เสถียรภาพต่อออกซิเดชันของน้ำมันหล่อลื่นไฮดรอลิกจากน้ำมันพืช

นางสาวสายนที เชื้อพงษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
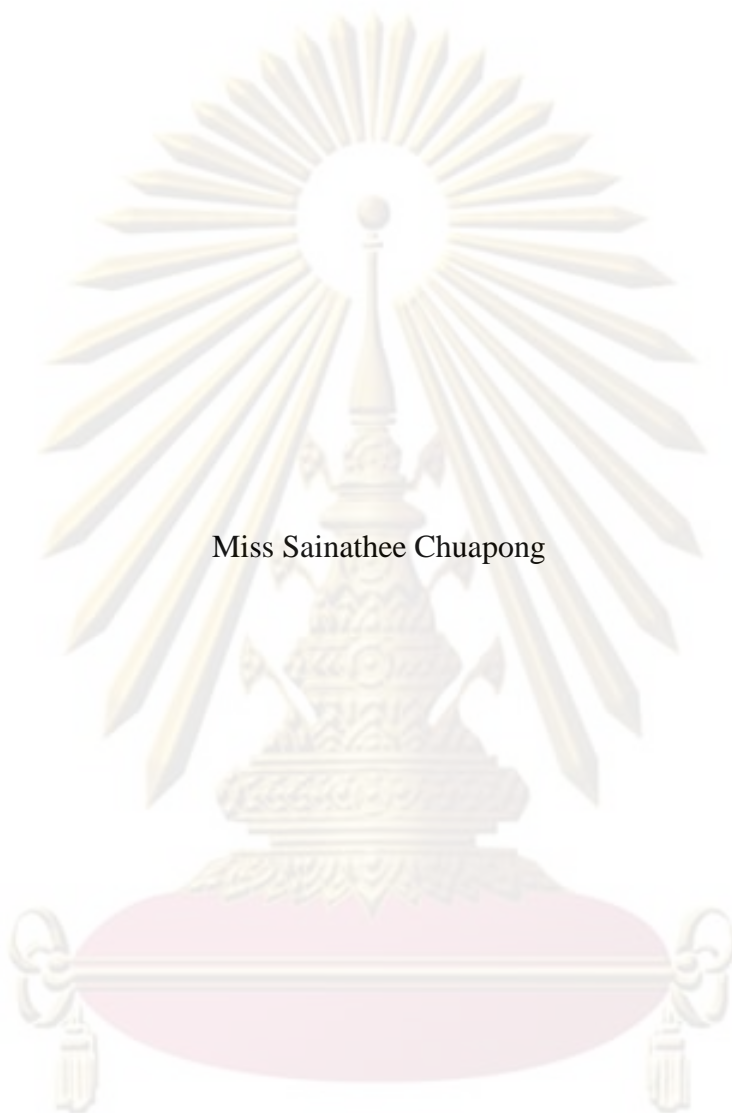สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
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ปีการศึกษา 2552
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

OXIDATION STABILITY OF HYDRAULIC LUBRICANTS FROM VEGETABLE OILS

Miss Sainathee Chuapong

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

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Academic Year 2009
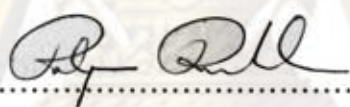
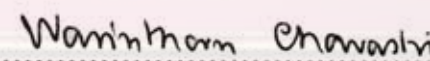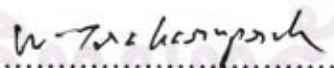|	
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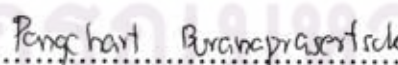
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VEGETABLE OILS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. วรินทร ชวศิริ, 46 หน้า

น้ำมันหล่อลื่นที่ผลิตจากน้ำมันปิโตรเลียมโดยทั่วไปมีความเป็นพิษต่อสิ่งแวดล้อมและยาก
ต่อการทำลายหลังการใช้งาน น้ำมันพืชสามารถนำมาใช้ทดแทนน้ำมันปิโตรเลียมได้เนื่องจาก
สมบัติการหล่อลื่นที่ดี สามารถย่อยสลายได้ตามธรรมชาติ สมบัติของความหนืดและการระเหยต่ำ
งานวิจัยนี้ได้ปรับสมบัติทางกายภาพของน้ำมันหล่อลื่นไฮครอลิกจากน้ำมันพืช ได้แก่ ความหนืด
ดัชนีความหนืด จุดวาบไฟและการต้านสึกหรอ เปรียบเทียบกับน้ำมันหล่อลื่นไฮครอลิกทาง- การค้า
OIL-HR เป็นน้ำมันหล่อลื่นจากน้ำมันรำข้าวแสดงสมบัติการหล่อลื่นที่ดีและสมบัติความหนืด
เมื่ออุณหภูมิเปลี่ยนแปลงเทียบเคียงกับน้ำมันหล่อลื่นไฮครอลิกที่ใช้ในทางการค้า เสถียรภาพต่อ
ออกซิเดชันของน้ำมันหล่อลื่นไฮครอลิกจากน้ำมันถั่วเหลืองและน้ำมันรำข้าว ทดสอบภายใต้ภาวะ
อุหภูมิสูงที่เติมสารไดฟีนิลลามีน 0.5 เปอร์เซ็นต์โดยน้ำหนัก มีสมบัติด้านออกซิเดชันที่ดี สมบัติ
การกัดกร่อนทองแดงของ OIL- HC, OIL-HP, OIL-HSFและ OIL-HR น้ำมันหล่อลื่นจาก
น้ำมันมะพร้าว น้ำมันปาล์ม น้ำมันทานตะวันและน้ำมันรำข้าว อยู่ในกลุ่ม 1a ซึ่งแสดงสมบัติการ
ด้านกัดกร่อนที่ดี น้ำมันหล่อลื่นไฮครอลิกจากน้ำมันรำข้าวแสดงสมบัติด้านสึกหรอและความ
หนืดเมื่ออุณหภูมิเปลี่ยนแปลงได้ดี

สาขาวิชา....ปิโครเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต..

ปีการศึกษา...........2552.........................ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.........................

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KEYWORDS: HYDRAULIC LUBRICANTS / VEGETABLE OILS / OXIDATION STABILITY

SAINATHEE CHUAPONG: OXIDATION STABILITY OF HYDRAULIC LUBRICANTS FROM VEGETABLE OILS. THESIS ADVISOR: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D., 46 pp.

The lubricants produced from petroleum base stock are generally toxic to environment and difficult to dispose after use. Vegetable oils can be used as an alternative base stock for lubricants besides petroleum base because of their excellent lubricity, biodegradability, viscosity characteristic and low volatility. The hydraulic lubricants from vegetable oil were manipulated in this research. Their physical properties including viscosity, viscosity index, flash point and four- ball wear were investigated comparing with those of commercial hydraulic lubricants. OIL-HR, lubricants produced from rice bran oil was exhibited excellent lubricity and viscosity–temperature properties in the same level as commercial industrial lubricants. The oxidation stability of manipulate hydraulic lubricants from soybean oil and rice bran oil under the tested conditions of oven oxidation test in the presence of 0.5% diphenylamine exhibited excellent antioxidant property. The copper corrosion behavior of hydraulic OIL-HC, OIL- HP, OIL-HSF and OIL-HR, lubricants produced from coconut, palm, sunflower and rice bran oil, respectively, revealed these blended oils were classified into **1a** class, which showed good anticorrosion. The hydraulic lubricant from rice barn oil displayed good anticorrosion and viscosity-temperature characteristic.

Field of study Petrochemistry and Polymer Science Student's signature...................................

Academic year.............2009......................... Advisor's signature ....

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
ºC	degree Celsius
cSt	Centistokes
F.P.	flash point
h	hour
mL	milliliter(s)
mmol	millimole
m.p.	melting point
PP	pour point
PV	peroxide value
S.G.	Specific gravity
TAN	total acid number
VI	viscosity index
ZDDC	zinc dialkyldithiocabarmate
ZDDP	zinc dialkyldithiophosphate

CHAPTER I

INTRODUCTION

There have been growing concerns worldwide for the use of mineral oils as lubricants because of the environmental issue. For the last three decades, certain industries have continuously put their efforts to formulate environmentally adopted lubricants with technical characteristics equal or superior to those based on mineral oils. Vegetable oils are a viable candidate for replacement of mineral oils due to their inherent biodegradability, non-toxicity and excellent lubricity. Additionally, vegetable oils are renewable resource, and their cost is reasonable compared with that of other alternative biodegradable fluids [1]. Other advantages include very low volatility due to the high molecular weight of the triglyceride molecule and excellent temperature viscosity properties. Their polar ester groups are able to adhere to metal surface, and therefore, good lubricity.

Chemically vegetable oils are carboxylic ester derived of glycerol and known as triglycerides. [2]
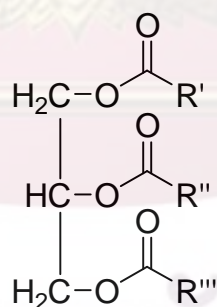
Triglyceride

The R groups are normally straight chain varying in chain length from 4 to 24 carbon atoms. They can be saturated, monounsaturated or polyunsaturated. The chain length of R groups as well as the degree and position of unsaturation determines the physical properties of the triglyceride.

The degree of saturation can be classified as follows:

Saturated - Each carbon atom contains the maximum number of hydrogen atom. No double bonds, *e.g.* stearic acid, C18:0.

Monounsaturated – Removal of two hydrogen atoms and replacement with a carbon-carbon double- bond, *e.g.* oleic acid, C18:3.

Polyunsaturated – Any molecule containing more than one double bond, *e.g.* linoleic acid, C18:2 or linolenic acid, C18:3.

Saturated triglycerides are more stable to oxidative degradation than mono-saturated triglycerides. Monosaturated triglycerides are more stable than poly-unsaturated triglycerides.

1.1   Lubricant Base Stocks [3]

1.1.1   Mineral Oils

Mineral stocks are refined by a number of processes of selection from the crude oil barrel. For this reason, the choice of crude is important. Most favored are paraffinic crudes, which give a good yield of high-viscosity (HVI) stocks, although they also contain a lot of wax. Distillation under atmospheric pressure removes the gasoline and distillate fuel components, leaving a "long residue" containing the lube oil and asphalt, further distillation under vacuum yields "neutral distillates" overhead and an asphalt residue. Finally, wax is removed by dissolving the oil in methyl ketone and chilling and filtering to yield oils with pour points in the -10 to -20°C range. At the refiner's option, the oils may be "finished" with hydrogen to remove sulfur, nitrogen and color bodies.

Paraffinic oil

Paraffinic oil is produced either by hydrocracking or solvent extraction process. Most hydrocarbon molecules of paraffinic oils have non-ring long chain structure. Paraffinic oil is relatively viscous and resistant to oxidation. They possess high flash point and high pour point. Paraffinic oils are used for manufacturing engine oil, industrial lubricants and as processing oil, in rubber, textile and paper industries.

Naphthenic oil

Naphthenic oil is produced from crude oil distillates. Most hydrocarbon molecules of naphthenic oil have saturated ring structure. Naphthenic oils possess low viscosity, low flash point, low pour point and low resistance to oxidation. Naphthenic oils used in moderate temperature application mainly for manufacturing transformer oil and metal working fluids.

Aromatic oil

Aromatic oil is the product of refining process in manufacture of paraffinic oils. Most hydrocarbon molecules of aromatic oils have non-saturated ring structure. They are dark and have high flash point. Aromatic oils are used for manufacturing seal compounds adhesive and as plasticizers in rubber and asphalt production.

1.1.2 Synthetic Base Stocks

Polyalphaolefin (PAO) is the most widely used synthetic lubricants. It was made by combining two or more decene molecules into an oligomer or short chain length polymer containing no sulfur phosphorus or metals. Because it is wax free, low pour points, usually below -40°C. Viscosity grades rang from 2 to 100 cSt.

Polyol esters are the diesters which are formed by the reaction of an acid and an alcohol. Polyol esters refer to the molecule with two alcohols in its structure *e.g.* neopentylglycol (NPG) and pentaerythritol (PE).

Polyalkylene glycols (PAGs) are polymers of alkylene oxides. Lubricant performance and properties of a particular PAG depend on the monomers used to manufacture it, molecular weight, and the nature of the terminal groups. PAGs have good high-temperature stability and high viscosity indexes, and they can be used over a wide temperature range. It exhibits low deposit formation, and tends to solubilize their decomposition products.

Phosphate esters are synthesized from phosphorus oxychloride and alcohols, or phenols. It is used both as base oils and as anti-wear in mineral and synthetic lubricants. Thermal stability is good, and pours point ranges from -25 to -5°C.

However, viscosity index is extremely low, ranging from 0 to -30, which limits their high-temperature capabilities.

1.1.3 Vegetable oils

Most vegetable oils contain triglyceride. Vegetable oil compositions are normally described in terms of their fatty acid content, referring to the acid ester moieties, actual fatty acids present in the oil known as free fatty acids. The triglyceride structure of vegetable oils provides qualities desirable in a lubricant. Long polar fatty acid chains provide high strength lubricant films that interact strongly with metallic surface, reducing both friction and wear. The strong intermolecular interactions are also resilient to change in temperature providing a more stable viscosity or high viscosity coefficient. The entire base oil is also a potential source of fatty acid.

The triglyceride structure is also the basis for the inherent disabilities of vegetable oils as lubricants. Unsaturated double bonds in the fatty acids are active sites for many reactions, including oxidation, lowering the oxidation stability of vegetable oils. Another concern is the susceptibility of the triglyceride ester of hydrolysis. The similarities of all vegetable oil structures mean that only a narrow range of viscosities is available for their potential use as lubricant. Differences in the physical and chemical properties of vegetable oils are largely dependent on the degree of unsaturation of the constituent of fatty acids as shown in Table 1.1. Vegetable oils with a high proportion of saturated fatty acid are solid or semisolid at room temperature.

The presence of double bond in the chains, which particularly owing to the *cis* configuration, is not able to pack together easily. This results in a lower melting point with a consequence that unsaturated vegetable oils are liquid and free of wax deposit at room temperature. However, the presence of double bonds does have an effect on oxidative stability. The allylic position is labile and hence susceptible to free radical abstraction and subsequent formation of peroxide. In polyunsaturated oils, the methylene group separating double bonds is doubly allylic and therefore particularly prone to oxidation. Hence, lubricant base on vegetable oil required both low-temperatures performance and oxidative stability.

Table 1.1 Typical fatty acid composition of some common vegetable oils [4]

| Oil or Fat | Unsat/ Sat ratio | Saturated | | | | | Mono unsaturated | Poly unsaturated | |
		Capric acid C10:0	Lauric acid C12:0	Myristic acid C14:0	Palmitic acid C16:0	Stearic acid C18:0	Oleic acid C18:1	Linoleic acid C18:2	Alpha Linoleic C18:3
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil	6.7	-	-		11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Safflower Oil	10.1	-	-	-	11	2	48	32	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil	7.3	-	-	-	7	5	19	68	1

1.2   Lubricant Additive

Additives are present in lubricants for a variety of reasons. Additive can be differentiated based on the physical or chemical properties of the base oil or modify the metal surface of the lubricant contact.

Antioxidant

These additives protect the base oil from the ravages of oxidation. Oxidation is a free radical process that is mechanistically divided into three steps: initiation, propagation, and termination. The oxidation process begins with the generation of alkyl free radicals under high temperature, UV light, or metal catalyst conditions. Antioxidants are compounds that disrupt the propagation step of free radical degradation. Antioxidants are classified according to their mode of action as radical scavenger and as hydroperoxide decomposers. Radical scavengers which interfere with propagation steps referred to as primary antioxidants, while hydroperoxide decomposers were labeled as secondary antioxidants.

Phenolic antioxidants

Sterically hindered mono-, di- and polynuclear phenol derivatives belong to the most effective antioxidants acting as radical scavenger and used for many applications. Typically, those referred to the phenols with the substituents present at 2 and 6 positions with tertiary butyl group. The most simple derivatives are 2,6-di-*tert*-butylphenol (2,6-DTB) and 2,6-di-*tert*-butyl-4-methyl phenol (BHT). The advantage of polynuclear phenols like 4,4′-methylene*bis*(2,6-di-*tert*-butylphenol) or another type with high molecular mass substituents at 4 position is the reduced volatility due to the higher molecular weight that makes these products suitable for high temperature applications.
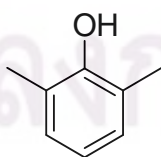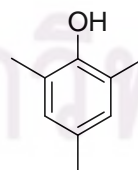
2, 6-di-*tert*-butylphenol   2,6-di-*tert*-butyl-4-methyl phenol
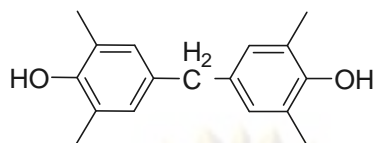
4, 4′-methylene*bis*(2,6-di-*tert*-butylphenol)

Aromatic amines

Aromatic amine represents another important class of antioxidants that act as radical scavengers. Typical products are a large number of alkylate diphenylamines, *N*-phenyl-1-naphthylamine (PANA) and the polymeric 2,2,4-trimethyldihydro-quinoline. Because of its poor solubility in mineral oil, the latter is commonly used in grease and polar lubricants.
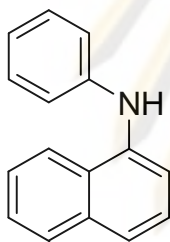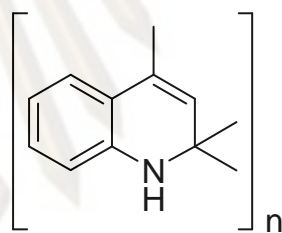
N-phenyl-1-naphthylamine   *2,2,4-trimethyldihydroquinoline*

Compounds containing sulfur and phosphorus

There are two classes of secondary antioxidants containing sulfur and phosphorus compounds *e.g.* zinc dithiophosphates, zinc dithiocarbamates and organo-phosphorus compounds *e.g.* aryl phosphites.
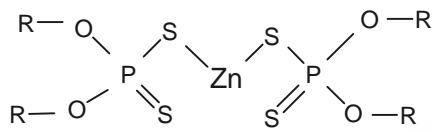
zinc dithiophosphates
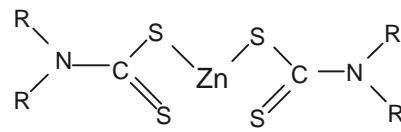
zinc dithiocarbamates
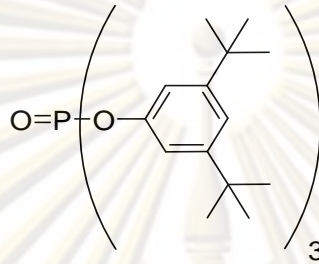
organophosphorus compounds

Antiwear (AW), extreme pressure (EP) and friction modifier (FM)

These additives are referred to as tribological additives, and reduce friction and wear when operating conditions become more severe *e.g.* high load, low speed. Fluid film lubrication is replaced with mixed film and then boundary lubrication when the thickness of the lubricating film is less than surface irregularities in the moving metal parts. Wear is the physical loss of material from a metal surface. Four wear mechanisms are delineated: adhesion, abrasion, corrosion and contact fatigue.

The mode of action from FM additive to AW additives and finally EP additives represents a shift toward increasingly harsh operating conditions – mixed lubrication to boundary lubrication. FM additives reduce friction and include fatty acids, fatty alcohols and fatty amines and amides. The polar functional groups of these species adsorb on metal surface and separate sliding metal surfaces. AW additive *e.g.* zinc dialkyldithiophosphate. Antiwear reacts with metal surface creating an anti-wear film that is less than shear resistant. EP additive target high stress conditions and like the AW additive form tribochemical reaction layers *e.g.* *bis*(diamyldithiocarbamate)zinc and methylene–*bis*(di-*n*-butyldithiocarbamate).

O=P(—O—⟨C₆H₄⟩—)₃

di-amyldithiocarbamate
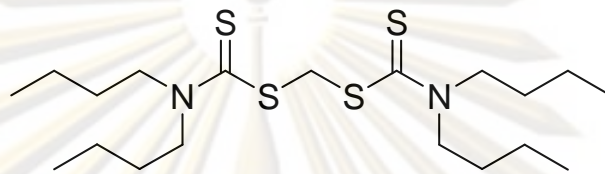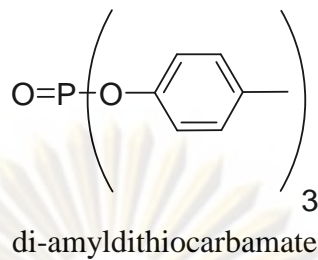
Methylene-bis(di-n-butyldithiocarbamate

1.3 Hydraulic Oil

Hydraulics describes the transfer of energy and signals through fluids; power transferred to drive, control and move. Hydraulic fluids based on mineral oils, synthetic fluids and fire-resistant fluids used in all type of machinery and equipment.

Hydraulic component manufacturers supply nearly all industries including the agriculture and construction machinery sectors, conveyor technology and packaging industries, woodworking and machine tools, shipbuilding, mining and steel industries, medicine, environmental technology, and chemicals.

Characteristics of Hydraulic Oil

- Transferring pressure and motion energy
- Transferring forces and moments when used as a lubricant
- Minimization of wear to sliding surfaces under boundary friction conditions
- Minimization of friction
- Protection of components against corrosion (ferrous and non-ferrous metals)
- Dissipation of heat
- Suitability for a wide range of temperatures, good viscosity-temperature behavior
- prolonging the life of machinery, *etc.*

The critical characteristics and performance attributes of hydraulic fluids are viscosity, viscosity index, wear protection capability, oxidation stability, antifoam and air separation characteristics, demulsibility, rust protection and compatibility.

Additives are specially designed chemical compounds that are added to lubricating oils to impart specific properties such as the ones mentioned above. Additionally hydraulic fluid additives are engineered to meet and exceed the requirements of major industry manufacturer's specification including [5]

- Denison HF-0, HF-1, HF-2
- Eaton- Vickers M-2950-S, I-286-S
- Cincinnati Lamb Landis P-68, P-69, P-70
- General Motors (LS2) LH-03-1, LH-04-1, LH-06-1
- DIN 51524 Parts 2
- US Steel 127

1.4 Principle properties of lubricants

1.4.1 Specific gravity, DIN 51757/ASTM D 1298 [6]

Specific gravity is defined as a quotient of the mass and the volume. In petroleum products, the mass/volume relation expressed as:

$$\text{Specific Gravity} = \frac{\text{Mass/ unit volume product at 60 °F}}{\text{Mass/ unit volume water at 60 °F}}$$

1.4.2 Viscosity, ASTM D445 [7]

Viscosity is one of the most important for characterization of lubricants and their flow and transport properties. The viscosity of a fluid is a measurement of its internal resistance to flow of cohesion between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and molecular weight of the constituent components. The instrument used to determine the viscosity of oil is called the viscometer. Kinematic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under

gravitational force at a standard temperature. Test temperatures are usually at 40 and 100 °C for centistokes units.

1.4.3 Viscosity index, ASTM D2270

The relationship of viscosity to temperature of fluid, high viscosity index fluids tends to display less change in viscosity with temperature than low viscosity index fluids. The viscosity index of lubricant is calculated from viscosities determined at two temperatures at 40°C and 100°C [8].

1.4.4 Flash point, ASTM D92 [9]

The flash point is reached at the lowest temperature at which the application of defined test flames causes the vapors above the surface to ignite. For the determination of the flash point closed and open cups are used. The open cup flash point is described according to ASTM D92 and the closed cup method according to ASTM D93.

1.4.5 Pour point, ASTM D97 [10]

The pour point is the lowest temperature expressed as a multiple of 3°C at which the test fluid is observed to flow when it is cooled and examined under defined conditions.

1.4.6 Water Content

There are in general two standard methods for determination of water content. For volumes of 0.05% and above, ASTM D95 [11] is used. This test procedure involves azeotropic reflux distillation of the oil with xylene with water separating from the reflux distillate.

For lower water contents between 50 and 1000 ppm, the Karl Fischer method (DIN 51777/1ASTM D1744) is more accurate. The sample is titrated with a standard solution of iodine pyridine and sulfur dioxide in methanol. The end point of the titration at which free iodine is hydrated may be registered either potentiometrically or by color indicator.

1.4.7 Acidity, alkalinity, ASTM D664 [12]

The total acid number (TAN/ASTM D664) is a method to determine acidic and basic constituents in petroleum products. The acidity of unused oils and fluids is normally derived from type and concentration of specific additive material whereas the acidity of used oil is of interest to measure the degree of oxidation of the fluid.

The total base number (TBN) characterizes the alkaline reserve in petroleum products. It is particularly used for engine oils where by acidic combustion products are used up the alkaline reserve.

1.4.8 Four-ball apparatus

The four-ball apparatus (Figure 1.1) is one of the oldest and best-known model test benches for liquid and solid lubricants. Because it furnishes very precise lubricants key values, it is used all over the world. A roller-bearing ball rotated under pressure and at a constant speed on three fixed steel balls of the same type in an oil bath or lubricated with a solid lubricant. The gradual increase in pressure enables the determination of weld loads, supplies key values concerning load ability, or enables allows the determination of the friction or start-up behavior in relation to the lubricant. In addition, the application of relatively small loads over a longer period of time enables the determination of key wear protection values and the friction values of lubricants. During these tests, the surface of the ball surface will produce wear impressions which when measured will lead to information on the effects of additives.
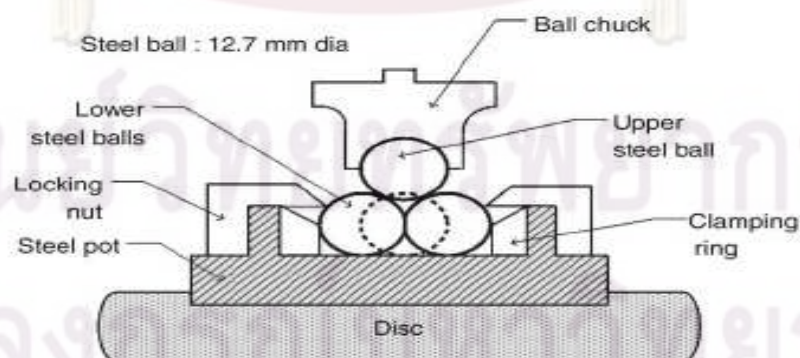
Figure 1.1 Four –ball apparatus [13].

1.5   Literature reviews

In 2004, He and co-workers [14] evaluated the tribological properties of S,P-containing triazine derivative, 2,4-*bis*-(diethylamino)-6-(*O,O′*dialkyldithio-phosphate)-*S*-1,3,5-triazine as a lubricating oil additive in vegetable oil using a four-ball tester. These compounds showed good load-carrying capacity, improved antiwear and friction-reducing properties. The action mechanism was estimated through the analysis of the worm surface with X-ray photoelectron spectroscopy and scanning electron microscope.

In 2005, Castro and co-workers [15] studied the effect of lubricant on the complexity of friction and wear under boundary conditions using a pin-on-disc machine and four-ball wear tester. The outcome showed that the chemical characteristic of both additive and base fluid have an important role on the effectiveness of additives.

In 2006, Erhan and co-workers [16] presented a systematic approach to improve the oxidation and cold flow behavior of vegetable oil derivatives using a synergistic combination of additives in high oleic vegetable oil blended with synthetic fluid. The oxidation properties were examined using pressure differential scanning colorimetry and rotary bomb oxidation test, while pour point measurements used to study low temperature properties. Vegetable oil-based lubricants formulated using the above approach exhibited superior oxidative stability, and improved low temperature properties such as pour point compared to commercially available industrial oils such as bio-based hydraulics fluids.

Jayadas and Nair [17] reported TGA of coconut, sesame, sunflower and commercial 2T oils under nitrogen and oxygen atmospheres as a part of the study on thermal and oxidative degradation of vegetable oils. Coconut oil showed lower weight gain, an indicator of oxidative stability, under oxidative environment and the highest pour point among the vegetable oils considered. This can be attributed to the predominantly saturated nature of its fatty acid constituents.

Fox and Stachowiak [18] described the methods used to assess and improve oxidation stability of vegetable oil-based lubricants. Vegetable oils being investigated

are a potential source of environmentally friendly lubricant, due to a combination of biodegradability, renewability and excellent lubrication performance.

In 2007, Jayadas and co-workers [19] evaluated the tribological properties of coconut oil using a four-ball tester and a test rig to test the wear on two stroke engines. The influence of an antiwear and extreme pressure (AW/EP) additive on the tribological performance of coconut oil was also evaluated experimentally. The addition of the AW/EP addition has brought about considerable reduction in wear with coconut oil as 2T oil.

In 2008, Moser and Erhan [20] reported the evaluation of four branch chain ether and soybean oil methyl ester against cloud point, pour point, oxidation stability, viscosity, lubricity and surface tension. All branched chain ethers exhibited excellent low temperature performance, oxidation stability and lubricity behavior. Thus, branch chain ether may aid in development of bio-based material for potential use as additives in bio-diesel fuel.

The objective of this research

The objective of this research is to prepare hydraulic lubricants and to investigate oxidative stability of hydraulic lubricants formulated from vegetable oils and additive in commercial industrial lubricants.

CHAPTER II

EXPERIMENTAL

2.1   Instruments and equipments

Viscometer, Model CANNON 9724 - E50 CANNON Instrument Company. Density Hydrometer, Model 300H, Amarell GmbH & Co,KG. Flash Point Tester, Model TANAKA ATG CANNON Instrument Company, USA. Automatic Karl Fischer Mettle's – DL32. Pour Point Tester, Model A82 HAKKE. Four Ball Tester, Model K93100, KOEHLER. Hotplates and Stirrers, BIBBY STERILIN. Volumetric and coulometric Karl Fischer titrators, Metrohm. Colorimeter, Fisher ASTM (D 1500). Oven & Incubator, Memmert Germany.

2.2   Raw materials and chemicals

The vegetable oils used in this study included coconut, palm kernel, rice bran, camellia seed, soybean, castor, sunflower, corn, olive, cottonseed, sesame and safflower oils were obtained from BRS INTERTRADE Co., Ltd. Some vegetable oils were purchased from department store and supplier.

Four types of commercial additives using in blending for hydraulic fluid including zinc dialkyldithiophosphate (ZDDP), zinc dialkyldithiocarbamate (ZDDC), diphenylamine and polymeric ester derivatives were obtained from BRS Intertrade Co., Ltd.

2.3   Experimental procedure

2.3.1   Viscosity, ASTM D445

Kinematic viscosity of oil was measured by viscometer at 40° and 100°C in oil bath as per ASTM Test Method D445.

2.3.2   Specific gravity/ Density, ASTM D1298

Specific gravity can be defined by hydrometer as per ASTM D1298. In petroleum product determination using a glass hydrometer, of the density, relative - density (specific gravity), or API gravity of crude petroleum, petroleum products, or

mixtures of petroleum and nonpetroleum products normally handled as liquids, and having a Reid vapor pressure of 101.325 kPa (14.696 psi) or less.

2.3.3 Flash Point, ASTM D92

The flash point is reached at the lowest temperature at which the application of defined test flames causes the vapors above the surface to ignite. For the determination of the flash point the closed cup described method according to ASTM D92.

2.3.4 Pour point, ASTMD97

Pour points are measured by following ASTMD97. A 50 mL of sample is placed in test jar, stopper. The stopper contains thermometer measuring from +20° to -80°C that is immersed into the sample. Temperature is measured in 3°C increments until the sample stops pouring. The pour point is defined as the temperature in °C at which the sample still pours when the jar is tilted.

2.3.5 Water content, ASTM D1744

The sample is titrated with a standard solution of iodine pyridine and sulfur dioxide in methanol. The end point of the titration at which free iodine is hydrated may be registered either potentiometrically or by color indicator. In this study, water content was quantified by the Karl Fischer method as per ASTM D 1744.

2.3.6 Peroxide value (PV)

Peroxide value (PV, meq O_2 kg^{-1} oil) is a measurement of oxidative rancidity and a guide to vegetable oils quality. PV determinations by standard method involve dissolution of appropriate amounts of oil (0.3-5 g according to the expected PV) in 25 mL acetic acid-chloroform solution (3:2). Then 1 mL of saturated KI solution is added and the flask stoppered. The mixture is stirred for 1 min and then kept in dark for exactly 5 min. After that, 75 mL of deionized water is added and the content is titrated with 0.01 N sodium thiosulfate solution in the presence of starch indicator (1%) until the discoloration of the mixture. The same procedure was carried out for a blank solution and was taken into-account in all the titrations.

PV is calculated using the following equation:

$$PV \ (\mathrm{mequiv.kg^{-1}}) \quad = \quad \frac{1000}{m} \ \text{x} \ 0.01(V\text{-}V_{\text{blank}})$$

Where V and V_{blank} in mL are the volume of thiosulfate used for titrating sample and blank solution, respectively and m in g is the mass of oil sample [21].

2.3.7 Preparation of hydraulic lubricants from vegetable oils

Formulating hydraulic fluids from raw material by combination of vegetable oils with antioxidant and anti-wear additive were conducted. The performance of prepared hydraulic oils was examined compared with commercial industrial oils.

2.3.8 Long-term oven oxidation stability test

Hydraulic fluid blends are placed into glass sample vials and kept in oven at 85°C for 28 days. The samples were determined for total acid number (TAN) as ASTM D664 at 0 and 28 days by Karl Fisher titrations.

2.3.9 Total acid value

Total acid value is a measurement for total amount of both weak and strong organic acids present in the lubricant. This is expressed as the amount of potassium hydroxide, KOH in mg required to neutralize free acids in 1 g of sample. The sample oil which was weighed accurately and dissolved with 75 mL of mixture solvent was titrated potentiometrically with 0.1 mol/L 2-propanal solution of KOH at room temperature.

2.3.10 Tribological test on four- ball tester

Anti-wear properties of sample lubricants were evaluated by four-ball wear test, which is regulated by ASTM D4172.

2.3.11 Foam characteristics

This test is the determination of the foaming characteristics of lubricating oils. The sample maintained at 24°C is blown with air at a constant rate for 5 min, and then allowed to settle for 10 min. The volume of foam is measured at the end of both periods. The test is repeated on a second sample at 93.5°C, and then after collapsing the foam at 24°C.

2.3.12 Copper corrosion behavior (Copper- Strip Test)

The detection of copper corrosion follows by ASTM D130. Timing in this test are 3 hours, at ambient temperature up to 150°C. At the end of the test period the copper strip is removed, washed and compared with the ASTM copper strip corrosion standards.

CHAPTER III
RESULTS AND DISCUSSION

The aim of this research was to manipulate hydraulic lubricants from vegetable oil and to investigate the properties of hydraulic lubricants comparing with those of commercial hydraulic lubricants. With the excellent lubricity, biodegradability, viscosity temperature characteristics and low volatility of vegetable oils, this natural resource was thought to be another alternative base stock for lubricants besides petroleum base.

3.1   Physical property of vegetable oil as lubricant base stock

Generally, lubricants contain two main components, *i.e.* base stock more than 90% and additive being approximately 10%. The base stock required for preparing lubricant must meet performance criteria in such aspects as viscosity properties, volatility, oxidative and hydrolytic stability, deposit forming tendencies, miscibility or compatibility with elastomeric and mechanic systems. There are two main candidates for being base stock: those derived from refinery petroleum crude oil and vegetable oils. In the past, almost of lubricants were produced from petroleum base. Nowadays, the tendency to use vegetable oil to replace petroleum base has been increased since the previous used lubricants were toxic to environment and depletion of petroleum oil. On the other hand, vegetable oils derived from renewable source possess biodegradable property. This main property is the advantage of vegetable oils.

In this study, twelve common vegetable oils namely soybean, palm, sunflower, castor, coconut, rice bran, safflower, camellia seed, olive, corn, castor and sesame oils were selected as base stock. The physical properties including kinematic viscosity, viscosity index, specific gravity, water content, flash point and pour point are presented in Table 3.1.

Table 3.1 Physical properties of selected vegetable oil and petroleum base

SAMPLE	Kinematic Viscosity (centistokes)		Viscosity Index	Specific Gravity	Water content	Flash Point	Pour point
	at 40°C	at 100°C	(VI)		%	°C	°C
Sunflower oil	40	6.7	123	0.900	0.100	260	-15
Soybean oil	31.17	7.62	228	0.900	0.120	262	-12
Palm oil	39.62	8.51	200	0.910	0.202	218	-18
Rice bran oil	39.75	8.23	188	0.911	0.090	>210	-10
Olive oil	38.72	8.38	201	0.907	0.100	>210	-9
Corn oil	35.59	8.74	239	0.900	0.181	>200	-20
Cotton seed oil	35.83	8.24	216	0.910	0.064	> 210	-24
Sufflower oil	39.31	8.36	196	0.920	0.195	>200	-20
Camellia seed oil	30.94	7.63	231	0.910	0.119	>340	-9
Castor oil	256.95	19.86	89	0.952	0.090	>250	-10
Coconut oil	39.50	9.20	226	0.900	0.100	>200	-15
Sesame oil	35.00	8.00	212	0.913	0.100	>200	-25
Petroleum base	40.74	6.23	99	0.872	0.09	226	-10

Two common properties using to consider for further application of hydraulic lubricant are kinematic viscosity and viscosity index. From Table 3.1, kinematic viscosity of sunflower, soybean, palm, rice bran, olive, corn, cotton seed, safflower, camellia abele seed, sesame and coconut oils at 40°C in the range of 31 to 40 centistokes and viscosity at 100°C is 6 to 10 centistokes. This property was the same as that of petroleum base oil, 200 SN. The kinematic viscosity of castor oil at 40 and 100°C were 257 centistokes and 20 centistokes, respectively, which found to be close to petroleum base number 600 SN.

The kinematic viscosity values of all selected vegetable oils are high due to high molecular weight of triglyceride present. Polar ester groups of triglycerides are behavior adhere to metal surfaces and therefore have behavior good lubricity.

As presented in Table 3.1, viscosity index (VI), which expressed the viscosity-temperature property of vegetable oil, is the relationship of viscosity with change to temperature. This index indicated lubricity of oil when temperature changes.

The viscosity index (VI) of oil is a number that indicates the effect of temperature changes on the viscosity of oil. A low VI signifies a relatively large change of

viscosity with changes of temperature. On the other hand, a high VI signifies relatively little change in viscosity over a wide temperature range.

For the proper operation of the hydraulic control system, the hydraulic fluid must have a sufficiently high VI to perform its functions at the extremes of the expected temperature range.

Flash point properties are reached at low temperature, when vapors above the surfaces ignite. As presented in Table 3.1, flash points of vegetable oils are more than 200°C. This property indicated low volatility of lubricant. Vegetable oils had high flash point due to high molecular weight of triglyceride. The flash point of oil is important since at the lowest temperature, the auto-ignition of the vapor occurs above the heated oil sample.

According to Table 3.1, seven selected vegetable oils have a pour point of -9° to -15°C while coconut, safflower, corn, soybean and sesame oils have pour point in the range of -12° to -25°C. Pour point is the low temperature flow property of oils, if base oil has poor pour point property, this will limit its use at low operating temperature, especially industrial oils. Generally, vegetable oil has a tendency to form microcrystalline structure at low temperature through uniform stacking of the triglyceride backbone. Such macro crystal restricts the easy flow of the system due to loss of kinetic energy of individual molecules between stacking.

Data of specific gravity and water content of all selected twelve vegetable oils are given in Table 3.1, the water content of vegetable base was in the range of 0.09 to 0.2% by weight. Water content indicates moisture in oils, if water contamination in hydraulic system part is finely dispersed, it will enter into the oil phase and depending on the density of oil, which water can separate from oil phase.

Specific gravity is the ratio of weight per unit volume of substance. In Table 3.1, specific gravity of vegetable oil and petroleum base is equal to 0.90 to 0.95. In the petroleum industry, specific gravity is important properties for calculation of the concentration, weight or volume of oils.

3.2   Peroxide value (*PV*) of vegetable oils

Unsaturated double bonds in fatty acids are active sites for many reactions, including oxidation, which lowered the oxidation stability of vegetable oils. Oxidation

stability of triglyceride is primarily limited by the degree of unsaturated double bonds. Peroxide value is a measurement of oxidation rancidity and the guide to vegetable oil quality. This method is a common parameter in the chemistry of fats. It shows the degree of oxidation and measures the amount of total peroxide in oil.

Lipid peroxidation is a free radical reaction that results in the formation of hydroperoxide, which unless prevented from propagation may simultaneously destroy native antioxidant compound. Vegetable oil oxidation initiated by formation of free radicals. Free radicals can formed from the removal of hydrogen atom from methylene group next to double bond. Free radicals rapidly react with oxygen to form a peroxy radical. The peroxy radical can attack a lipid molecule to remove a hydrogen atom to form a hydroperoxide in process. The peroxide values of selected vegetable oils are quantified and collected in Table 3.2.

Table 3.2   Peroxide value (*PV*) of vegetable oils.

Item	Raw Material	*PV* meqO$_2$ /kg fat
1	Coconut oil	1.50
2	Palm oil	3.57
3	Rice bran oil	4.76
4	Camellia seed oil	6.25
5	Soybean oil	6.35
6	Castor oil	7.57
7	Sunflower oil	9.20
8	Corn oil	12.40
9	Olive oil	13.55
10	Cotton seed oil	24.19
11	Sesame oil	24.51
12	Safflower oils	102.30

Peroxide values of sunflower, soybean, palm, rice bran, camellia abele seed, castor and coconut oils without antioxidant are in the range of 1-10 $meqO_2$/kg fat, whereas those of olive, corn, cotton seed, sesame and safflower oils are 13.55, 12.40, 24.19, 24.51 and 102.30 $meqO_2$/kg fat, respectively. The higher proportion of unsaturated fatty chains in oil can be the reason supported these observed results. The kinetics of the oxidative process can be accelerated by light, oxygen or high temperature. Therefore, the promising vegetable oil candidates for lubricant base fluids should have low hydroperoxide value.

The composition of fatty acids in safflower oil includes approximately 13% of monounsaturated, 78% of polyunsaturated, and 9% of saturated fatty acid (Table 1.1). From the amount of unsaturated composition, it shows poor oxidation stability. Safflower oil has peroxide value of 102.30 $meqO_2$/kg fat, indicating that safflower oil was not proper to replace petroleum base stock because of poor oxidation stability.

Sesame oil has 41% of monounsaturated, 45% of polyunsaturated, and 13% of saturated fatty acid with peroxide values of 24.51 $meqO_2$/kg fat while cotton seed oil has approximate 19% of monounsaturated, 55% of polyunsaturated, and 26% of saturated fatty acid (Table 1.1) with the peroxide value of 24.19 $meqO_2$/kg fat. Based upon these obtained data, this vegetable oil cannot be used in lubricant fluids due to their high unsaturated of fatty acid, thus providing poor oxidation stability. As the number of double bond increases, it would become more sites to be susceptible to the abstraction of a hydrogen atom and the autoxidation process can occur at fast rate. Vegetable oils containing a high percentage of monounsaturated fatty acid will typically autoxidize only at high temperature, while the oils containing polyunsaturated will autoxidize at room temperature.

Increased level of hydroperoxide would increase wear during boundary of the oxidation. Increasing wear was also linked to the degradation of triglyceride fatty acids. It was uncertain as to which factor had the most impact either the presence of hydroperoxide or the degradation of triglyceride fatty acid. Vegetable oil will decay during lifetime and applications in lubricant fluid, which the changes of physical and chemical properties have affected on the lubricant performance. Therefore, vegetable oils as base lubricant must have low peroxide value and high oxidation stability property.

The kinematic viscosity at 40° and 100°C, pour point and *PV* of five selected vegetable oils were determined as presented in Tables 3.1 and 3.2. It appears that kinematic viscosity and pour point of coconut, palm, soybean, sunflower and rice bran oils have the properties very closed to petroleum base stock. These vegetable oils exhibited the qualities closed to that in common lubricant used. Long polar fatty acid chains provide high strength lubricant films that interact strongly with metallic surfaces, reducing both friction and wear. The strong intermolecular interactions are also resilient to change in temperature providing a more stable viscosity, or high viscosity coefficient.

A *PV* value in this work was found in the range of control *PV* value at 1- 10 meqO$_2$/kg fat. Moreover, prices of five vegetable base oils selected are not high-price. With this reason, it is interesting to explore whether these vegetable base oils can replace base oils from crude petroleum stock.

3.3 Oxidation stability

Antioxidants are additives to protect base oil deteriorate from the ravages of oxidation. Oxidation is a free radical process that the mechanism is broken down into three steps: initiation, propagation and termination. The oxidation process begins with the generation of alkyl free radicals under hard conditions such as high temperature or in the presence of metal catalyst. Oxidation reaction was impaction to lubricant fluid; the effect of oxidation caused high viscosity in lubricant due to base oil thickener, which impact of increase acidic value in oil. There are three classes of additives including radical scavenger, peroxide decomposer and multifunctional additives. Chain breaking antioxidants react with radicals to form stable compounds and prevent propagation of the oxidation reaction.

The oxidation tests were comparatively performed using neat vegetable oil and vegetable oil with ZDDP, ZDDC, diphenylamine and polymeric ester antioxidants as presented in Figs 3.1 and 3.2. The test temperature at 85°C was selected which is suitable for hydraulic application. TAN or acid value measures the amount of acidic substance in the oils. The acidic characteristics of most of the oxidation products generally caused danger corrosion. The impact of alkylperoxy radicals on the metal

surface is caused for corrosive wear. As a result, these additives were selected for use in the vegetable oil in this study.
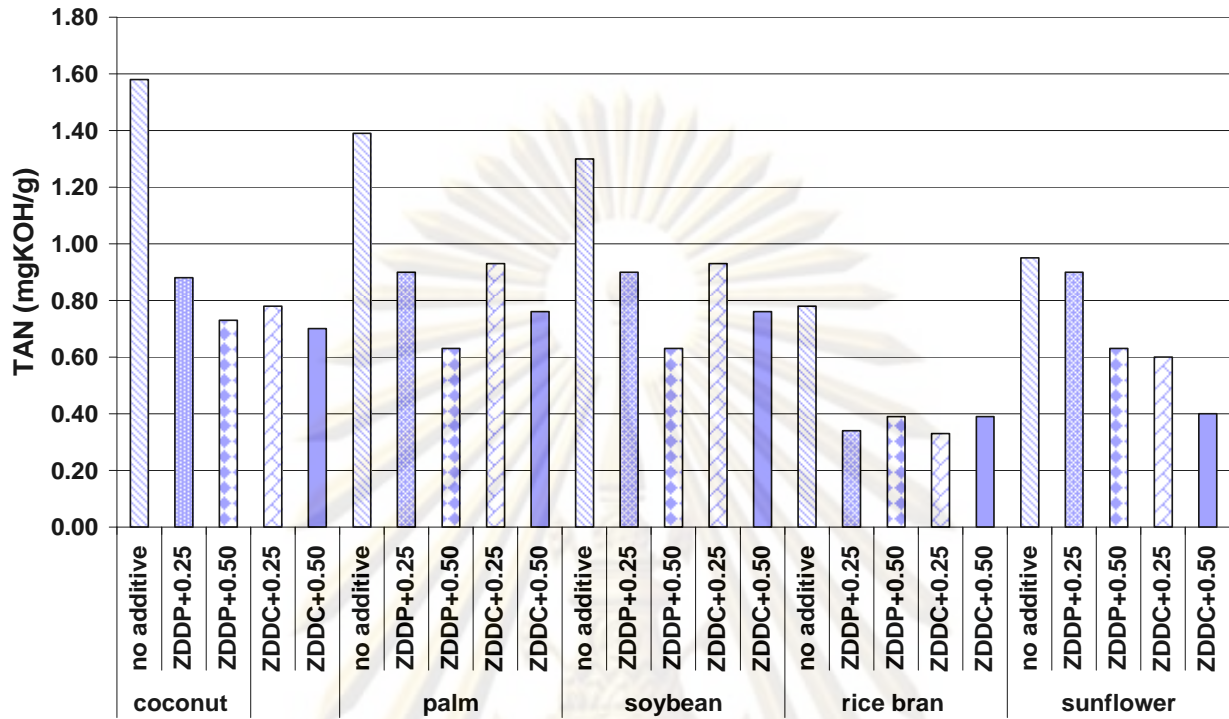
Figure 3.1 Total acid value of vegetable oil added ZDDP and ZDDC test at 85°C for 28 days.
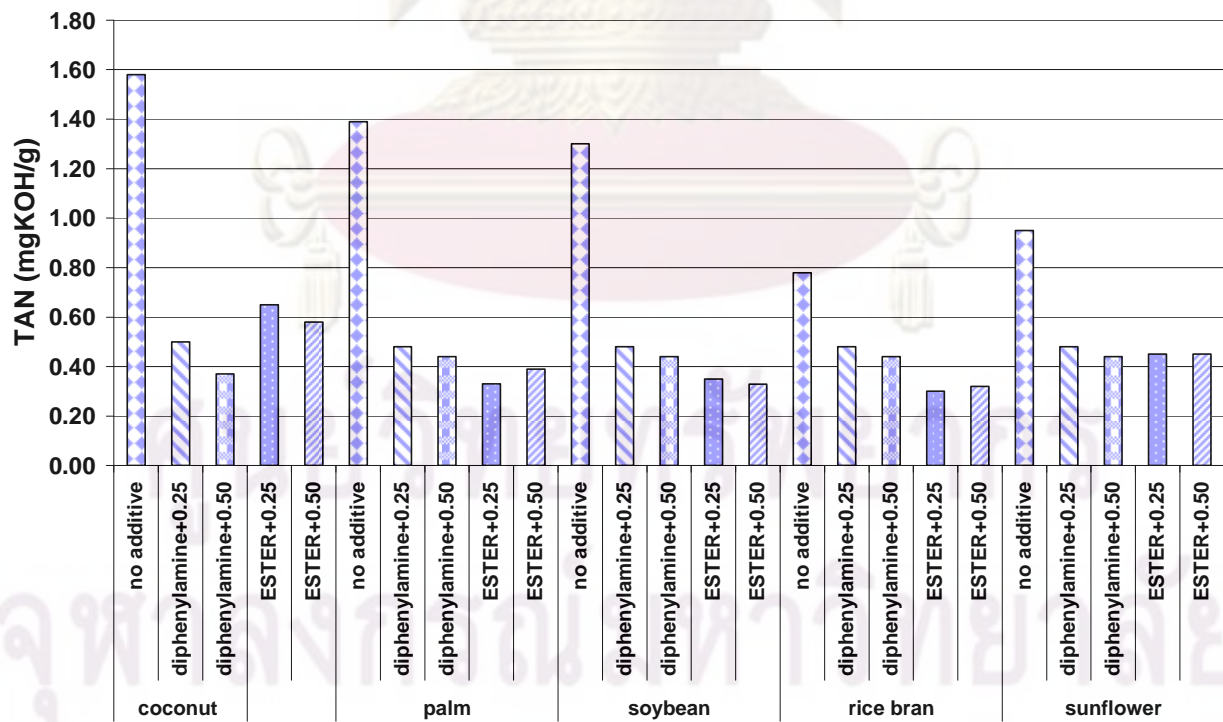
Figure 3.2 Total acid value of vegetable oil added diphenylamine and polymeric ester test at 85°C for 28 days.

3.3.1 Zinc dialkyldithiophosphate (ZDDP)

The total acid values of selected vegetable oil adding ZDDP at 85°C for 28 days are presented in Fig 3.1. The total acid values of coconut, palm, soybean, rice bran and sunflower oils in the presence of 0.25% ZDDP are 0.88, 0.90, 0.90, 0.34 and 0.90 mgKOH/g. Increasing the amount of ZDDP to 0.50%, the total acid values are 0.73, 0.63, 0.63, 0.39 and 0.63 mg KOH/g respectively.

ZDDP's are a family of coordination compounds that feature zinc bound to the anion of dithiophosphoric acid as shown in Fig 3.3.
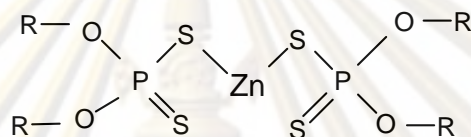
Figure 3.3 Structure of zinc dialkyldithiophosphate.

The alkyl groups can be either branch or linear alkanes between 1-14 carbons length, 2-butyl, 1,3-dimethylbutyl, heptyl, octyl, isooctyl(2-ethylhexyl), 6-methyl heptyl, 1-methylpropyl and dodecylphenyl. The mechanism of ZDDP as antioxidant can be illustrated by the following reactions:

$$[(RO)_2PS_2]_2Zn + ROOH \rightarrow [(RO)_2PS_2]ZnOH + (RO)_2PS_2\bullet$$

$$(RO)_2PS_2\bullet + ROOH \rightarrow (RO)_2PS_2H + ROO\bullet$$

$$[(RO)_2PS_2]_2Zn + ROO\bullet \rightarrow RO_2^- + (RO)_2PS_2Zn^+\bullet + (RO)_2PS_2\bullet$$
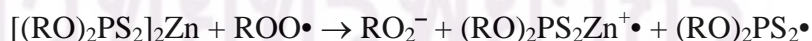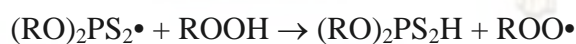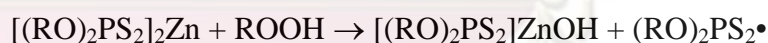
The mechanism of the oxidation inhibition by ZDDP involves complex interactionsbetween alkylperoxy radicals, organic hydroperoxides and intermediate decomposition products of initial compounds. Comparing the result of neat oil with the vegetable oils with additive, it was found that in the presence of 0.5% ZDDP, the oxidation stability of vegetable oils increased.

3.3.2. Zinc dialkyldithiocarbamate

As shown in Fig 3.1, the total acid values of coconut, palm, soybean, rice bran and sunflower oils with 0.25% additive are 0.78, 0.93, 0.92, 0.34 and 0.60 mgKOH/g. The total acid numbers of those mentioned vegetable oils in the presence of 0.50 % additive are 0.70, 0.76, 0.76, 0.39 and 0.40 mgKOH/g.
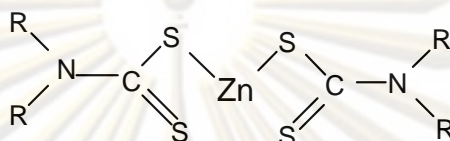
Figure 3.4 Structure of zinc dialkyldithiocarbamate.

$$[R_2NCS_2]_2Zn + ROOH \rightarrow R_2N\!\!-\!\!CS_2ZnS\!\!=\!\!OC\!\!=\!\!SNR_2$$

$$ROOH \rightarrow\rightarrow RN\!\!=\!\!C\!\!=\!\!S + SO_3/ H_2SO_4$$
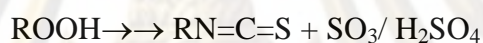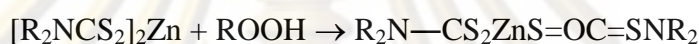
ZDDC was claimed as a hydroperoxide decomposer. It converts the hydroperoxide formed during the oxidation process to nonradical products, thus preventing propagation. From this study, the oxidation inhibition process was very effective at 0.5% ZDDC.

3.3.3 Aromatic amines

The oxidation stabilities of neat oil and those of vegetable oils with the addition of additives are compared as presented in Fig 3.2. The oxidation stability performance in the presence of 0.25% and 0.50% of diphenylamine additive was compared. The results revealed that the addition of 0.5% diphenylamine in vegetable oil was an efficient antioxidant in vegetable oils. The reaction of diphenylamine is dependent on temperature. At low temperature, the interaction with peroxyl radicals predominated as presented in Figure 3.5.
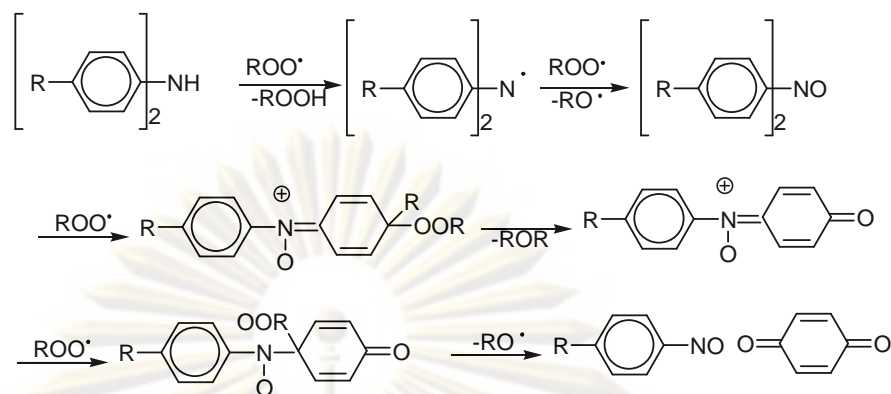
Figure 3.5 Reaction mechanism of diphenylamine compound.

According to Fig 3.5, the reaction of one diphenylamine molecule eliminates four peroxy radicals. By definition, the stoichiometric factor is four. Hence, diphenylamines perform as good peroxy radical scavengers at temperature less than 120 °C.

3.3.4 Polymeric ester

From the data obtained, with polymeric ester at 0.50%, the antioxidant behavior is good. The total acid values with polymeric esters at 0.25 and 0.50% weight are in the range of 0.20 to 0.60 mg KOH/g. Hence, polymeric ester performs as an excellent antioxidant preventing the oxidation of lubricants from vegetable oils. Using four mentioned antioxidants, the trend of oxidation stability was increased when the amount of the added antioxidant increased. However, the use of 0.75% antioxidant, the outcome result did not reveal any significant difference. Therefore, only 0.50% of antioxidant was required. Furthermore, diphenylamine was found to be the best antioxidant comparing with other antioxidants examined.

3.4 Thermal oxidation stability of vegetable oil

When vegetable oil was treated at high temperature or heating for a long time, the color of the oil was turned to dark, probably due to the oxidation. This phenomena could be visualized from the increment of total acid number. The oxidation products

were formed by thermo-oxidation degradation of the oil, and oxidation occurred due to the inherent unsaturated of vegetable oils.

In this research, the controlled conditions were at 150°C for 1,000 h, the results demonstrated the relationships between the acid values and the heating time for vegetable oil added 0.5 % polymeric ester and diphenylamine that revealed the acid value of oil when heat and time of the reaction were increased and accelerated. In addition, thermo-oxidative stability was investigated to evaluate the antioxidant performance of vegetable oils containing diphenylamine and polymeric ester at high temperature.

The thermo-oxidative degradation of vegetable oil is similar to that of the petroleum base stocks. In primary step, triglycerides are cleaved thermally forming radicals; these radicals react with oxygen and become peroxides. The primary antioxidants trap the formed radical, whereas secondary antioxidant was involved with the decomposition of peroxides. In the second step, oligomer forms sludge and deposits. It is important to determine effectiveness of this antioxidant.

Figs 3.6 and 3.7 display the total acid value of vegetable oil with the addition antioxidant after heating at 150°C for 1,000 h. The total acid number of coconut and palm oil with the addition of diphenylamine was increased after 600 h, while those of rice bran, soybean and sunflower oils were increased after 200 h. On the other hand, when vegetable oils were combined with polymeric ester, the total acid numbers were increased after 200 h. From these obtained results, diphenylamine was disclosed to be the most effective antioxidant for high-temperature oxidation. The difference in antioxidant properties at high temperature was related to the mechanism of the additive and the structure of vegetable oils.
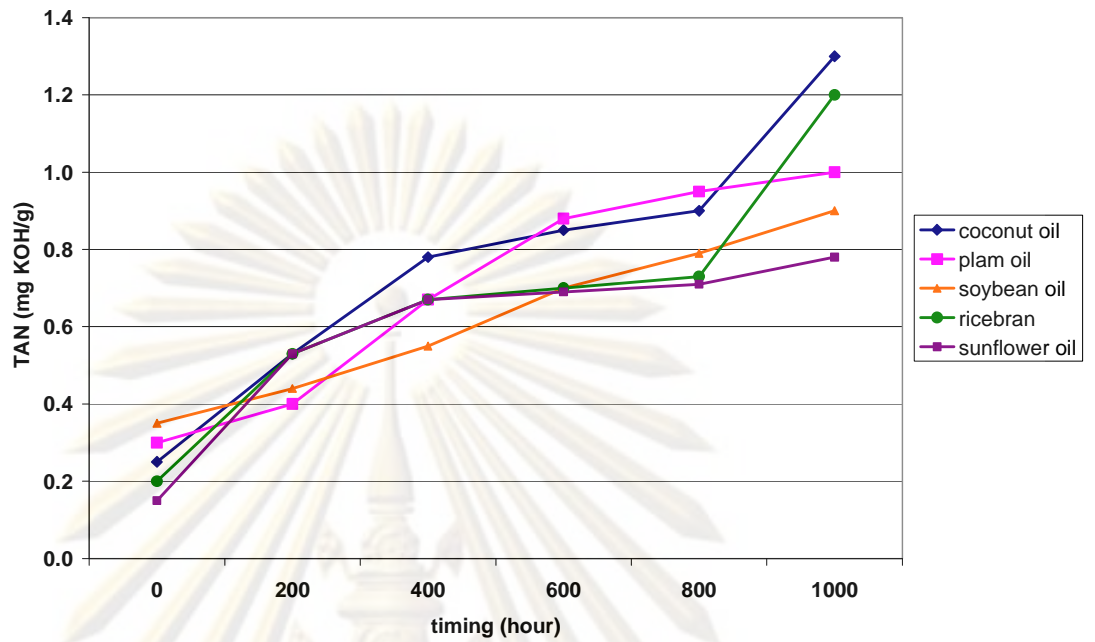
Figure 3.6 Total acid value of vegetable oil with the addition of polymeric ester.
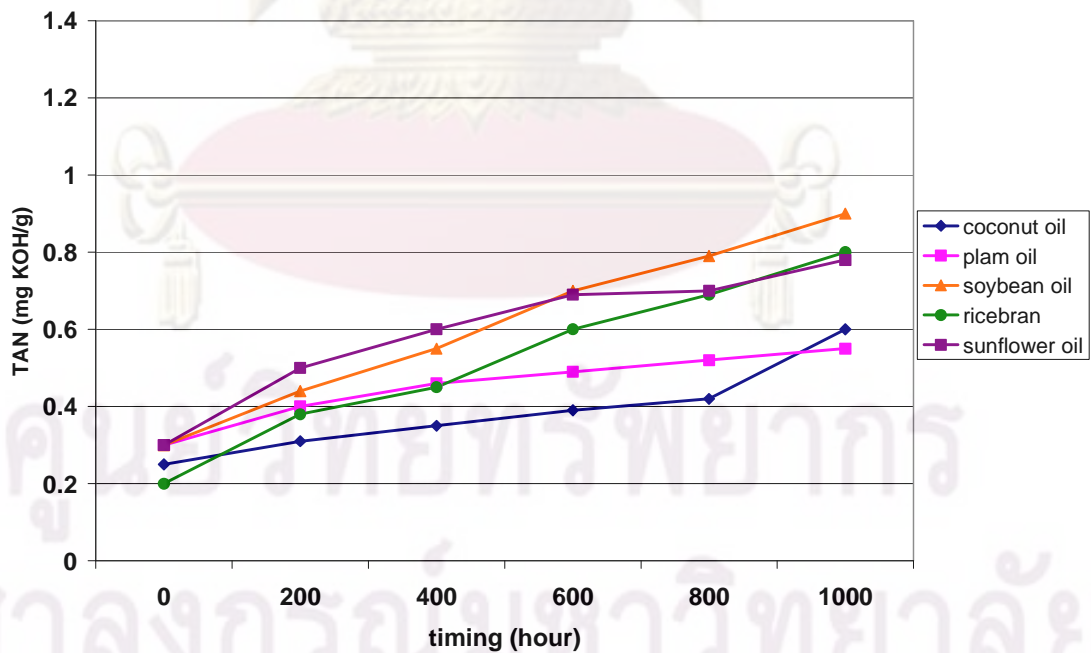
Figure 3.7 Total acid value of vegetable oil with the addition of diphenylamine.

Vegetable oils containing a high percentage of monounsaturated fatty acid will typically autoxidize only at high temperature, whereas those comprising of poly-unsaturated will autoxidize initially at room temperature. Additionally, diphenylamine performs as peroxy radical scavenger at low temperature <120°C and high temperature > 120°C.

As mentioned earlier, the oxidation of oils undergoes three oxidation stages, the first stage is the inhibition period. The inhibition period is predominantly affected by temperature and concentration of antioxidant. The second stage is the breakdown stage, in which the oxidation is not influenced by antioxidant. The most effect on oxidation rate can be observed in its compositions and properties.

The final oxidation stage can be characterized by a slow oxidation rate due to a high oil viscosity. Oil contains a high concentration of oxidation product which can partly be a polymerization of oil. Oxidation products are acidic and can give rise to corrosive attack. Furthermore, the oxidation of oil leads to the increment of viscosity and polymerization leads to the formation of varnish and sludge deposit. The results of kinematics viscosity and VI of certain vegetable oils in the presence of antioxidant are displayed in Tables 3.3 and 3.4.

Table 3.3 Viscosity characteristics of certain vegetable oils in the presence of antioxidant

SAMPLE	Kinematic Viscosity (cSt)		VI
	at 40°C	at 100°C	
Oil-Cox	38.70	9.00	225
Oil-Pox	39.00	8.20	192
Oil-Rox	39.52	8.11	185
Oil-Sbox	41.53	7.64	155
Oil-Snox	40.15	9.38	228

Oil-Cox is coconut oil, Oil-Pox is palm oil, Oil-Rox is rice bran oil, Oil- Sbox is soybean oil and Oil-Snox is sunflower oil.

Table 3.3 presents the viscosity characteristics of vegetable oils combined with 0.5% diphenylamine which was similar to those of native vegetable oils. Viscosity at 40°C is in the range from 38 to 42 cSt and viscosity at 100°C is about 8 to 9 cSt.

Table 3.4 Viscosity characteristics of vegetable oils after oxidation test

SAMPLE	Kinematic Viscosity (cSt)		VI
	at 40°C	at 100°C	
Oil - Cox	45.16	10.05	218
Oil- Pox	49.53	11.70	240
Oil- Rox	49.81	12.18	251
Oil- Sbox	59.67	13.32	232
Oil- Snox	63.40	15.10	254

Oil-Cox is coconut oil, Oil-Pox is palm oil, Oil-Rox is rice bran oil,
Oil-Sbox is soybean oil and Oil-Snox is sunflower oil.

The viscosity characteristics after the oxidation test are listed in Table 3.4. The viscosity at 40°C is in the range from 45 to 49 cSt, except for Oil-Sbox and Oil-Snox having the viscosity more than 50 cSt. While the viscosity characteristics at 100°C was about 10 to 15 cSt.

The physical properties of the vegetable oils after oxidation test are displayed in Figs 3.8 and 3.9. The viscosity at 40°C of Oil-Cox, Oil-Pox and Oil-Rox are increased by 17, 27 and 26%, respectively, while the viscosity change of Oil-Sbox and Oil-Snox increased to 44 and 57%. In addition, the viscosity at 100°C of Oil-Pox, Oil- Rox, Oil- Sbox and Oil- Snox was found to increase from 40 to 74%. The only exception could be seen from Oil-Cox whose viscosity was lower than other oil.
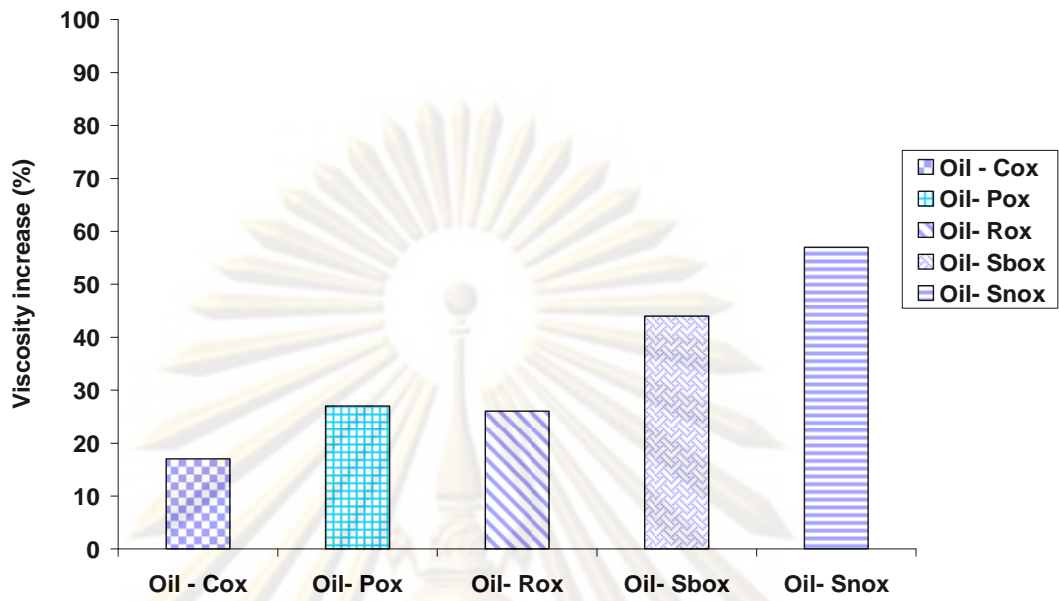
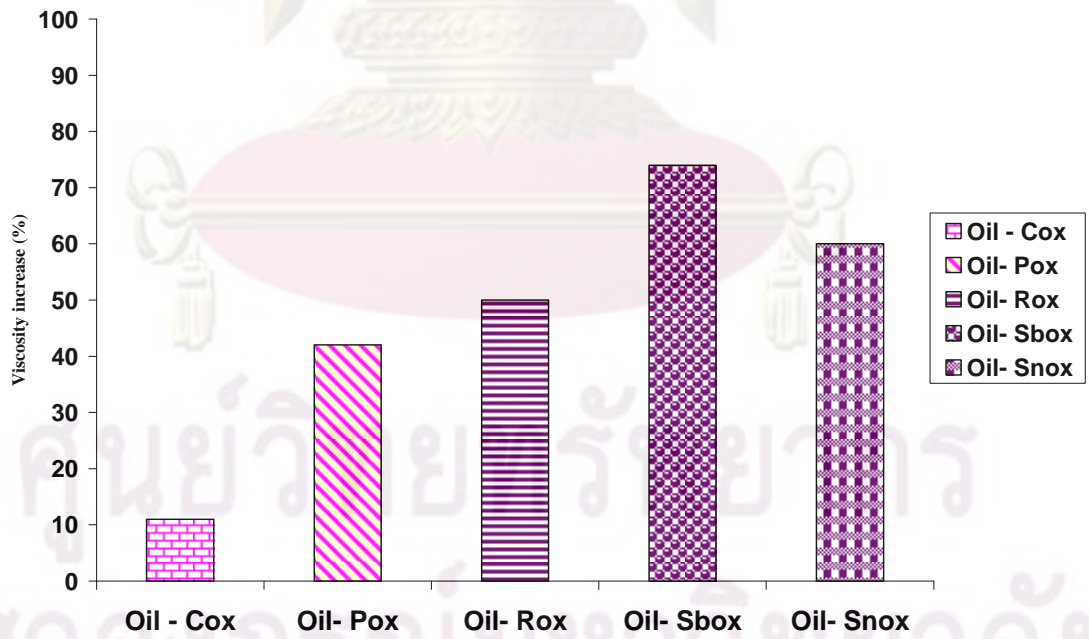**Figure 3.8** Viscosity increase at 40°C after thermal oxidation test.

Figure 3.9 Viscosity increase at 100°C after thermal oxidation test.

The measurement of internal friction in a fluid is viscosity. It is one of the most important properties for characterization of lubricants. The viscosity and TAN have chosen to describe the degree of aging of the hydraulic lubricants.

The oxidation stability of oils by viscosity measurement affected on the thermal oxidative. Their degradation during thermal and oxidative aging can lead to a viscosity decrease while low or moderate extent of oil oxidation proceeds. That effect could be observed more pronounced at high temperatures of viscosity measurement. The viscosities at 40 and 100°C were increased indicating of the degradation of vegetable oils at high temperature. The coconut, palm and rice bran oils displayed higher oxidative stability than soybean and sunflower oils.

Although vegetable-base lubricant is a potential lubricant, its main drawback is its narrow range of available viscosities. The viscosity test result in thermal oxidative showed that Oil-Snox had a higher viscosity than the other oils. The high viscosity of Oil-Snox can be explained due to the presence of polyunsaturated triglyceride.

3.5 Formulation of hydraulic lubricant from vegetable oils

The formulation of hydraulic lubricant from vegetable oils is presented in Table 3.5.

Table 3.5 Composition of hydraulic lubricant

Sample	Description
Oil- HP	Palm oil 98.9% + diphenylamine 0.5% + AW 0.6 %
Oil- HC	Coconut oil 98.9% + diphenylamine 0.5% + AW 0.6 %
Oil- HS	Soybean oil 90.9%+Castor oil 8% + diphenylamine 0.5% + AW 0.6 %
Oil- HR	Rice bran oil 95.9%Castor oil 3% + diphenylamine 0.5% + AW 0.6 %
Oil - HSF	Sunflower oil 98.9% +diphenylamine 0.5% + AW 0.6 %

Table 3.5 describes the formulation of hydraulic oil from vegetable oil, which is the combination between vegetable oil with diphenylamine as antioxidant and commercial antiwear (AW) additive.

3.6 Characteristic of hydraulic lubricants from vegetable oils

The characteristics of the formulated hydraulic lubricants from vegetable oil are exhibited in Table 3.6.

Table 3.6 The characteristics of hydraulic lubricants from vegetable oil

Characteristics	ASTM	OIL - HC	OIL - HP	OIL - HS	OIL-HSF	OIL-HR	COM-HYD
Kinematic viscosity at 40°C(cSt)	D445	42.67	38.79	41.5	40.5	39.05	46.08
Kinematic viscosity at 100°C(cSt)	D445	7.51	8.32	6.8	6.86	8.33	6.64
Viscosity Index	D2270	144	198	120	128	197	95
Flash point (°C)	D92	268	215	200	190	190	212
Pour point (°C)	D97	-12	-15	-10	-9	-15	-18
TAN (mg KOH/ g)	D664	0.427	0.38	0.301	0.573	0.33	0.327
Cu strip corrosion	D130	1a	1a	1b	1a	1a	1a
Four ball wear (mm)	D2266	0.38	0.32	0.35	0.335	0.29	0.305
Foam tendency	D892						
Sequence I (mL)		75/10	90/20	100/30	75/10	50/30	50/10
Sequence II (mL)		75/10	90/10	100/30	80/0	50/10	50/0
Sequence III (mL)		75/10	90/20	150/30	75/10	50/30	50/10

From the data obtained, the viscosities at 40 and 100°C of sample showed similar characteristics to that derived from the hydraulic lubricant petroleum base. As shown in Table 3.6, the oil sample exhibited higher VI value. The higher viscosity index of sample could be explained by the fact that the vegetable base oil contained triglyceride that maintained stronger intermolecular interactions when temperature was increased. It may be possible to provide more evidence regarding hydrogen bonding among the triglyceride molecules in oil sample, hence higher viscosity index was observed. Additionally, this formulated oil exhibited excellent lubricity and viscosity-temperature properties in the same level as commercial industrial oils.

3.6.2 Flash Point

Table 3.6 shows the flash point of oil sample blended with antioxidant and antiwear additive. Flash point properties of sample were lower than neat vegetable oils. Even though the sample had low flash point, that property is almost the same as that of hydraulic oil derived from petroleum base. This property also indicated low volatility of lubricant.

3.6.3 Pour point

As presented in Table 3.6, the hydraulic lubricants made from vegetable oils had a pour point of -9 to -15°C. According to pour point test, at low temperature, the sample has poor pour point properties. This would limit its use at low operating temperature in industrial oil.

3.6.4 Effect of antioxidant and antiwear

Table 3.6 displays the oxidation stability of hydraulic oils as evaluated by total acid number in oven test at 85°C for 28 days. This study was focused on the effect of an additive, which was the combination of 0.5% diphenylamine as antioxidant and 0.6% ZDDP as antiwear additive. The effectiveness of this additive combination was the increment of the oxidation stability of hydraulic lubricant. ZDDP has reported to function both as radical scavenger and hydroperoxide decomposer. The mechanism of the oxidation inhibition appeared to be very effective. The possible reason was possibly by the synergism between antioxidant and antiwear additive.

The TAN's of hydraulic lubricant from vegetable oil are in the range of 0.3 to 0.5 mg KOH/g. This result is not different from commercial hydraulic oil. Under the test conditions of the oven oxidation test, the additive combination used in this study act as an excellent additive by preventing the oxidation of hydraulic lubricants from vegetable oils.

3.6.5 Tribological characteristics

When two contacting parts of machinery start to move and the hydrodynamic lubrication has not yet built up or in the case of severe stress and strong forces, the lubricating system runs in the area of mixed friction. The effect of ZDDP addition on

the antiwear properties is evaluated by standard Four- Ball friction test. This study investigated tribological properties of hydraulic bio-base as shown in Table 3.6. The wear scar diameter of OIL-HC, OIL-HP, OIL-HS, OIL-HSF and OIL-HR were 0.38, 0.32, 0.35, 0.34 and 0.29 mm, respectively. From this data, the sample OIL-HR is excellent lubricity.

3.6.6 Foam tendency

Surface foaming occurs when the air release speed is greater than the speed at which the bubbles at the surface of the fluid collapse, *i.e.* more bubbles are created more than collapse. In the worst cases, this foam can be forced out of tank vents or opening or can be drawn into the pump. Foaming behavior defined by DIN 51566. The volume of foam, which gathers on the surface of the fluids is measured as aging time at different temperatures. As displayed in Table 3.6, foam tendency of hydraulic bio-based meets minimum requirement of hydraulic fluids – ISO 6473.

3.6.7 Copper Corrosion

Corrosion tests usually involve bringing the oil sample into contact with a metal surface under control conditions. Discoloration of the metal, change in surface condition or weight loss may be used to measure the corrosion tendency of the oil. The lubricant should not contain components which promote corrosion of metal parts in machine. According to DIN 51579, corrosion to copper can be taken as the form of discoloration or flaking. A ground copper strip is submerged in the fluid to be tested for a given time and temperature. Hydraulic oils are normally tested for 3 h at 100°C. The degree of corrosion are: **1** as slightly discolor, **2** as moderately discolor, **3** as heavy discolor and **4** as corrosion, dark color.

In general, the specification of hydraulic lubricants control copper corrosion should not be over degree number **2**. Table 3.6 presents the copper corrosion behavior of hydraulic lubricants from vegetable oils in **1a** and **1b** classes. From these results, it shows good anticorrosion in this manipulated lubricant.

3.7 Cost evaluation

The comparison of the manipulation cost of hydraulic lubricants from vegetable oil and commercial hydraulic oils is outlined in Table 3.7.

Table 3.7 Cost of hydraulic lubricants from vegetable oils**.**

	component	S.G. 25 °C	THEORETICAL % WEIGHT	%VOLUME	RAWMAT. COST/LT. (BAHT)	VOLUME 1 LT. (BAHT)
Commercial Hydraulic	petroleum base	0.8966	98.75	98.92	45.94	45.44
	Additive	1.0380	1.25	1.08	250.00	2.70
	TOTAL		100.00	100.00		48.15
Oil - HP	Vegetable base	0.9100	98.90	99.50	33.00	32.83
	AW-additive	1.0930	0.60	0.50	230.00	1.16
	Antioxidant	0.9730	0.50	0.47	250.00	1.18
	TOTAL		100.00	100.00		33.99
Oil - HC	Vegetable base	0.9000	98.90	99.50	28.00	27.86
	AW-additive	1.0930	0.60	0.50	250.00	1.24
	Antioxidant	0.9730	0.50	0.47	250.00	1.16
	TOTAL		100.00	100.00		29.10
Oil - HS	Vegetable base	0.9000	98.90	99.50	35.00	34.83
	AW-additive	1.0930	0.60	0.50	250.00	1.24
	Antioxidant	0.9730	0.50	0.47	250.00	1.16
	TOTAL		100.00	100.00		36.07
Oil - HSF	Vegetable base	0.9000	98.90	99.50	40.00	39.80
	AW-additive	1.0930	0.60	0.50	250.00	1.24
	Antioxidant	0.9730	0.50	0.47	250.00	1.16
	TOTAL		100.00	100.00		41.04
Oil - HR	Vegetable base	0.9110	98.90	99.50	45.00	44.77
	AW-additive	1.0930	0.60	0.50	250.00	1.26
	Antioxidant	0.9730	0.50	0.47	250.00	1.18
	TOTAL		100.00	100.00		46.03

Table 3.7 describes the cost evaluation of hydraulic oil from vegetable oil compared with commercial hydraulic oils. From this data, the hydraulic lubricants manipulated from vegetable-based can clearly lessen the cost of production**.**

CHAPTER IV

CONCLUSION

Vegetable oils are a renewable source. Their cost is reasonable compared with petroleum crude oil. The purpose of this research was to manipulate hydraulic lubricants from vegetable oil and to investigate the physical properties compared with the commercial hydraulic lubricants.

Physical properties of vegetable oil were determined by American Society for Testing and Material (ASTM) method. It was found that viscosity and pour point characteristics of coconut, palm, rice bran, soybean and sunflower oils were very close to those of petroleum base stock. The oxidation stability of oil at temperature <120°C, was evaluated by total acid number (TAN). The TAN's of oil in the presence of 0.25 and 0.50% of diphenylamine and polymeric esters were in the range of 0.20 to 0.60 mgKOH/g. The results revealed that polymeric ester and diphenylamine compound were an efficient antioxidant in oil. On the other hand, at >120°C the polymeric ester was low efficient antioxidant in oil, whereas diphenylamine was disclosed to be the most effective antioxidant for high-temperature oxidation.

Compared hydraulic bio-based with commercial hydraulic oils as shown in Table 3.6, it was founded that the viscosity at 40° and 100°C of sample showed similar characteristics to hydraulic lubricant petroleum base. The oxidation stability of vegetable oils with 0.5% diphenylamine revealed excellent preventing oxidation of lubricants. The tribological properties test by Four-ball apparatus was conducted and founded that the wear scar diameter of OIL-HR was 0.29 mm. According to these results, the hydraulic oils derived from rice bran oil have excellent lubricity. The other required properties including flash point, copper corrosion and foam characteristics were measured and found that the blended hydraulic bio-based oils were well fitted with those requirements for hydraulic fluid-ISO 6473

Overture for the future work

Since vegetable oils have poor oxidative stability due to the presence of *bis*-allyic protons, chemical modification of triglyceride is one of the most important tasks necessary to perform to make polyunsaturation part possess better oxidation stability.

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APPENDICES

| **Cu-Strip** | **Oil-HC** | **Oil-HP** | **Oil-HSF** | **Oil-HR** | **Oil-HS** | **Com-HYD** |
| | Class 1a | Class 1a | Class 1a | Class 1a | Class 1b | Class 1a |

Figure 1. Copper strip corrosion test.
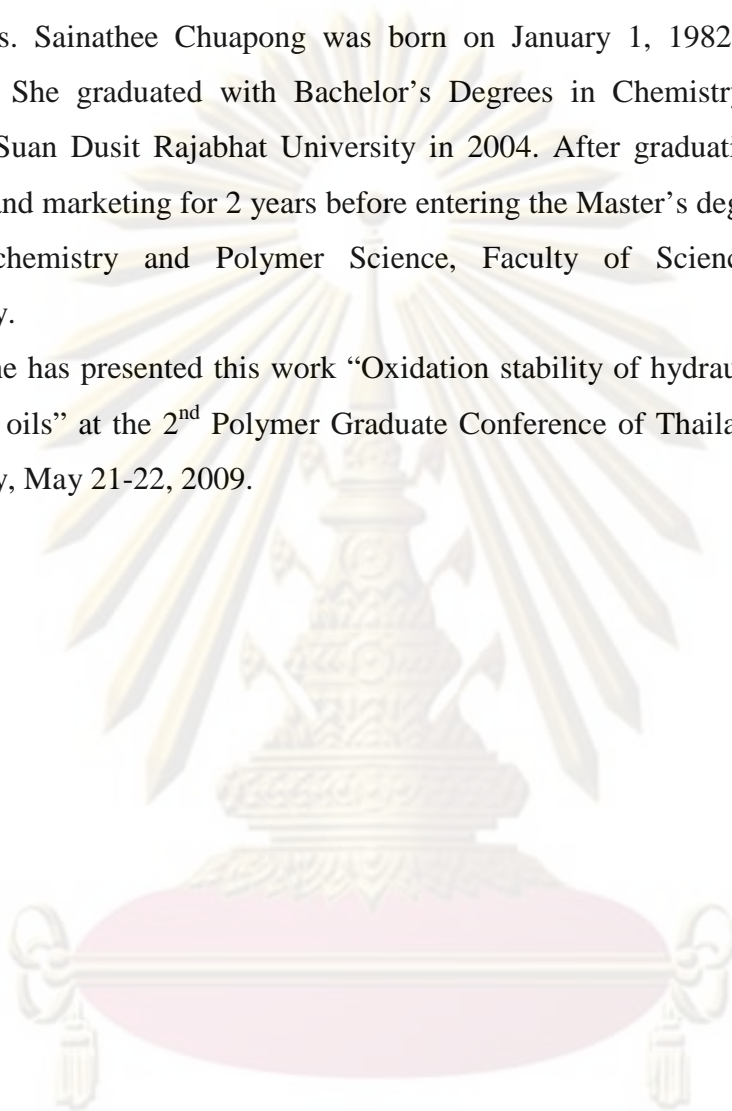
Figure 2. ASTM Copper strip corrosion standards

VITA

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