upon thickness of the oil or viscosity. Generally, the thickness of this film is in between 1-100 micron. It is found that, thick oil film will separated the surfaces of the rubbing components (Gangopadhyay et al., 2007). In order for achieving those properties, suitable additives are added into base stock.

Base stock is an important compound in lubricant production. Typically it can be divided into either petroleum or bio based. A mineral or petroleum based oil used nowadays caught people attention toward environment effect. Spilling of these lubricants is harmful to the ecological system such as aquatic marine species and wildlife (Rani et al., 2015). Due to that effect, bio based oil has gain interest worldwide because of it environmental benefits including renewability, biodegradability, non-toxicity and environmental friendly (Shahabuddin et al., 2013).

1.2 Potential of vegetable base oil

Lubricant made from vegetables and plants had been studied recently to replace current mineral base stock which caused environment pollution. Padavich and Honary, (1995), stated that mineral based being used as hydraulic fluids were consumed approximately 5 million metric tons per year. Due to that, hydraulic fluids have the highest need to be produce from biodegradable source. On the other hand, Susan (2005), has reported that, vegetable oils used as cutting fluid provides consistent alignment of oil’s lubricity to the specimen being machined. This lubricity affects the tool wear performance whereby reduction in flank wear and surface roughness was observed when vegetable oil used as cutting fluid (Xavior et al., 2009).

Bio based lubricant can be derived from either edible or non-edible plants. Many researches have proved the suitability of edible vegetable oil as lubricant such as sunflower oils, olive oils, rapeseed oils, and others. A study by Mendoza et al., (2011), mentioned that, sunflower oil has a potential to be used as hydraulic fluids for an agricultural tractor. This is due to high oleic acid content in sunflower oils with capability to be biodegradable without toxic. This argument was also supported by Randles and Wright, (1992), which stated that, vegetable oils with high oleic acid content make this new source suitable to replace the conventional mineral oil with an addition to be non-toxic and biodegradable. Apart from that, high amount of oleic acid contents can also be found inside olive oil as studied by Kalam et al., (2017). The results show olive oils give lower coefficient of friction, lower wear scar diameter, and lower worn scar surface area. Wu et al., (2000), on the other hand found that, better friction reducing and extreme pressure abilities are achievable when epoxidized rapeseed oil was use as bio based lubricant.

There were also studied perform on non-edible vegetable oils to be use as bio based lubricant. The non-edible vegetable oils which are currently being studied include Jojoba oils, Karanja oils, rubber seed oils, Linseed oils and many more. Aravind et al., (2015) has reviewed the characteristic of rubber seed oil that makes this source suitable as lubricant based stock. This non-edible source is renewable, because every year a healthy rubber tree gives 500g of seeds containing 50 to 60 wt% of oil on average as being studied by Kumar et al., (2011). Allawzi et al., (1998) on the other hand reported that Jojoba oils showed constant chemical structure, kinematic viscosity, and refractive index during experiment provided the temperature ranging from 40 to 200 degree centigrade. Apart from that, lower coefficient of friction and wear scar diameter values were obtained from blending of Karanja oil with an additive 2Wt % of ZDDP as compared to mineral oil SAE20W-40 as studied by Mahipal et al., (2014). Apart from usage as a lubricant based stock, vegetable oils also has a potential to be an additive which help improving tribological properties of a lubricant. Good anti-wear and lubricity was found when Castor oil methyl ester proved to be used as an additive in diesel fuel as being studied by Madankar et al., (2013). Another study carried by Ertugirul Durak, (2004), had shown the suitability of rapeseed oil as an additive with base oil.

1.3 Problem statement

Lubricant derived from petroleum is undergoing depletion day by day. As reported to Club of Rome with and additional of two oil crisis in 1979 and 1983, that mineral oil is on principle a limited resource. Another concern was on the method to disposal of used oils due to industrial development. Millions of tons of lubricant end up in the environment when viewed worldwide every year as result from leak, emission and spillage (Haus et al., 2001).

Environmental pollution, dermatitis to operators, soil contamination during disposal and water pollution are the adverse effects due to use of conventional cutting fluids. Besides, the mining process to obtain this mineral base has led to environmental issues. Brundtland et al., (1987), stated that, environmental problem is obviously associated with the production and use of chemical in mining process with a limited capacity to tolerate with pollution. The contamination of ecosystem by petroleum based consists of hydrocarbon and additives have viewed great environmental problems as reported by many researches.

Due to environment trait, a search for an alternative resource due declining amount of mineral oil base left in the earth has caught attention amongst researchers. Base stock derived from vegetable oils has undergoing rapid development as base stock for fluid used in industrial application (Bartz, 1998). This bio base ester derived from plants and vegetables also gives excellent performance with lower cost compared to synthetic ester as reported by Kodali, (2002).

In nature, typical vegetable oils by its chemical structure are long fatty acid tri-ester of glycerol is proved to provide most of lubrication properties such as good boundary lubrication, high viscosity index, high flash point and low volatility (Adhvaryu et al. 2004). Vegetable based oils stick to a metal surface more tightly compared to petroleum based oils due to vegetable oils molecules have polar charge which different from the metal surface. Hutching et al., (1992), reported that, vegetable oils contain molecules with boundary lubricating (BL) properties. A good boundary lubricating properties of vegetable oils is due to presence of polar functional group as mentioned by Waara et al., (2001). This observation was also reported by Farooq et al., (2011), which revealed that presence of hydroxyl group in the Castor oil structure make this vegetable oil polar. As the polarity of molecules increases, the higher affinity for the molecules to bind to steel surfaces (Suarez et al., 2010). A studied by Ding et al., (2010), reported that, leakage and volatilization of grinding fluid using mineral base cause pollution. Vegetable oils pose higher boiling point, which could atomized and turned into gas provide lesser pollution made by mineral base.

Apart from advantages offer by vegetable base oils, it has main disadvantage when applied in both low and high thermal operation. Due to these deficiencies, chemical compound is added to improve vegetable oils lubrication properties known as additive. Various additives are blended into based oil to enhance the lubrication properties of a lubricant. These additives function when the asperities of moving surfaces are in contact. It is known as boundary lubrication regime. There are several mechanisms by which the boundary lubricating films can function such as sacrificial layer, low shear interfacial lubricating layer, friction modifying layer, shear resistant layer, and load-bearing solids (Hsu et al., 2005).

Additives for lubricating oils were used since 1940 as being outlined by many researches (Rowe et al., 1967, Rounds et al., 1975, Harrison et al., 1991, Wu et al., 1997, Willermet et al., 1995). Commonly use additives for vegetable oil are anti-wear, anti-friction and friction modifiers. Anti-wear additive is used to react with surfaces in contact to form protective layer, which ensures that irregular asperity contacts do not lead to severe wear (Hsu et al., 2005). This is done by an additive commercially known as Zinc dialkyl dithiophosphate (ZDDP).

According to Ito et al., (2006), study on bearing steel cylinders skated against the plate in PAO with and without addition of Zinc dialkyl dithiophosphate (ZDDP) and the results showed the friction was 0.06 to 0.08 when ZDDP is presence. This was similarly observed by Liu et al., (2002), when the liquid paraffin added with ZDDP produced lower coefficient of friction compared to boron-permeated AISI-1045 steel disc slid against AISI-52100 steel ball lubricated with only liquid paraffin. In contrast, a study carried out by Wan et al., (1997), show larger wear produced when steel was slide opposed aluminium alloy lubricated with paraffin ZDDP added.

Friction modifiers are additives that reduce friction. It can be divided into two type namely organic and molybdenum compound. Molybdenum containing compound proved to be effective friction modifier. Ratoi et al., (2007), reported that, friction modifiers reducing film were formed on zinc phosphate. Difference between anti-wear additives and friction modifiers is mechanical properties. The friction modifiers are closely packed array of multi-molecular layer, loosely adhering to each other which allow the outer film to shear off easily (Kenbeek et al., 2003).

Blending various additives sometimes lead to worsening rather than improvement. A study by Unnikrishnan et al., (2002), mentioned that the frictional properties of MoDTP do not change by the addition of ZDDP. The usual level of the anti-wear additives in lubricants lies between 1 to 2 wt% (Stachowiak et al., 2005). However, the most desirable blending concentration has not been established. Therefore, this study is concern on finding the most desirable concentration of ZDDP and MoDTP in lubricant oil for improvement in tribological properties and environment concern.

1.4 Objectives

From the above discussions, the objectives of this study are stated below:

1. To blend concentration of anti-wear and friction modifier in bio lubricant.
2. To test and characterize new developed bio lubricant.

1.5 Scope of research

To obtain desired objectives, the scope is limited to:

1. Blending the concentration of ZDDP and MoDTP to be added in corn oil.
2. Testing of the optimized bio lubricant using ASTM D6595 for the dilution of ZDDP and MoDTP.
3. Characterization of the optimized bio lubricant using ASTM4172 on tribological properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of lubricant

Lubricant can be classified according to three physical states which include solid lubricant, liquid lubricant, and semi-solid lubricant. Each types of lubricant have its own physical properties and chemical properties. These properties determine the suitability for each types of lubricant to be applied at different contact surface and conditions.

2.1.1 Solid lubricant

According to Erdemir, (1995), friction and wear can be controlled by the presence of solid lubricant in a severe service condition. Such severe conditions can be in vacuum, extreme pressure, radiation, and more. Based on preliminary studies by other researchers, it was found that solid lubricant has the ability to disperse in water, oils, and greases. This ability in turn, improves the friction and wear resistant. Besides, solid lubricant is preferable in high temperature application due to lower evaporation capability. This low evaporation rate will cause the lubricant to adhere on the contacting surfaces thus support the applied load over temperature range which further reduce the friction between contacting surfaces as studied by Iliuc, (1980). A solid lubricant can be also classified into several classes. Table 2.1 displays classes of solid lubricant and typical range of friction coefficient.

Lamellar structure is a layer lattice whereby atoms in individual layers are held with strong covalent or ionic force. In this individual layer, atoms are arranged in hexagon configuration. A relatively weak ionic or van der Waals force is held between each individual layers formed a stack of hexagonal sheet. This relatively weak ionic force between individual layers proofed to cause reduction in coefficient of friction as studied by Rudnick, (2008). Examples of lamellar structure solid lubricants commonly encountered includes transition metal dichalcogenide (example molybdenum disulphide), and graphite. Transition metal dichalcogenide such as molybdenum disulphide was known to exhibit lowest friction both in dry and vacuum environment (Winer, 1967; Donnet et al., 1996). Amongst transition metal dichalcogenide, molybdenum disulphide (MoS_2) is mostly used due to it availability as natural mineral in form of molybdenite. MoS_2 has another advantage compared to graphite which it does not require any form of moisture in order to provide lubrication. Apart from independence of moisture, MoS_2 can withstand temperature up to approximately 500℃. Apart from that, the hardness of stainless steel was found to increase due MoS_2 added into the stainless steel-MoS_2 composition (Mahathanabodee et al., 2013). The increment in hardness was further explored by Napara et al., (1997), which stated that, molybdenum (Mo) element was diffused into stainless steel matrix due to decompose of MoS_2.

2.1.2 Semi solid lubricant

This group of lubricant is also known as cohesive lubricant. Cohesion can be defined as attraction between each particle to stick together. This property causes grease to resist from flowing. Semi solid lubricant found to be in three types which are grease, paste, and waxes. Waxes typically consist of high molecular weight of hydrocarbon. It is suitable to be use at boundary lubrication regime during low speed condition. Grease on the other hand is made using base oil and addition of thickener. The application of grease can be found during elasto-hydrodynamic and boundary lubrication regime. Apart from grease and wax, semi solid lubricant can be in form of paste. Paste is made from high percent of solid lubricant.

Amongst solid lubricant listed, the widely used in industries and study, is grease. Previously mentioned, grease is made by high percentage of base oil and least percentage of thickener. Lugt, (2016), mentioned that greases are classified based on it thickening agent such as lithium, calcium, and barium. These agents physically reacted with base oil to provide consistency. Consistency is a characteristic which under the application of force measures the magnitude for grease to resist plastic deformation.

Another characteristic related to grease is apparent viscosity. Grease is a material that will not flow if the shear stress yield point is not exceed. This makes grease to be group as a non-Newtonian material (Pirro et al., 2001). The importance of apparent viscosity is to predict the tendency of leakage.

Leakage in turns causing the bearing to destroy prematurely as well as contaminate the environment as previously studied done by Society of Japanese tribologist, (2007). This problem relates to another characteristic which is the compatibility. Grease can be in combination with another type of grease to enhance the performance and physical properties of individual grease. Performance of equipment lubricates by grease, degrade because of wrong grease mixture. Hiraoka, (2012), highlighted that, lack of compatibility between Perfluoropolyether (PFPE) and mineral oil grease contributes to leakage.

2.1.3 Liquid lubricant

The most commonly used lubricant is known as lubricating oils or liquid lubricant, encountered includes petroleum, synthetic, and bio based which from animals and vegetables. According to Delebecq et al., (1983), lubricating oil gives several functions such as increase mechanical strength maintains engine cleanliness, reducing friction and wear, transport or removes particles, and protecting the engine from oxidation as well as corrosion. Besides, lubricating oils are capable of rejecting more heat with appropriate design of lubrication systems.

When two interacting bodies separate, the molecular-interaction and mechanical interaction is reducing. Due to ability of liquid lubricant to shear, elastic-plastic deformed, and micro-welding, its actually contribute to pliability. This pliability causes load to distribute evenly over the contacting area. There are several criteria in selection of type of lubricants. In selecting lubricating oil compared to semi solid and solid lubricant, criteria includes operating environment, viscosity,