UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EFFECT OF ZDDP ADDITION IN CORN OIL AS ANTIOXIDIZING AGENT FOR LUBRICATION APPLICATION

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

………………………………

(Muhamad Azwar bin Azhari)

ABSTRAK

Minyak mineral digunakan secara meluas dalam bidang pelinciran. Masalah timbul apabila mereka mendapati bahawa pelupusan minyak mineral biasanya kompleks dan ia boleh menyumbang kepada pencemaran alam sekitar. Tujuan kajian ini adalah untuk menghasilkan minyak pelincir alternatif dengan penambahan agen antioksida ke dalam minyak sayur-sayuran. Minyak masak jagung dipilih untuk menjadi minyak induk pelincir. Kestabilan pengoksidaan adalah penting untuk dimaksimumkan dalam minyak pelincir. Minyak sayuran mempunyai kestabilan pengoksidaan yang sangat miskin kerana kandungannya asid lemak tak tepu yang terdiri daripada struktur trigliserida. Ikatan dua dalam wujud dalam struktur trigliserida menyumbang kepada kebarangkalian yang lebih tinggi daripada diserang oleh oksigen dengan itu, menjadikan proses lebih tinggi pengoksidaan yang kemudiannya akan menyebabkan prestasi degradasi minyak. Untuk menyelesaikan masalah ini , pengenalan tambahan antioksidan dijalankan dalam kajian ini. Zink Dialkyldithiophosphate (ZDDP) mempunyai keupayaan melaksanakan ejen antiwear yang berkesan dan juga agen antioksidan. Dengan melarutkan ZDDP dalam minyak jagung menggunakan teknik mandi air , minyak pelincir yang baru dibangunkan dihasilkan dan ujian sampel dan pencirian telah dijalankan. Sampel kemudiannya diuji untuk kelikatan kinematik , kiraan zarah dan kandungan logam. Dalam pencirian sampel , pin pada keputusan ujian cakera menunjukkan bahawa pekali geseran menurun kepekatan meningkat dengan kenaikan beban. Keputusan menunjukkan bahawa 5 % berat daripada ZDDP menunjukkan ciri-ciri yang terbaik ke arah penggunaan pelinciran. Kesan penambahan antioksidan dalam minyak memberikan pelbagai keputusan dan ia bergantung kepada kepekatan optimum bahan tambah dan yang paling penting alam sekitar dimana penggunaan minyak tersebut.

ABSTRACT

Mineral based oil is being widely used in the field of lubrication. The problems aroused when they found that the disposal of the mineral oil is generally complex and it may contribute to the pollution to the environment. Due to these consequences, this study focuses more on the use of vegetable oil. The purpose of this study is to produce alternative lubricant oil with the addition of the antioxidizing agent into the vegetable oil. Commercialized cooking corn oil is chosen to be the parent oil of the lubricant. The oxidation stability is important to be maximized in lubricant oil. Vegetable oil has very poor oxidation stability due to its content of unsaturated fatty acids which made up of triglycerides structure. The double bond in exists in the structure of triglyceride contributes to higher probability of being attacked by the oxygen thus, making the higher process of oxidation which will then results in the degradation performance of the oil. To resolve this problem, the introduction of antioxidant additive is conducted in this study. Zinc Dialkyldithiophosphate (ZDDP) has the capability of performing the effective antiwear agent as well as antioxidant agent. By dissolving the ZDDP in corn oil using water bath technique, newly developed lubricant oil is produced and sample testing and characterization were conducted. The samples were then tested for its kinematic viscosity, particle count and metal content. In sample characterization, pin on disc test result showed that the friction of coefficient decreased as the concentration increased with increment of load. The greater the amount of ZDDP, the better the results of coefficient of friction and it shows that 5 wt % of ZDDP showed the best characteristics towards lubrication application. the effect of the addition of antioxidant in oil gave a variety of results in each of the test conducted and it is dependable on the optimum concentration of the additive and most importantly the environment that the oil will be introduced to.

DEDICATION

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

ACKNOWLEDGEMENT

This thesis is based on the research conducted on the applicability of vegetable oil (corn oil) with addition of Zinc Dialkyldithiophosphate (ZDDP) to be used as lubricant oil. I am grateful for number friends and colleagues in encouraging me to start the work, to preserve it and finally to book it. I would like to include a special note of thanks to my friends, Siti Hasnaa and Abdul Shukor for always lend a valuable help throughout the time we have spent together in completing each other thesis. Thank you for helping me doing the laboratory test, thank you for not giving up on getting the laboratory test results and not to forget, thank you for helping me out on completing my thesis. I know it has been a whole lot of works for the whole semester but I am grateful we are finally made it. I would like to dedicate my thanks to my supervisor, Mr Muhamad Azwar bin Azhari to have me as part of your PSM members. I have learnt a lot from my supervisor starting from the very basic of lubrication fundamental, the writing skills, until now that I have produced my own thesis. Thank you for always there to keep supporting me throughout the two semesters. Finally I would like to acknowledge with gratitude, the support and love of my family – my beloved mother; Rasidah bt Mohammad, my sister; Siti Quratulaini bt Mohd Zamri and my brother; Muhammad Quayyum bin Sufian. They all keep me going and without them, this thesis would not have been possible without them.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

API	-	American Petroleum Institute
ASTM	-	American Society for Testing and Materials
CO	-	Corn oil
EVA	-	Ethylene–vinylacetate copolymer
EC	-	Ethylcellulose
FTIR	-	Fourier Transform infrared
HYD	-	Hydraulic oil
IFM	-	Cemicroscopy
JAT	-	Jatropha oil
ME	-	Molybdenum ester
PTFE	-	Polytetrafluorethylene
PS	-	Pentasulfide
PNMR	-	Phosphorus nuclear magnetic resonance
PAO	-	Polyalphaolefin oil
PO	-	Palm olein
PFAD	-	Palm fatty acid distillate
POV	-	Peroxide values
PPM	-	Part per million
RDE/AES	-	Rotating disc electrode atomic emission spectroscopy
SRO	-	Sulfuration modified rapeseed oil
SEM	-	Scanning electron microscope
SFM	-	Scanning force microscopy
SMCO	-	Sulfide-modified corn oil
STP	-	Stamping oil
TAN	-	Total acid number
TBN	-	Total base number
VI	-	Viscosity index
WSD	-	Wear scar diameter

v	-	Kinematic viscosity
n	-	Dynamic viscosity
ρ	-	Density of liquid
St	-	Stokes
cSt	-	Centistokes
mg	-	Milligram
kg	-	Kilogram
µg	-	Microgram
mL	-	Millilitre
µL	-	Microlitre
W_1	-	Mass of water titrated
W_2	-	Mass of sample used
V_1	-	Volume of water titrated
V_2	-	Volume of sample used

CHAPTER 1

INTRODUCTION

1.1 Introduction to Lubricant

Existing of lubrication is undeniable in most of the industrial area. It is the action of keeping two or more surfaces separated by the existence of oil or grease. Lubrication offers the objects in contact to move well against each other, thus, spreading out the friction heat and also flash away the contaminants. If the ability of a substance is to create a film between surfaces in order to prevent contact and reduce friction, it can be considered a lubricant.

Lubricant contains of base oil and several types of additives. The significant function of the base oil is to lubricate as well as a carrier to the additives. The primary properties which the base oil carries can be further enhanced by the addition of additive thus, producing a new formulated lubricant (Ahmed & Nassar, 2011).

1.2 Function of Lubrication

Lubrication carries several benefits in order to make the equipment or machine last longer. The primary purpose of lubrication is to minimize the friction between contacting surfaces by providing the barrier between them alongside reducing the occurrence of wear. In summation to that special function, lubricant is made to preserve the internal cleanliness by flushing out all the undesirable contaminants in the fluid from adhering to components. Keeping the internal part cool is equally important too, because lubricants can absorb heat from contacting surfaces and transfer the heat so that it can be safely dispersed. Furthermore, lubricant acts as a shock absorber because the highly film of the fluid can withstand rupture and disperse the energy spikes over a broader contact area. Henceforth, wear and damaging forces can be brought down and extending the useful lifetime of the component. Protection is one of the important functions carried by the lubricant. It protects the internal component form corrode because the composition of the oil containing lubricant itself.

1.3 Vegetable oil in Motor Lubricant

The base stocks used to formulate lubricants are normally of mineral (oil) or synthetic stock, although vegetable oils may be utilized for specialized applications. Synthetics can be produced from petroleum or vegetable oil feed stocks. Vegetable oils are being explored as a source of environmentally acceptable lubricant because they have exposed their anti wear and fatigue resistance properties rather than mineral oils, as well as improved deterioration load carrying capacity (Emmanuel & Mudiakeoghene, 2008).

Specific application trials have displayed the potential capability of the vegetable oil in a range of areas including engine oils, hydraulic fluids and transmission oils. It has been shown that vegetable oils are beneficial in reducing wear and friction, but are restricted by low stability and poor low temperature properties. Biolubricants have very low or almost negligible toxicity and are, in most cases, readily biodegradable.

Chemical structures of oil are the one biodegradability will depend on. Usually, the high chemical stability will result in reduced degradation rates. Plant oil lubricants also obtain most of the properties required for lubricants such as high viscosity indices because of their high molecular weights, low volatility (they have an approximately 20% lower rate of evaporation than mineral-oilbased fluids) and good lubricity because their ester bonds enable the oil molecules to stick to metal surfaces through physical bonding and offer better boundary lubricity than nonpolar petroleum-based mineral oil (Nadia et. al, 2013).

Oxidation stability of vegetable oil is one of the problems in formulating the vegetable oils. The high content of unsaturated fatty acids in vegetable oils produces the oil less cooperative in stabilizing the oxidation. In order to solve this situation, the modification of the vegetable oil or addition of antioxidant additives could help in stabilizing the oxidation process (Fox & Stachowiak, 2003). The application of vegetable oil for industrial purposes, and specifically lubrication has been in practice for many years. Characteristic drawbacks and the availability of inexpensive options have brought the low utilization of vegetable oils for industrial lubrication.

Vegetable oil does not volatilize without decomposing. Reasons for the use of vegetable oils in the science of lubrication abound. Their superior lubricity and emulsifying characteristics increase their desirability as additives to the cheaper but less effective mineral oil based lubricants. The benefits that inspire the use of vegetable oils include their relatively low viscosity-temperature variation; that is their high viscosity indices, which are about twice those of mineral oils. Additionally, they have low volatilities as manifested by their high flash points. Significantly, they are environmentally friendly, renewable, non toxic and biodegradable. In instant, engine lubricants formulated from vegetable oils have the following advantages deriving from their base stock chemistry:

- Higher Lubricity resulting in lower friction losses, and hence more power and better fuel economy.
- Lower volatility resulting in decreased exhaust emissions.
- Higher viscosity indices.
- Higher shear stability.
- Higher detergency eliminating the need for detergent additives.
- Higher dispersancy.

Rapid biodegradation hence decreased environmental / toxicological hazards (Emmanuel & Mudiakeoghene, 2008)

1.4 Problem Statement

Mineral oil is not readily biodegradable and a few environmental issues started to arise due to the difficulties to manage mineral oils waste. Henceforth, this study is concerned about the use of vegetable oil replacing the mineral oil as an alternative way to overcome the issues which have arises (M.K. & Hayder A, 2009). These oils offer significant environmental benefits with respect to resource renewability and biodegradability, as well as providing satisfactory performance in a wide array of applications. Other than that, it is a non-toxic, good boundary lubrication property, excellent thin film strength due to adherence to the surface of metals, low volatility, higher flash and fire points, and also naturally high viscosity index. Mineral oil or synthetic esterbased fluids may also offer these advantages, but their cost can be excessively high.

Once poured into the engine, an automotive lubricant fluid undergoes oxidation in air due to a number of factors including heat, severe pressure and the presence of metal (Canter, 2008). Maximum oxidation process will degrade the composition of the oil by breaking the bonding between the molecules. The oxidation process can be stabilized by the addition of antioxidizing agent. Antioxidant will maximize the stabilisation of oxidation process. It exists in two classes; primary and secondary.

However, there are some of disadvantages of using vegetable oil lubricant. The use of it is limited in industrial use due to poor thermal and oxidation stability. This is the biggest problem carried by vegetable oil in order to make them as a lubricant. Other disadvantages are; low cold flow behaviour, shorter life and storage time and also poor seal compatibility (need modifications). The introduction to antioxidant additive (ZDDP) into the vegetable oil will overcome this problem since ZDDP is an effective antioxidant. A few sample tests will be carried out to test the effectiveness of the ZDDP in the vegetable oil (corn oil). ZDDP will not only act as antioxidant, but as well as it provides anti wear function. The hypothesis have been made by a researcher, their presence of glassy compound, phosphorus as polyphosphate and iron sulphide as a ternary eutectic with iron oxide, provides the ant/wear function of ZDDP (Watkins, 1982).

1.5 Objectives

Based on the introduction and problem statement stated above, the objectives of this study are stated below.

i. To prepare an alternative lubricant oil with the addition of antioxidizing agent.
ii. To test and characterize the newly prepared lubricant oil.

1.6 Scopes

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

i. Prepare alternative lubricant oil using commercialized cooking corn oil with the addition of ZDDP as an antioxidizing agent.
ii. Determine the cooperating action between the vegetable base oil, corn oil and the antioxidizing agent, ZDDP using the direct method.
iii. Conducting a few sample tests upon new developed oil using laboratory machines to test and characterize the oil.
iv. Conducting the application test upon the new developed oil on pin on disc test.

CHAPTER 2

LITERATURE REVIEW

2.1 Based Oil Lubricant

All liquids provide lubrication based on their properties. Lubrication is desirable in most of the modern equipment to extend the useful life of the equipment. A lubricant carries several functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage. Lubricant comprises a base fluid and an additive package. The primary function of the base fluid is to lubricate and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, anti-wear performance, and corrosion control. Engine oil needs exceedingly frequent changes of oil in automotive era. The principal function of the lubricant is to extend the life of moving parts operating under many different conditions of speed, temperature, and pressure.

At low temperatures the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At higher temperatures they are expected to keep the moving parts apart to minimize wear. The lubricant does this by reducing friction and removing heat from moving parts (Nehal S. & Amal M., 2011). Contaminants pose an additional problem, as they accumulate in the engine during operation. The contaminants may be wear debris, sludges, soot particles, acids, or peroxides. An important function of the lubricant is to prevent these contaminants from doing any damage.

Base oil is the origin of the lubricating oil as it provides the basic lubricating necessities of an engine application. Mineral (petroleum) or synthetic, vegetable stocks and animal stocks can be used as a base oil lubricant. Based oil lubricants create a significant percentage of the completed lubricants, ranging from 70% of automotive engine oils to 99% of some industrial oils. The base stocks donate significant performance characteristics to measure the selection criteria in areas such as thermal stability, viscosity, volatility, the ability to dissolve additives and contaminants (oil degradation materials, combustion by-products, etc.), low temperature properties, demulsibility, air release/foam resistance, and oxidation stability. In order to attend the balanced performance of the lubricant, those list are important to know the process and selection alongside to get acknowledged with the additives and the mixing procedures (Pirro & Wessol, 2001).

Base oil technology has undergone many stages of development. Animal fats were used as a lubricant in the first form. Ancient inscriptions date back to 1400 century show beef and mutton fat (tallow) being applied to chariot axles. Petroleum-based oils first became presented in 1852. (Kramer, et al., 2011) claimed that they were not widely assumed at first because they did not do as good as many of the animal-based merchandise. Raw, crude did not produce very good lubricant. Merely as the need for automobiles grew, and then did the need for better lubricants. Crude oil has been discovered to be improved by refining the crude into narrow distillation cuts with varying viscosity. By 1923 the Society of Automotive Engineers classified engine oils by viscosity: light, medium, and heavy. Engine oils contained no additives and had to be replaced every 800-1000 knots. In the 1920s more lubrication manufacturers started “processing” their base oils to improve their action. Three popular processing routes were:

Clay Treating

Clay was used to soak up and remove some of the worst components in the petroleum base oil. It has high polar compounds of sulphur and nitrogen and has been usually aromatic.

Acid Treating

Concentrated sulphuric acid was used to convert the base oil into an emission which can be flash away. It is an expensive process although this process excellently cleaned up the oil.

SO_2 Treating

SO_2 treating was a original extraction process, using recyclable solvent, to get cleared of the worst elements in the lube oil. However, highly toxic of the solvent was produced. Although it also has been practically phased out, it was a beneficial stepping stone to conventional solvent extraction (Kramer, et al., 2011).

2.2 Mineral oil

Petroleum, or crude oil, is useful for numerous resolutions. Fuel, gasoline, kerosene, solvents, fuel oil, diesel fuel, lubricating products, and industrial specialty product are the made from petroleum origin. Frequently, there are two stages crude oil is refined: refining of light products and refining of lubricating oils and waxes. (Pirro & Wessol, 2001).

2.2.1 Fluid lubricants (Oils)

Mineral fluid lubricants are based on mineral oils. Mineral oils (petroleum oils) are products of refining crude oil. There are three types of mineral oil: paraffinic, naphtenic and aromatic.

1. Paraffinic oils are formed by hydrocracking or solvent extraction process. Hydrocarbon molecules of paraffinic oils mostly have non-ring long-chained structure. It is relatively viscous, oxidation resistor, have high flash point and

high pour point. Paraffinic oils have widely applied to manufacturing engine oils, and industrial lubricants.

2. Naphtenic oils are product of crude oil distillates. They have saturated ring structure comes from hydrocarbon molecules. The properties of naphtenic oils are they have low viscosity, low flash point, low pour point and low resistance to oxidation. It is used in modest temperature applications, primarily for manufacturing transformer oils and metal working fluids.
3. Aromatic oils exist from manufacture of paraffinic oils which have non-saturated ring structure. Aromatic oils are dark and have high flash point. Aromatic oils are used for manufacturing seal compounds, adhesives and as plasiticezers in rubber and asphalt production.

2.2.2 Semi-fluid lubricants (greases)

Semi-fluid lubricants (greases) are produced by emulsifying oils or fats with metallic soap and water at 400-600°F (204-316°C). Typical mineral oil base grease is vaseline. Grease properties are determined by a type of oil (mineral, synthetic, vegetable, animal fat), type of soap (lithium, sodium, calcium, etc. salts of long-chained fatty acids) and additives (extra pressure, corrosion protection, anti-oxidation, etc.). Semi-fluid lubricants (greases) are used in variety applications where fluid oil is not applicable and where thick lubrication film is required: lubrication of roller bearings in railway car wheels, rolling mill bearings, steam turbines, spindles, jet engine bearings and other various machinery bearings.

2.2.3 Solid lubricants

Solid lubricants possess lamellar structure preventing direct contact between the sliding surfaces even at high loads. Graphite and molybdenum disulfide particles are common Solid lubricants. Boron nitride, tungsten disulfide and polytetrafluorethylene (PTFE) are other solid lubricants. Solid lubricants are mainly