UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ADDITION OF ZINC DIAMYLDITHIOCARBAMATE (ZDDC) IN CANOLA OIL AS PHYSICAL PROPERTIES IMPROVER FOR LUBRICANT SUBSTITUTION

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 (Maintenance Techonology) (Hons.). The member of the supervisory is as follow:

Muhamad Azwar Bin Azhari
(Project Supervisor)

ABSTRACT

The purpose of this study is to prepare an alternative substitution to existing lubricants with the addition of Zinc Diamyldithiocarbamate (ZDDC) as anti-friction, friction modifier agent and anti-wear. Being non-renewable ad non-biodegradable, other alternative for mineral oil as lubricant needs to be studied. Vegetable oils are considered suitable due to the superior characteristics of the oil compared to mineral oil. Lacking in oxidation stability, additional additive needs to be blended with the vegetable oil to enhance the oil performance. Canola oil was used as vegetable oil for base oil which was directly introduced with ZDDC and blended in a water bath of 50°C for 20 minutes. The canola oil was added with 0wt%, 1wt%, 2wt%, 3wt% and 4wt% of ZDDC. The newly developed oil was tested using American Society for Testing and Materials (ASTM) methods as well as characterized using four-ball test and upright laser microscope to determine the metal content, kinematic viscosity, coefficient of friction (COF), and wear scar diameters (WSD). It was found that from the tests and characterizations, 2 wt% composition of ZDDC inside canola oil gives the best results. For the kinematic viscosity, 2 wt% gives the lowest kinematic viscosity result of 36.73cSt. The COF obtained from the 2 wt% was 0.08278µ which was the lowest amongst the other results. Furthermore, the WSD obtained was the lowest which was 65.20 µm. From the results, 2 wt% ZDDC is proved to be the desirable concentration of additive to be added into canola oil. To conclude, the objective in preparing newly developed lubricant oil has been achieved which resulted in the formation of the new lubricant with 2 wt% composition of ZDDC additive inside canola base parent oil. The tests results indicated the stated composition is the critical value of ZDDC concentration in producing the best oil lubricant.

ABSTRAK

Tujuan kajian ini adalah untuk menyediakan satu alternatif kepada pelincir sedia ada dengan mencampurkan Zinc Diamyldithiocarbate (ZDDC) sebagai agen anti-geseran dan agen pengubah geseran. Disebabkan tidak boleh diperbaharui dan tidak boleh dibiodegredasi, alternatif lain untuk minyak mineral sebagai pelincir perlu dikaji. Minyak sayuran dianggap sesuai kerana mempunyai sifat karakteristik yang lebih baik berbanding minyak mineral. Kekurangan kestabilan pengoksidaan, bahan penambah perlu dicampur dengan minyak sayuran untuk memperelok keupayaan minyak tersebut. Minyak canola akan digunakan sebagai minyak sayuran untuk minyak asas yang akan dicampur secara terus dengan ZDDC dan akan dikisar di dalam rendaman air pada suhu 50°C selama 20 minit. Minyak canola ini akan dicampur dengan 0bt%, 1bt%, 2bt%, 3bt%, dan 4bt% ZDDC. Minyak baru ini akan diuji menggunakan kaedah "American Society for Testing and Materials (ASTM)" serta dikaraktersifikasi menggunakan ujian "pin-on-disc", "four-ball", dan "upright laser microscope" untuk mengetahui kandungan logam, kelikatan kinematic, pekali geseran dan diameter kehausan parut. Daripada ujian dan karakterifikasi, campuran 2 bt% ZDDC kedalan minyak canola memberikan keputusan yang paling baik. Untuk kelikatan kinematic, 2 bt% memberikan keputusan kelikatan kinematic yang paling rendah iaitu 36.73 cSt. Pekali geseran yang diperolehi daripada 2 bt% ialah yang paling rendah berbanding keputusan yang lain iaitu 0.08278 μ. Tambahan pula, diamteter kehausan parut yang diperolehi ialah yang paling rendah iaitu 65.20 μm. Daripada keputusan ujian, 2 bt% ZDDC telah dibuktikan ialah kepekatan penambah yang wajar dicampurkan kedalam minyak canola. Sebagai kesimpulan, objektif dalam menghasilkan minyak pelincir baharu telah dicapai dengan penghasilan minyak pelincir dengan campuran 2 bt% ZDDC kedalam minyak canola. Keputusan ujian menunjukkan bahawa komposisi yang dinyatakan ialah nilai kritikal kepekatan ZDDC dalam menghasilkan minyak pelincir yang terbaik.

DEDICATIONS

To my beloved parent, Zakaria Bin Dahalan and Bakiah Binti Thani.

To my cherished siblings, Siti Zubaidah Binti Zakaria and Siti Zuriani Binti Zakaria.

To my respected supervisor, Muhamad Azwar Bin Azhari.

To my helpful friends.

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LIST OF SYMBOLS AND ABBREVIATIONS

A*	-	Activated Additive
ADDC	-	Antimony Dialkyldithiocarbamate
AH	-	Additive
ASTM	-	American Society for Testing and Materials
AW	-	Anti-Wear
BHT	-	Butylated Hydroxytoluene
BN	-	Boron Nitride
bt%	-	Peratus Berat
$C_{15}H_{31}COOH$	-	Palmitic Acid
CN	-	Amide Group
COF	-	Coefficient of Friction
cSt	-	Centistokes
EDTA	-	Ethylenediaminetetraacetic Acid
EHD	-	Elastohydrodynamic
FeF_3	-	Iron (III) Fluoride
FeS_2	-	Iron (II) Sulfide
g	-	Gram
g/cm^3	-	Relative Density (gram per cubic centimeter)
GMO	-	Glycerol-mono-oleate
H	-	Hydrogen
H*	-	Hydrogen ion
HDL	-	Full Film Hydrodynamic
Hrs	-	Hours
HSL	-	Full Film Hydrostatic
IF	-	Fullerene-like
IIIG	-	Engine Oxidation Test
mm	-	Millimeter
mm^2/sec	-	Kinematic Viscosity (millimeter square per second)

J/g	-	Specific Heat (Joule per gram)
K	-	Kelvin
ml	-	Milliliter
Mo	-	Molybdenum
MoSx	-	Molybdenum Disulfide
MXx	-	Metal Dichalcogenides
N	-	Newton
NaOH	-	Sodium Hydroxide/Caustic Soda
nD	-	Refractive Index
NLGI	-	National Lubricating Grease Institute
No.	-	Number
nm	-	Nanometer
OH	-	Hydroxide
P	-	Phosphorus
PAO	-	Polyalphaolefin
PPD	-	Pour-Point Depressant
ppm	-	Particles per million
PSO	-	Polimerized Soybean Oil
PTFE	-	Polytetrafluoroethylene
R	-	Radical
R*	-	Radical Ion
R1, R2, R3, R4	-	Alkyl Groups
RDE-AES	-	Rotating Disc Electrode Atomic Emission Spectroscopy
ROO*	-	Peroxide Radical
ROOH	-	Organic Acid
rpm	-	Rotation per Minute
S	-	Sulfur
SAP	-	Sulfur, Ash and Phosphorous
SBO	-	Soybean Oil
Se	-	Selenium
SEM	-	Scanning Electron Microscopy
SiO2	-	Silicon Dioxide
ta-C	-	Tetrahedral Amorphous Carbon

TiF3	-	Titanium (III) Fluoride
VI	-	Viscosity Indices
W	-	Tungsten
W/m.K	-	Thermal Conductivity (Weight per meter Kelvin)
WS_2	-	Tungsten Disulfide
WSD	-	Wear Scar Diameter
wt%	-	Weight Percent
ZDDC	-	Zinc Diamyldithiocarbamate
ZDDP	-	Zinc Dialkyldithiophosphate
°C	-	Decree Celcius
µm	-	Micro-metre
%	-	Percent
µ	-	Micron
µm	-	Micro Meter

CHAPTER 1
INTRODUCTION

1.0 Introduction

Lubricant is an important aspect in many systems and effective lubrication is important to obtain a reliable functioning as well as energy efficient systems (Bhushan and Gupta, 1997). The manner of lubrication is that it separates two moving surfaces be it by a fluid layer (hydrodynamic lubrication) or a low shear and durable lubricant film (boundary lubrication) as in the case of contacts with high load. The film assists in reducing material wear and loss of energy due to friction (Morina et al., 2014). Natural products such as vegetable oils and animal fats were used until 19^{th} century as there are no other competitive options until the extraction of mineral oils in the second half of 19^{th} century as they were available in large quantities and cheaper replacement for lubricants (Suhane et al., 2012). Mineral based oils have been widely used as the main source of lubrication and have been used since the development of steam engines. Crude oil will be predicted to be used, as long as crude oil is available, mineral based oils which originate from the distillation of crude oil (Bekal and Bhat, 2012). Moreover, mineral oil combustion is accountable for the release of metal traces for example zinc, calcium, magnesium, phosphorous, and iron nanoparticles (Miller et al., 2007). Apart from that, disposing the mineral oil tends to be a problem as wrong disposal leads to marine and terrestrial ecosystem pollutions (Ssempebwa and Carpenter, 2009).

Current and future prospects of mineral oil as lubricants have been analyzed (Tung and McMillan, 2004), and unfavorable future prospects have been predicted. Hence, suitable solutions to replace mineral based oil are being made. Usage of low sulfur, ash and phosphorous (low SAP) have been studied (Igartua et al., 2009) and it have been found out that they are biodegradable and harmless to aquatic environments. It has been stated that the use of synthetic esters as bio-lubricants haves similar values in coefficient of friction compared to mineral lubricants (Barriga et al., 2006).

1.1 Functions of Lubricant

The basic functions of a lubricant includes reducing friction, wear, temperature, corrosion, shock, contamination as well as the energy required to do the work (Bannister, 1996). Any lubricant, at any time can be anticipated to perform up to those seven stated functions simultaneously. Basic lubrication film conditions can be specified into four conditions. They are full film hydrodynamic (HDL), full film hydrostatic (HSL), elastohydrodynamic (EHD) and boundary layer. Full film is the perfect or favored condition for sliding friction. In another sense, the moving surfaces are fully apart and separated by a continuous fluid film. Full film lubrication can be categorized into hydrodynamic and hydrostatic lubrication. The difference between hydrostatic and hydrodynamic lubrication is that in hydrostatic lubrication, an external device is required to produce the lift pressure and separating the moving elements whereas hydrodynamic lubrication relies on the natural lifting away of the journal due to the increasing rotational speed and it squeezes the lubricant between itself and the surface. Elastohydrodynamic film depends on some conditions such as surface speeds, loads, lubricant viscosity and pressure-viscosity relationship. It is formed by the applied pressure or load and is mostly found in rolling element bearings. In the other hand, the condition when a bearing is at rest and when the bearing is in motion in the final condition that happens before component failure is called boundary layer. This is usually the result of insufficient lubricant supply or the incorrect choice of lubricant unable to support the external load it is placed upon. Sometimes, boundary layer is referred as thin film lubrication.

1.2 Introduction of Vegetable Oil as Lubricant

Another alternative is available to replace mineral oil, which is the use of vegetable oils. Vegetable oils may be used from the sources such as rapeseed, soybean, sunflower, safflower, cotton seed, peanut, jatropa and palm (Kwon et al., 2015). Some other less commonly known oils are rice bran oil, tiger nut oil, patua oil, keome oil, niger seed oil, and piririma oil (Aluyor and Ori-Jesu, 2008). The vegetable oil has excellent lubricity with as it is biodegradable, less toxic and renewable. This makes the vegetable oil more favorable compared to mineral based oil (Bekal and Bhat, 2012). High viscosity index, low coefficient of friction, high flash point, high volatile and high shear stability properties of vegetable oil make it superior and more suitable to be used as a lubricant over mineral oil (Balamurugan et al., 2010). The usage of vegetable oils are mainly effective as boundary lubricants (Fox and Stachowiak, 2007). The entire base oil by having high polarity permits solid interactions with the lubricated surfaces. The lubricant molecules which is attracted to the surface affects the boundary lubrication performance and also by potential reaction with the surface.

However, vegetable oils lacks in term of thermal stability due to the presence of bis-allylic protons (Erhan et al., 2006). These active sites are extremely liable to radical attack and consequently the molecules undergo oxidative degradation and form polar oxy compounds. This results in the formation of insoluble deposits and rise in oil acidity and viscosity (Liu et al., 2015). The oils were effective as lubricants with zero failures, but the viscosity increases over time and produced deposits on the bore (Fox and Stachowiak, 2007). This study shows an approach to enhance the oxidation behavior of canola oil which has been selected as a choice of vegetable oil combined with zinc diamyldithiocarbamate (ZDDC) as antioxidant.

1.3 Problem Statement

Industries nowadays have started to highlight on environmental pollution awareness (Aluyor and Ori-Jesu, 2008). Due to the increase in crude oil prices, studies on vegetable oil as alternative lubricant were made as the existing mineral base oil comes from a depleting source (Bartz, 1998). On top of that, difficulty in managing mineral oils waste is also among the factors contributing to environmental pollution. Therefore, initiative of this study involves the utilization of vegetable oil as a replacement for mineral oil as an alternative to overcome the surfacing issues (Nizam, 2009). The characteristics of vegetable oil which are biodegradable and originate from a renewable source makes vegetable oil a superior substitute compared to mineral oil. Their anti-wear and fatigue resistance properties of vegetable oil compared to mineral oil have been considered as a source of environmentally acceptable lubricant. Apart from that, vegetable oil has outstanding thin film strength due to its adherence to the surface of metals, besides having high flash and fire point, low volatility, and also high viscosity index.

One of the drawbacks of vegetable oils is their poor oxidation stability (Liu et al., 2015). This is primarily due to the existence of bis-allylic protons. These protons are highly susceptible and vulnerable to radical attack. Subsequently, they undergo oxidative degradation to form polar oxy compounds, which ultimately forms insoluble deposit and results in the increment of oil acidity, viscosity, corrosion, and volatility when used as lubricant based oils. Furthermore, it has been found out that the fatty acid compound in vegetable oils is not the only reason for its oxidative stability (Przybylski and Zambiazi, 2007). It was found that the minor endogenous components also affect the stability of the oils. The amount and types of compounds can play a big role in the oxidation stability of vegetable oil. If this is true, there would be many issues if engine oil or lubrication oil was made with different samples of vegetable oils grown in different locations or during different growing seasons. The lubrication oils or engine oils might have to be retested every time a new batch of vegetable oil is used. This would be very costly and would ensure that no lubricant marketer or additive company would be willing to make the investment required. Moreover, the deficiency of competition and low incentive in developing bio-based products has limited development and market acceptance of these products (Johnson et al., 2002).

The introduction of antioxidant additive, Zinc Diamyldithiocarbamate (ZDDC) into the vegetable oil will overcome this problem since ZDDC is an effective antioxidant. ZDDC will act as radical scavenger and hydroperoxide decomposer. It alters the formed hydroperoxides due to oxidation process to non-radical products; hence, avoiding chain propagation (Erhan et al., 2006). This is a modification to other oil alternatives, which is an innovation from vegetable oil, mainly canola oil for this study. ZDDC will not only act as antioxidant, but it acts as corrosion and wear additives by halting or interrupting oxidation of the oil and also by forming protective film on metal surfaces. Thus, ZDDC is a good additive for oil in heavy duty services because it functions as anti-oxidant, anti-wear and extreme pressure agents (Marinkovic, 2008). Therefore, Zinc Diamyldithiocarbamate (ZDDC) is selected as anti-oxidant and will be used in this study to be blended with commercialized cooking canola oil to overcome the problem and boost the lubricant properties.

1.4 Objectives

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

1. To prepare an alternative lubricant oil with the addition of anti-friction and anti-wear additive.
2. To test and characterize the newly prepared lubricant oil.

1.5 Scopes

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

1. Preparing alternative lubricant oil using commercialized cooking canola oil with the addition of ZDDC as anti-friction and anti-wear additive.
2. Testing of the newly developed oil using standard laboratory test methods.
3. Characterizing of the newly developed oil by conducting four-ball test and upright laser microscope.

CHAPTER 2

LITERATURE REVIEW

2.0 Lubricant

Generally, lubricant can be divided into three states or forms. They are solid, semi-solid/grease and liquid lubricants. Each of this appearance has different industrial functions and usages. Further descriptions on these lubricants are discussed in the next sections.

2.0.1 Solid Lubricant

The small particles have been employed both as solid lubricants and as additives in lubricants for many years with the size in the order of 0.5 µm or more. Some examples are graphite, boron nitride (BN), mica, Molybdenum Disulfide (MoS_2), Tungsten Disulfide (WS_2) and polytetrafluoroethylene (PTFE). Due to being relatively large size and tribological properties remaining poor in the presence of humidity and oxygen, these particles have a tendency to deposit during use. Thus, this limits their practical applications. There have are many studies on the addition of nanoparticles with the typical size in the range of 2–120 nm to lubricants as friction modifiers to efficiently reduce friction and wear (Tang and Li, 2014). To be specific, nanoparticles are based on carbon compound, metal, metal oxide, metal carbonate, metal sulfide, metal borate, rare earth compound and Silicon Dioxide (SiO_2). The level of crystallinity (defect), size, shape and concentration affect the tribological performances as friction modifiers.

The mechanisms of friction modifier and anti-wear of nanoparticles in lubricants can be represented as follows: rolling effect, protective film, mending effect and polishing effect. The rolling effect and protective film mechanisms belong to the direct effect of nanoparticles on lubrication enhancement. For the rolling effect, no chemical or mechanical reaction happens. The spherical nanoparticles will be rolling between the friction surfaces and transform the pure sliding friction to the mixed sliding–rolling friction. The protective film mechanism on the other hand, involves the interaction of the nanoparticles with the friction surfaces and forms a thin protective film on the surfaces. Hence, these reduce the friction and wear (Tang and Li, 2014). Besides that, the mending effect and polishing effect mechanisms belong to surface improvement effect of nanoparticles. For the mending effect, the nanoparticles create a physical tribo-film to compensate for the loss of mass as it may deposit on the friction surfaces and. For the polishing effect, the abrasiveness of the hard nanoparticles reduces the roughness of the rubbing surfaces. The roughness of the worn surfaces depends on the size of nanoparticles.

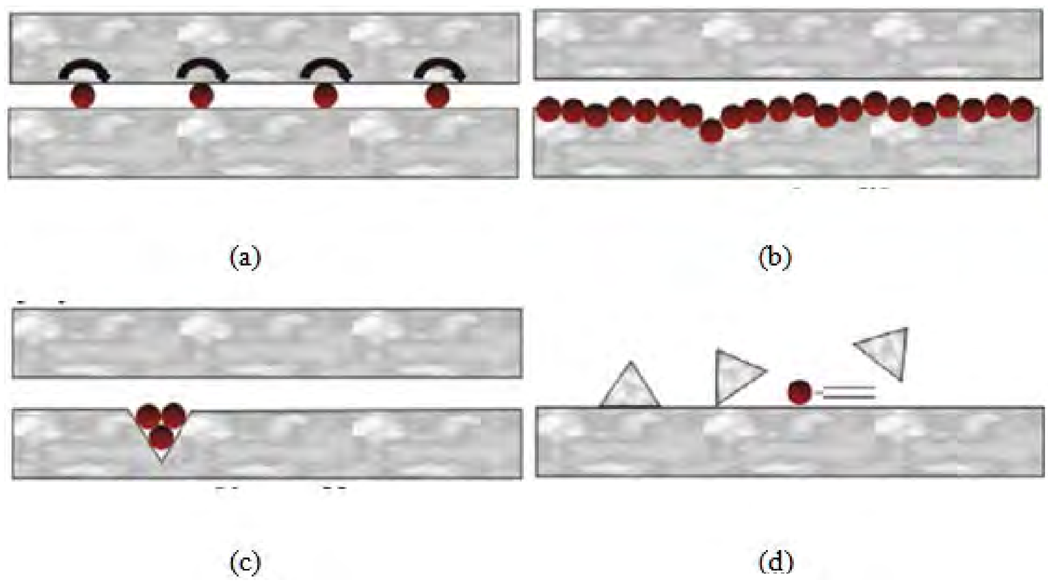

Figure 2.1: Lubrication mechanisms of nanoparticles as friction modifiers: (a) rolling effect, (b) protective film, (c) mending effect, and (d) polishing effect (Tang and Li, 2014).

Fullerene-like (IF) metal dichalcogenides, MX_2 which are inorganic in nature, (M =Molybdenum (Mo) or Tungsten (W) and X = Sulfur (S) or Selenium

(Se)) that have structures similar to carbon fullerenes and. The structures have been widely used for lubrication and showed superior lubricating properties as a friction modifier to those of 2H platelets under various conditions because the composite may act as roller bearing during friction process. The IF-nanoparticles lubrication mechanisms as friction modifiers have been stated as the following three effects:

- Rolling effect: the spherical shape of IF-nanoparticles functions as a ball bearing between the rubbing surfaces under low load conditions;
- Sliding effect: the IF-nanoparticles act as spacer and remove metal/metal contact between the asperities of the two surfaces under slightly higher load conditions;
- Third body: exfoliation of the IF-nanoparticles and the external layers gradually transfer onto the asperities of the friction surfaces giving easy shearing under high load conditions, where the third body can be considered as a combination of oil, nanoparticles and wear particles.

2.0.2 Semi-Solid Lubricant

Semi-solid lubricant is also known as grease. Greases are not just very viscous lubricating oils. They are combinations of lubricating oils and thickeners (Williams, 1994). In order to produce a stable colloidal structure or gel, the thickeners are spread in lubricating oils. So, grease contains oil constrained by minute thickener fibers. It provides semi-permanent lubrication since the oil is constrained and unable to flow. Because of this reason, despite certain limitations in performance, greases are widely used. Low-maintenance, semi-permanent lubricants in rolling contact bearings and some gears is the most extensive application of greases is as. The grease may be left for a period of several months or longer before being replaced after being filled into a bearing or gear set.

The lubricating performance of greases is mediocre to mineral oils except at low sliding speeds where some greases may be better. Greases are to meet the same