ผลการเสริมและการต้านต่อเสถียรภาพออกซิเดชันของสารต้านออกซิเดชันในน้ำมันหล่อลื่นพื้นฐานชนิดเอสเทอร์สังเคราะห์

นางสาวสุมิตรา ดวงแก้วมณี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาปิโตรเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2553

SYNERGISTIC AND ANTAGONISTIC EFFECTS ON OXIDATION STABILITY OF ANTIOXIDANTS IN A SYNTHETIC ESTER BASE OIL

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Science Program in Petrochemistry
Faculty of Science
Chulalongkorn University
Academic Year 2010

Thesis Title	SYNERGISTIC AND ANTAGONISTIC EFFECTS ON OXIDATION STABILITY OF ANTIOXIDANTS IN A SYNTHETIC ESTER BASE OIL
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Field of Study	Petrochemistry
Thesis Advisor	Associate Professor Amorn Petsom, Ph.D.

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สุมิตรา ดวงแก้วมณี : ผลการเสริมและการต้านต่อเสถียรภาพออกซิเดชันของสารต้านออกซิเดชันในน้ำมันหล่อลื่นพื้นฐานชนิดเอสเทอร์สังเคราะห์ (SYNERGISTIC AND ANTAGONISTIC EFFECTS ON OXIDATION STABILITY OF ANTIOXIDANTS IN A SYNTHETIC ESTER BASE OIL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. อมร เพชรสม 93 หน้า.

ผลการเสริมและการต้านประสิทธิภาพของสารต้านออกซิเดชันประเภทที่ปราศจากซัลเฟอร์ ฟอสฟอรัส และโลหะหนัก เป็นส่วนประกอบ อันได้แก่ ออกทิล ไดเฟนิลเอมีน, ฮินเดอร์ บิสฟีนอล, ออกทิล เฟนิล อัลฟา แนฟทาลีน และอนุพันธ์ โทลูไทรเอโซล ต่อเสถียรภาพออกซิเดชัน ความเสถียรทางความร้อน คุณสมบัติทางเคมีและกายภาพของน้ำมันหล่อลื่น ไดออกทิล ซีบาเคต จากผลการทดสอบความเสถียรภาพต่อออกซิเดชันด้วยเครื่องโรเททิง บอมบ์ ออกซิเดชัน เทสเทอร์ (RBOT) ได้แสดงถึงการต้านประสิทธิภาพของสารต้านออกซิเดชัน เมื่อมีการเติมออกทิล ไดเฟนิล เอมีน ลงในน้ำมันหล่อลื่น แต่ในน้ำมันหล่อลื่นที่มีการผสมฮินเดอร์ บิสฟีนอล, ออกทิล เฟนิล อัลฟา แนฟทาลีน และอนุพันธ์โทลูไทรเอโซล จะปรากฏผลการเสริมประสิทธิภาพต่อเสถียรภาพออกซิเดชันได้ดีที่สุด นอกจากนี้น้ำมันหล่อลื่นดังกล่าวยังมีความเสถียรต่อความร้อนมากขึ้น เมื่อวิเคราะห์ด้วยเทคนิคเทอร์โมกราวิเมทริก ซึ่งสามารถยืนยันผลการวิเคราะห์ของการเสริมและการต้านต่อเสถียรภาพออกซิเดชันของสารต้านออกซิเดชันในน้ำมันหล่อลื่นได้ด้วยวิธีการของอิเลคตรอน สปิน เรโซแนนซ์ สเปกโทรสโกปี (ESR)

สาขาวิชา ปิโตรเคมี ลายมือชื่อนิสิต
ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

5073891223 : MAJOR PETROCHEMISTRY

KEYWORDS: LUBRICANT ADDITIVE / SYNERGISM / THERMAL STABILITY / ANTIOXIDANTS

SUMITTRA DUANGKAEWMANEE : SYNERGISTIC AND ANTAGONISTIC EFFECTS ON OXIDATION STABILITY OF ANTIOXIDANTS IN A SYNTHETIC ESTER BASE OIL. THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D., 93 pp.

Synergistic and antagonistic effects have been observed with the four sulfur-, phosphorus- and heavy metal-free antioxidants, hindered bis-phenol (HP), octylated diphenylamine (ODPA), octylated phenyl-alpha-naphthylamine (OPANA) and tolutriazole derivative (TZ), on the oxidation stability, thermal and physicochemical properties of dioctyl sebacate base oil. The oxidation stability was evaluated using a rotating bomb oxidation tester (RBOT). The results from isothermal and catalytic oxidation tests suggested that octylated diphenylamine has an antagonistic effect on the oxidation induction time (OIT). The combination of hindered bis-phenol: octylated phenyl-alpha-naphthylamine: tolutriazole derivative exhibited the highest synergistic antioxidant activity. Furthermore, synergism was observed in terms of both oxidation and thermal stabilities through thermogravimetric analysis (TGA).The confirmation has been studied by means of electron spin resonance spectroscopy (ESR) to obtain information on the thermal oxidation mechanism of the synergistic antioxidant.

Field of Study : Petrochemistry .... Student's Signature Sumi
Academic Year : 2010 .... Advisor's Signature ....

ACKNOWLEDGEMENTS

The author would like to express her deepest appreciation and sincere gratitude to her advisor, Associate Professor Dr. Amorn Petsom for providing valuable advice, encouragement and assistance throughout the course of this research. In addition, the author also wishes to express deep appreciation to Professor Dr. Pattarapan Prasassarakich, Professor Dr. Sophon Roengsumran, Associate Professor Dr. Wimonrat Trakarnpruk and Dr. Kunn Kangvansaichol for their valuable suggestion and comments.

The author would like to express special thank to Mr. Motoharu Akiyama and Mr. Ishiguro Sadaki at NMB-Minebea Thai company for their suggestion, helping and teaching her the experimental techniques throughout this work. Moreover, the author would like to thank the Faculty of Science, Graduate School, Chulalongkorn University for financial support. Appreciation is also extended to the Program of Petrochemistry, Faculty of Science, Chulalongkorn University and NMB-Minebea Thai company for providing of experimental facilities.

Gratitude is expressed towards everyone who has contributed suggestions and support throughout this work. Finally, the author is very appreciated to her family and her good friends whose names are not mentioned here for their love, assistance and encouragement throughout her entire education. Without them, the author would have never been able to achieve this goal.

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LIST OF ABBREVIATION

HDD = hard disk drive
FDB = fluid dynamic bearing
NRRO = nonrepeatable runout
PAO = poly alpha olefins
ME = molybdate ester
MC = organic molybdenum complex
DODPA = p,p’dioctyldiphenylamine
DOS = dioctyl sebacate
ODPA = octylated diphenylamine
HP = hindered bis-phenolic
TZ = tolutriazole
OPANA = octylated phenyl-alpha-naphthylamine
TCP = tricresyl phosphate
ZDTP = zinc dialkyldithiophosphate
PTFE = poly tetra fluoro ethylene
EP = extreme pressure additive
AW = antiwear
s = second
wt = weight
mPa = milliPascal
kPa = kilogram.Pascal
rpm = round per minute
N = Newton
m = meter
cm = centimetre
mm = millimetre
cSt = centistokes
ml = millilitre
g = gram
mg = milligram

mmHg = millimetre of Hg
min = minute
psi = pound per square inch
kgf = kilogram force
Hz = hertz
^{o}C = degree Celsius
ppm = part per million
m/z = mass to charge ratio
Cu = copper
TAN = total acid number
KOH = potassium hydroxide
ASTM = american standard test method
TGA = thermo gravity analyzer
GC/MS = gas chromatography and Mass Spectrometry
SRV = oscillation friction and wear testing machine
RBOT = rotating bomb oxidation tester
ESR = electron Spin Resonance
FTIR = fourier transform infrared spectroscopy
DSC = differential scanning calorimetry
HOT = hot oil oxidation
PMOT = penn state micro oxidation test
TOST = turbine oil stability test
OIT = oxidation induction time
IOT = incipient oxidation temperature

CHAPTER I

INTRODUCTION

The deterioration of lubricants often leads to the buildup of insoluble deposits or sludge and an increased viscosity during use. In order to avoid or temporally delay these problems, lubricants need to possess superior oxidation stability. Therefore, antioxidants are the key additive that protects the lubricant from oxidative degradation, allowing the oil to meet the demanding requirements for use in industrial applications.

In order to meet the latest technical, economical and environmental requirements the lowest possible level of sulfur and phosphorus content of any additive has to be used in the formulation of industrial oils [1, 2]. In order to achieve these increasing demands of lubricating oil properties, synergistic performance of commercial antioxidants using sulfur-, phosphorus- and heavy metal-free organic compounds is desirable in industrial applications. Along these lines, although previous investigations of the role of dissolved oxygen in the synergistic lubrication mechanism of oils containing organic sulfurides by the four-ball tester method revealed that diphenyl disulfide and antioxidant additives exhibited a superior load carrying capacity to that of reactive dibenzyl disulfide when tested at high temperatures and high oxygen contents [3]. In contrast, in two-step constant temperature tests with a high concentration of oxygen, the oil containing antioxidant additives alone showed a better performance than oils containing diphenyl disulfide or dibenzyl disulfide. The oil soluble additive, molybdate ester (ME), blended with dioctyldiphenylamine (DODPA) in poly alpha olefin (PAO) lubricants showed a good oxidative synergism with the DODPA antioxidant, as evaluated by differential scanning calorimetry (DSC) and hot oil oxidation (HOO) tests [4]. Hu *et al.* [5] also prepared and studied an oil soluble sulfur- and phosphorus-free organic molybdenum complex (MC). The antioxidant properties of this MC and methylene bis(di-n-butyldithiocarbamate) (V 7723) containing PAO lubricants, as evaluated by the oxidation induction time (OIT), using DSC and a modified Penn State micro oxidation test (PMOT), were improved and the weight loss was also reduced, by the addition of MC.

From the above reports, it appears that combinations of antioxidants can exhibit good oxidation inhibition at higher temperatures. Moreover, some antioxidants are also reported to have a good synergistic effect with sulfur-containing additives, such as zinc dialkyldithiophosphate (ZDTP), 1,3,4-thiadiazole and dithiocarbamate compounds [6-8]. However, the evaluation of the synergistic antioxidation properties of the group of sulfur- , phosphorus- and heavy metal-free organic compounds, such as octylated diphenylamine (ODPA), hindered bis-phenol (HP), octylated phenyl-alpha-naphthylamine (OPANA) and tolutriazole (TZ), in synthetic ester base oil by the rotary bomb oxidation test (RBOT) is scarce in the current literature. Rather, for the investigation of oil oxidation stability, a large number of reports on the physical and chemical degradation of lubricants, including thin film tests, such as pressurized differential scanning calorimetry (PDSC), DSC or PMOT are known. In contrast, only a few reports on bulk oil oxidation test, such as RBOT or the turbine oil stability test (TOST) are known.

According to the present study, the antioxidation property of four commercial sulfur-, phosphorus- and heavy metal-free organic antioxidants in a synthetic ester base oil was investigated by rotating bomb oxidation tester (RBOT) which this technique was different from other reports [4-5,7-8] which mostly used differential scanning calorimetry (DSC). The advantage and disadvantage points of RBOT and DSC as showed in Table 1.1.

Table 1.1 The advantage and disadvantage points of RBOT and DSC

Differential Scanning Calorimetry (DSC)	Rotating Bomb Oxidation Tester (RBOT)
Simple	Complicate
Less time-consuming	Long time-consuming
Using small volume sample	Using large volume sample
Thermal oxidation	Oxidation representation

Moreover, the confirmation has been also studies by means of electron spin resonance spectroscopy (ESR) to obtain information about the thermal oxidation mechanism of the synergistic antioxidant.

Objectives

To study and evaluate the synergistic and antagonistic effects on oxidation stability of antioxidant additives in synthetic ester base oil.

Scope of the research

Synergistic and antagonistic effects have been observed in several kinds of sulfur- , phosphorus- and heavy metal-free antioxidants as octylated diphenylamine, hindered bis-phenolic, octylated phenyl-alpha-naphthylamine and tolutriazole derivative on oxidation stability, thermal stability and physicochemical properties as additives in dioctyl sebacate (DOS) base oil. The oxidation stability property analysis is investigated through oxidation induction time (OIT) form by using rotary bomb oxidation (RBOT). Furthermore, the good synergistic performance of antioxidant additives will be prepared with addition of 0.5% TCP for finished lubricants and their properties will be assessed and optimized. Finally, the confirmation has been studied by means of electron spin resonance spectroscopy (ESR) to obtain information about the thermal oxidation mechanism of the synergistic antioxidant.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Lubricants

A lubricant is a substance introduced between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective film which allows for two touching surfaces to be separated and "smoothed," thus lessening the friction between them. Lubricants chemically interact with all surfaces so that contact only occurs with the smooth and free lubricant.

Typically lubricants contain 90% base oil and less than 10% additives as shown in Figure 2.1. Vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicone, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc.

Base oil + Additive → Lubricant

Figure 2.1 Typical compositions of lubricant.

Non-liquid lubricants include grease, powders (dry graphite, PTFE, Molybdenum disulfide, tungsten disulfide, etc.), teflon tape used in plumbing, air cushion and others. Dry lubricants such as graphite, molybdenum disulfide and tungsten disulfide also offer lubrication at temperatures (up to 350 °C) higher than liquid and oil-based lubricants are able to operate. Limited interest has been shown in low friction properties of compacted oxide glaze layers formed at several hundred degrees Celsius in metallic sliding systems, however, practical use is still many years away due to their physically unstable nature.

Generally, lubricant can be classified as below.

- Grease lubricant
- Solid lubricant
- Oil lubricant

Grease lubricant [9]

Grease is a lubricant used on the bearings. Grease is used for numerous types of bearings which the reason behind this is its thickness. A poor quality of bearing grease leads to the flow of grease onto the brake linings thereby causing safety hazards. Commonly, grease lubrication is carried out on ball or roller bearings. Grease lubrication exhibits a property of self-sealing which means the contaminants are prevented from entering the bearing.

A grease is lubricating oil thickened with a gelling agent such as a metallic soap or a nonmelting powder. For design simplicity, decreased sealing requirements, and low maintenance, greases are given first consideration for lubricating ball or roller bearings in electric motors, aircraft accessories, household appliances, machine tools, automotive wheel bearings, instruments and railroad and construction equipment. Greases are also a common choice for slow-speed sliding applications and small gear units.

- Oils in greases

Petroleum mineral oils are used in 98-99% of the grease produced. Oils in this viscosity range provide low volatility for long life at elevated temperature together with sufficiently low torque for use down to subzero temperatures.

Higher-viscosity oils up to the 450 to 650 mm^2/s range at 40 °C are employed for some high-temperature greases and for compounding with extreme pressure additives in greases for high-contact stresses at relatively low speeds.

Synthetic oils are employed in about 1-2% of current greases, where their higher cost is justified by unusual temperature conditions or other demands that cannot be met with mineral oil greases.

- Thickeners

Gelling agents used include fatty acid soaps of lithium, calcium, aluminum and sodium in concentrations of 6 - 20 wt%. Lithium soaps predominate with use in about 65% of grease production. Fatty acids employed are usually oleic, palmitic, stearic, and other carboxylic acids obtained from tallow, hydrogenated fish oil and castor oil. The relatively low upper temperature limit of 65 - 80 °C with traditional simple soap calcium and aluminum greases can be raised to the 120 - 125 °C range with new complex soaps. Calcium complex soaps, for instance are prepared by reacting both a high molecular weight fatty acid such as stearic acid and low molecular weight acetic acid with calcium hydroxide dispersed in mineral oil.

Solid lubricant [9]

Solid lubricants are made of lubricant materials, such as graphite or molybdenum. The friction of the solid soft film lubricants does not depend on the temperature, and they do not change to gas or vapor form in the space or terrestrial vacuum environments. Solid lubricants provide thin films of a solid between two moving surfaces to reduce friction and wear, usually for high temperatures, aerospace and other environments not tolerated by conventional oils and greases. The samples of solid lubricant are graphite, molybdenum disulphide, teflon and boron nitride.

Oil lubricant [9]

Oil is used as a lubricant on bearings and it is considered to be very effective. Oil is preferred when the surface speed or the operating temperature of the rollers or balls is high. The speed limits are enforced by the cage design and the size of the bearing. Oil can be used even at higher temperatures and speeds. In general, mineral oils are used as lubricants. Whereas, at very low or very high temperatures, synthetic oils such as synthetic esters, phosphate esters, silicate esters, poly alpha olefins (PAO), poly alkylene glycols (PAG) and ionic fluids are used. The application of oil on the bearings is based on the bearing running speed. For low and medium running speeds of the bearing, splash systems and oil bath are adapted. The circulation systems are adapted for medium running speeds and spraying off or mist is adapted for higher running speeds.

Liquid lubricants may be characterized in many different ways. One of the most common ways is by the type of base oil used. Following are the most common types.

- Mineral oils
- Polyalpha-olefin (PAO)
- Synthetic esters
- Alkylated naphthalenes (AN)
- Silicate esters
- Ionic fluids

The extensive use of esters as lubricants started during Word War II to meet the low temperature requirements of military applications. As a results, the military developed many specifications that require the use of esters. Today, many important industrial lubricating applications use esters because of their many advantages. As already mentioned, some esters show extremely good low temperature properties with most pour points below -30^{o}C. Some ester also possess better temperature-viscosity properties as indicated by their high viscosity index (VI) and show high biodegradability, although results can vary based on the biodegradability test used. Some European nations, concerned about the environment, enacted legislation to require the use of biodegradable lubricants in some applications that resulted in some companies switching to biodegradable lubricants. Currently, the main disadvantage of esters relates to the higher cost when compared with conventional mineral oils. However, ester lubricant applications will likely continue to increase due to their many advantages.

2.1.1 Purpose of lubricants

The resistance motion that is produced between the moving surfaces is reduced to a great extent. Lubricants perform the following key functions.

- Keep moving parts apart
- Reduce friction
- Transmit power
- Protect against wear
- Prevent corrosion

Keep moving parts apart

Lubricants are typically used to separate moving parts in a system. This has the benefit of reducing friction and surface fatigue together with reduced heat generation, operating noise and vibrations. Lubricants achieve this by several ways.
In cases of high surface pressures or temperatures the fluid film is much thinner and some of the forces are transmitted between the surfaces through the lubricant. This is termed elasto-hydrodynamic lubrication.

Reduce friction

Typically the lubricant-to-surface friction is much less than surface-to-surface friction in a system without any lubrication. Thus use of a lubricant reduces the overall system friction. Reduced friction has the benefit of reducing heat generation and reduced formation of wear particles as well as improved efficiency. Lubricants may contain additives known as friction modifiers that chemically bind to metal surfaces to reduce surface friction even when there is insufficient bulk lubricant present for hydrodynamic lubrication, e.g. protecting the valve train in a car engine at startup.

Transfer heat

Liquid lubricants can transfer heat. Liquid lubricants are much more effective on account of their high specific heat capacity. Typically the liquid lubricant is constantly circulated to and from a cooler part of the system, although lubricants may be used to warm as well as to cool when a regulated temperature is required. This circulating flow also determines the amount of heat that is carried away in any given unit of time. High flow systems can carry away a lot of heat and have the additional benefit of reducing the thermal stress on the lubricant. Thus lower cost liquid lubricants may be used. Non-flowing lubricants such as greases & pastes are not effective at heat transfer although they do contribute by reducing the generation of heat in the first place.

Protect against wear

Lubricants prevent wear by keeping the moving parts apart. Lubricants may also contain anti-wear or extreme pressure additives to boost their performance against wear and fatigue.

Prevent corrosion

Good quality lubricants are typically formulated with additives that form chemical bonds with surfaces to prevent corrosion and rust.

2.1.2 Properties of lubricants

- Antioxidant
- Corrosion resistance

- Thermal resistance
- Conductivity
- Viscosity

Antioxidant

By resisting oxidation reaction, bearing lubricants help in preventing damage and also protect the bearings from the corrosive effects of harmful chemicals.

Corrosion Resistance

It is the property that exhibits resistance towards atmospheric corrosion. Bearing lubricants possess higher corrosion resistance.

Thermal Resistance

Thermal resistance refers to the resistance offered by the substance when it is exposed to heat. In general, bearing lubricants have high thermal resistance. The thermal resistance of bearing grease is lower than that of bearing oil thermal resistance.

Conductivity

It is the property of transference of heat. Bearing lubricants exhibit poor conductivity.

Viscosity [10]

Viscosity is defined as the resistance to flow of a fluid under gravity with respect temperature. The viscosity is important property which has effect to friction of bearing and the relationships between friction and oil's viscosity can be shown as equation 2.1

$$F/A = ZN \tag{2.1}$$

$$P = ZN$$

So,

$$\mu = (ZN)/P \tag{2.2}$$

Where, μ denotes friction coefficient

Z denotes dynamic viscosity in mPa.s unit

N denotes velocity in rpm unit

P denotes ratio of friction per moving plate area in N/m^2 unit

F denotes friction in N unit

A denotes moving plate area in m^2 unit

Equation 2.2 is shown the relationships of each factor as shown in Stribeck's curve (Figure 2.2).

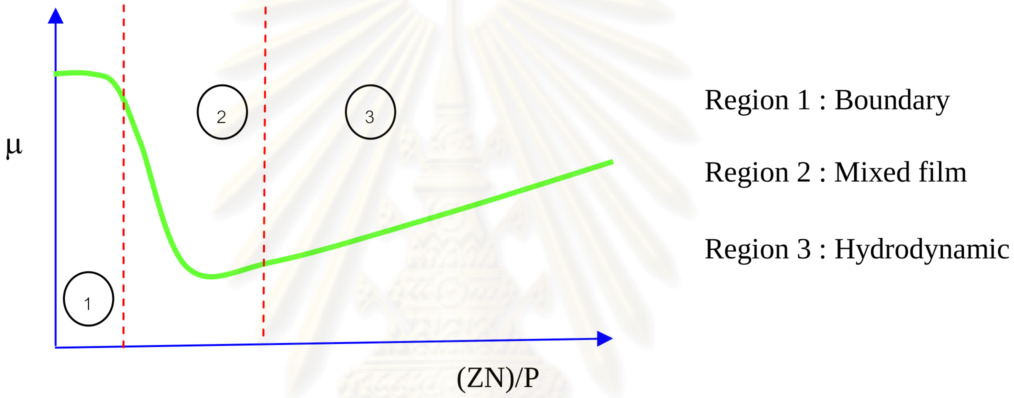

Figure 2.2 Stribek's curve.

The coefficient of friction in a lubricated bearing varies depending upon the absolute viscosity, the speed and the pressure per unit projected area, but has the same general form shown in this 'Stribeck' plot which can be separated lubrication conditions to 3 regions :

Region 1 : Boundary Lubrication

If the speed is very low there will be no pressure build up in the lubricant at all and hence the loading is for 100% carried by the asperities in the contact area, protected by adsorbed molecules of the lubricant and/or a thin oxide layer. Characteristic for boundary lubrication is the absence of hydrodynamic pressure. Dry contact is excluded from boundary lubrication.

Region 2 : Mixed Lubrication

A hydrodynamic pressure is build up in the lubricant when the speed increases. Characteristic for mixed lubrication is that the loading is carried by a combination of the hydrodynamic pressure and the contact pressure between the asperities of both surfaces. It is the intermediate region between boundary lubrication and hydrodynamic lubrication.

Region 3 : Hydrodynamic Lubrication

At high speed the hydrodynamic pressure increases such that the surface asperities are completely separated by a lubricant film. Characteristic for hydrodynamic lubrication is that the load and hydrodynamic pressure are in equilibrium.

Furthermore, oil’s viscosity also has effect to torque property as show the relation by mention to Newton’s law of viscous flow as follows.

Newton’s law of viscous flow [10]

In general, in any flow, layers move at different velocities and the fluid's thickness arises from the shear stress between the layers that ultimately opposes any applied force. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid's viscosity. Laminar shear, the non-linear gradient, is a result of the geometry the fluid is flowing through as illustrated Figure 2.3.

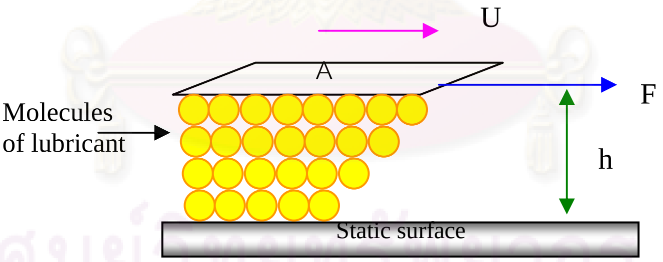

Figure 2.3 Illustration of oil’s flow in linear direction.

2.2 Lubricant additives [9, 24]

Lubricants perform many functions such as some are specific to individual pieces of machinery, other may be required by a whole range of equipment. These functions include dissipation of heat, reduction of friction and wear, detergency, sealing of critical areas, ability to separate water, and many more characteristics essential to proper operation of equipment.

Untreated or nonformulate, lubricants (mineral base stock and synthetic base stock) do not inherently possess the properties required for successful performance in today’s demanding lubrication environments. Base stock fluids need support from chemical additives to perform those functions properly; the proportionally larger base stock component generally provided or enhanced by he use of additive. Additives can also improve the resistance of the base stock to degradation in the presence of oxygen and catalytic materials.

2.2.1 Additive

An additive is material that imparts a new or desirable property not naturally occurring in the lubricant base stock. An additive may also reinforce a desirable property that the base stock already possesses to some degree.

A formulated fluid consists of a base stock and a performance package. The performance package may contain a number of additives that improve the lubricating ability of the base fluid. The quality and quantity of the additives in the performance package may depend also on the quality of the base stock and the use proposed for the finished lubricant.

Lubricant additives can be broadly categorized as either chemically active or chemically inert. Chemically active additives have the capacity to interact chemically with metals to form protective films and with polar oxidation and degradation products to make them harmless. These additives include :

- Dispersant
- Detergents
- Anti wear agents (AW)
- Extreme pressure agent (EP)
- Anti oxidation
- Rust inhibitor
- Corrosion inhibitor

Chemically inert additives improve the physical properties that are critical to the effective performance to the lubricant. These additives include:

- Emulsifiers / Demulsifies
- Pour point depressant
- Foam inhibitor
- Viscosity index improver

2.2.2 History of additives

A history of the use of additives goes back even before the alchemists attempted to change lead into gold some 2000 years ago. Some of the earliest chemists to use additives were the perfume markers, hundreds of year before Christ. Perfume making was one of the earliest industries. The chemists were primarily women who produced products to male the bathing and the odiferous nature of the times more acceptable. Some 2000 to 3000 B.C., Egyptian societies used bitumen and additives for embalming and mummification. Around 1500 B.C. Egyptians may have also used water-based additives to deliver the huge stones to the building sites of the early Pyramids. Most certainly, there were earlier applications involving he lubrication of wheels and axles with the mixtures of animal fats and natural oils. The earliest reported evidence of solid film lubrication were metal inserts in wooden implements found in the middle ages, around 500 A.D. The rapid growth of the additive market in the 1900s is found on Figure 2.4.

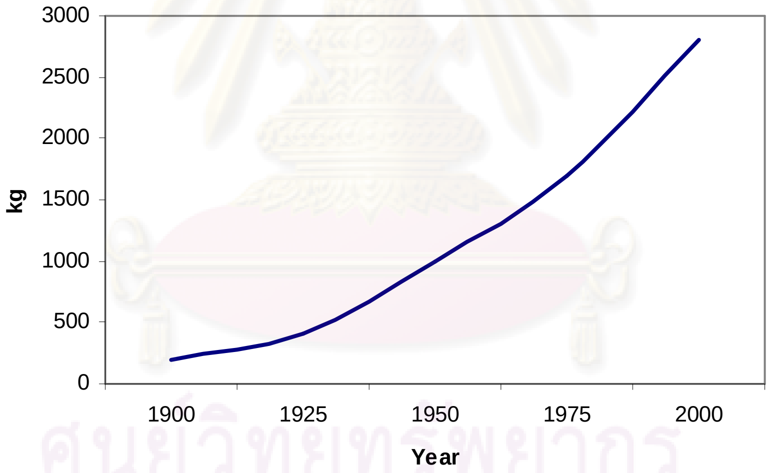

Figure 2.4 Trend of additive growth.

2.2.3 Desire additive properties

Each industry as know it today has its own history and additive culture. For the most part, the types of additives used in different industries can differ significantly. For example, additive used in food processing have different performance and health and safety requirements than they do when use fuels and lubricants in the automotive industry. On the other hand, there are many chemical compounds used as additives in different industries with the same or similar chemical structures. Although most industries have specific performance requirements related to their use of additives, some general requirement of additives apply to all application.

2.2.4 Type of additives

Some of the common types of additives and their functions are shown in Table 2.1 and 2.2. The additives may also be characterized by their functions, i.e., physical interaction or chemical interaction. Those listed as functioning by physical interaction. Table 1, act through physical adsorption-desorption phenomena (pour point depressants, oiliness compounds, color stabilizer), changes in structural from with changes in temperature (VI improver), changes in surface or interfacial tension (antifoam, emulsifier), formation of structures that trap base fluid (thickener, filler), evaporation, partial pressure, or structure bond changes (odorants, color stabilizers).

Those interacting chemically react with the surface or other chemical species in the fluid system. A chemical process can also increase the physical process. Oxidation results in increases in volatility when the antioxidants do not effectively control the oxidation. The oxidation of the base fluid results in degradation, producing smaller molecule that are more volatile than the original molecules.

Table 2.1 Function of additive by physical interaction

Additive	Function
Water stability	Impart water resistance to lubricant
Pour point depressant	Lowers low-temperature fluidity by slowing formation of waxy crystals
Viscosity index improver	Improve viscosity-temperature characteristics
Antifoam	Prevents the formation of stable foam
Emulsifier	Reduce interfacial tension, allows dispersion of water
Thickener	Converts oil into solid or semisolid lubricant
Color stabilizer	Slows darkening of fluids
Oiliness	Improve sliding of surface
Odor control	Prevent or mask undesirable odors or maintain odor level

Table 2.2 Function of additive by chemical interaction

Additive	Function
Antioxidant	Slow oxidation and oil deterioration, increase oil and machine life
Anti corrosion	Protect surfaces against chemical attack
Anti wear	Reduce thin film, boundary wear
Detergent	Keep surfaces clean
Dispersant	Suspend and disperse under desirable combustion, wear, and oxidation products
Oiliness	Reduce friction, increase lubricity
Extreme pressure	Prevent seizing, increase load carrying ability
Metal deactivator	Counteracts catalytic effects of surfaces by passivating surface

Some additives involve both physical and chemical process. Oiliness additives, depending on their structure, can absorb on the surface to form film that reduce friction between the moving surfaces. A polar head adsorbs onto the surface with long slippery hydro carbon chain exposed to the moving surfaces, reducing the friction.

The functional groups of chemically active and inert additives identified above, as well as friction modifiers and other additives, are described more fully as follow.

- Dispersant and Detergent

Dispersants are additives that are used to suspend oil soluble resinous oxidation products and particulate contaminants in the oils. They minimize sludge formation, particulate related wear, viscosity increase and oxygen related deposit formation.

Dispersants ate used primary in gasoline engine oils, heavy duty diesel and railroad engine oils, natural gas engine oil and aviation piston engine oils.

Detergents perform function similar to those of dispersants. Additionally, detergents neutralize acidic combustion and oxidation products, thereby controlling rust, corrosion and resinous buildup in an engine.

Detergents are used in lubricants to keep oil soluble by products of combustion and oil oxidation in suspension. Depending on the end use of the lubricant, insoluble by products can be coke, acidic decomposition products.

- Anti wear and Extreme pressure agents

Wear is a phenomenon occurring in all equipment that has moving parts. Three conditions that can lead to wear are the surface to surface contact that causes frictional wear; the surface contact with foreign matter that produces abrasive materials and corrosion wear; and exposure to corrosive materials or corrosive wear. Abrasive wear and erosion can be prevented by installing an efficient filtration mechanism to remove the offending debris. Corrosive wear can be controlled by using additives that can neutralize the chemically reactive species that attack the surface.

Under normal conditions of speed and load, two metal surfaces are effectively separated by a lubricant film, a condition known as hydrodynamic or thick film lubrication. An increase in load or a decrease in speed reduces the oil film, promoting metal to metal contact and raising the temperature of the contact zone because of frictional heat. As a result, the lubricant loses viscosity which decreases the film forming ability of the lubricant and its ability to minimize metal to metal contact. Under these conditions, the nature of lubricant changes from hydrodynamic to mixed film to boundary or thin film lubrication. Anti wear additives and extreme pressure agents offer protection under mixed film and boundary conditions

Anti wear and extreme pressure additives provide their protection by a similar mechanism; both function by thermal decomposition and by forming products that react with the metal surface to form a solid protective layer. This solid metal alloy film fills surface asperities, thereby reducing friction and preventing welding and surface wear. However, the extreme pressure additives typically require higher activation temperatures and loading conditions than the anti wear additive. Simply stated, anti wear additive perform under mild conditions and extreme pressure additive under severe conditions. The severity of conditions is determined by the load factor. Heavy loading requires extreme pressure additive and mild loading requires anti wear additive.

Since most anti wear and extreme pressure additives contain sulfur, chlorine, phosphorus, boron or combinations. Therefore, lubricants are typically formulated to optimize a balance between anti wear and extreme pressure protection and corrosiveness.

- Friction modifier

Lubrication is essential to facilitate the counter movement of two sliding surfaces. Using friction modifiers can make this function, usually performed by mineral oil these additives control friction, thereby preventing and reducing wear.

Friction modifier are long chain molecule with a polar end group and a non polar hydrocarbon chain. They differ from anti wear and extreme pressure additives in that they form the protective film through physical adsorption instead of chemical reaction. The polar end group physically adsorbs to metal surface, whereas the hydrocarbon chain strengthens the lubricant film through its attraction to the mineral oil. Under heavy load conditions, the extreme pressure additive replaces the friction modifier and assumes the function of damage prevention. As the load eases off. The friction modifier resumes its role. Friction modifiers have a finite life related to their oxygen resistance and thermal stability.

- Corrosion inhibitor

The term of rust and corrosion describe the damage done to metal surfaces by atmospheric oxygen and acidic products. Rates of rust and corrosion, ordinarily low, increase dramatically in the presence of water and polar impurities. Corrosion inhibitor provide a barrier between the metal surface and these harmful elements.

- Emulsifier and demulsifier

Emulsifiers and demulsifiers are basically surfactants with hydrophobic and hydrophilic ends. Emulsifiers are chemical compounds that reduce the surface tension of water, thus facilitating thorough mixing of oil and water and enabling two immiscible fluid to form an intimate are often used as lubricants in many industries for a variety of application. Such lubricants are inexpensive properties. Emulsions of water and mineral oil are chiefly used in metal working and hydraulic applications.

Emulsions have to possess a number of desirable properties. They should be table over long periods of time, possess good lubricating abilities, resist attacking seals and metals and be easy to demulsify for disposal.

Demulsifiers perform the opposite function by enhancing water separation. These materials concentrate at the water oil interface and create low viscosity zones and gravity driven phase separation.

- Pour point depressant

The pour point is the lowest temperature at which a fuel or and oil will pour when cooled under defined conditions. In general, the pour point reflects the amount of wax or straight chain paraffin in oil. At low temperature, wax tends to separate as crystals with a lattice like structure. These wax crystals can trap a substantial amount of oil, inhibit oil flow and impede proper lubrication of the equipment.

Base oil manufactures remove most of the wax during petroleum refining. However, complete dewaxing of the base oils is not practical because of process limitation and economics, not is it desirable. Pour point depressant enable mineral oils to function efficiently at low temperatures.

- Foam inhibitor

Almost every lubricant application involves some kind of agitation which encourages foam formation through air entrainment. Excessive foaming results in ineffective lubrication and over time promotes oxidative degradation of the lubricant. The viscosity of the lubricant and its surface tension determine the stability of the foam. Low viscosity oil produces foams with the large bubble that tend to burst quickly. High viscosity oils, generate stable foams containing fine bubbles that are difficult to break. The presence of surface active materials, such as dispersants and detergents, further increases the foaming tendency of the lubricant.

Foam inhibitors inhibit foam formation by altering the surface tension of the oil and by facilitating the separation of air bubbles from the oil phase. Because these additives generally have limited solubility in oil, they are added as very fine dispersions. Foam inhibitors are effective at low level, e.g. 3-150 rpm.

- Viscosity modifier

The principal function of viscosity modifier is to minimize temperature driven variations in viscosity. The viscosity index, derived from the viscosity of an oil at 40^{o}C and 100^{o}C, was formerly considered an accurate measure of the response of an oil to temperature changes. It is significant today because modern equipment operates at extreme temperature. At these temperatures, viscosities do not conform to those anticipated by the viscosity index.

Viscosity modifiers (Figure 2.5) are typically added to low viscosity oil to improve its high temperature lubricating characteristics. These are organic polymers that minimize viscosity changes with changes in temperature. They offer a practical means of extending the operating range of mineral oil to high temperature without adversely affecting their low temperature fluidity.

At low temperature, when the polymer molecules occupy a small volume and therefore have minimal association with bulk oil, viscosity remains virtually unchanged. However, the situation is reversed at high temperatures because added thermal energy causes polymer chain to expand or lengthen. Their increased surface area facilitates association with the bulk oil, thus slowing the thinning of the oil.

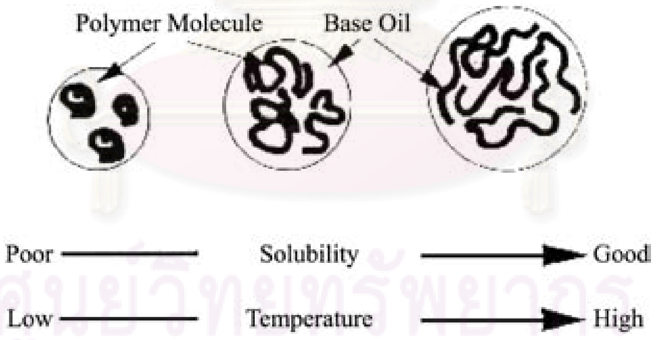

Figure 2.5 Viscosity improver and mechanism of thickening.

Thickening efficiency and shear stability are two important considerations when selecting a polymer for use as a viscosity index improver. The thickening efficiency of a polymer is a direct function of its molecular weight. On and equal weight basis, a high molecular weight polymer offers a higher viscosity than a low molecular weight polymer. Shear stability, the ability of the polymer to withstand the mechanical shearing forces encountered during use, is inversely related to its molecular weight.

In addition to the major classes of additives described above, all lubricants are susceptible to oxidation. Each type of base stock, whether mineral oil or synthetic has a stable threshold, beyond which stabilizer or anti oxidation are need to retard oxidation.

- Antioxidant

In the industrial lubricant sector, antioxidants play a critical role in controlling the level of sludge, acid and deposits that can be generated during use and lead to premature failure. There are two main types of antioxidants that function in different manners. Primary antioxidants donate hydrogen atoms by neutralizing the formation and propagation of reactive radicals. Antioxidant molecules are sacrificed as part of this process and, therefore, become depleted. Examples of primary antioxidants used in the lubricant industry are phenolics and aminics.

Secondary antioxidants represent the other category and are utilized mainly to decompose peroxides into stable products. This antioxidant type is primarily used in plastic resins, such as polyolefins.

Autoxidation is initiated by heat, light (high energy radiation), mechanical stress, catalyst residues, or reaction with impurities. Free radicals are formed and react in the presence of oxygen to form peroxy radicals, which further react with organic material leading to hydroperoxides (ROOH).

As these reactions ultimately lead to a change in chemical composition and such lubricant properties as molecular weight, they have immediate impacts on properties that determine the service life of lubricants. Some results of lubricant degradation are discoloration, viscosity changes, char formation, cracking and loss of adhesion.

The important aspect of this scheme is that once oxidation starts, it sets off a chain reaction that accelerates degradation, unless stabilizers are used to interrupt the oxidation cycle. Under standard aerobic conditions, polymer degradation generally follows two predominant mechanisms.

Antioxidants interrupt the degradation process in different ways, according to their structure. The different mechanisms and families of antioxidants are described in antioxidants families.

Antioxidant families [25]

Antioxidants interrupt the degradation process in different ways, according to their structure. The major classifications of antioxidants are listed below:

Primary antioxidants

Primary or free radical scavenging antioxidants (Figure 2.6) inhibit oxidation via chain terminating reactions. They have reactive OH or NH groups. (hindered phenols and secondary aromatic amines). Inhibition occurs via a transfer of a proton to the free radical species. The resulting radical is stable and does not abstract a proton from the polymer chain.

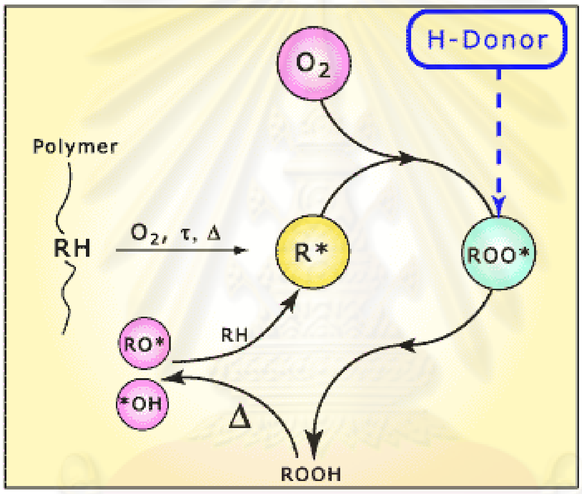

Figure 2.6 Mechanism of primary antioxidants.

Secondary antioxidants

Secondary antioxidants (Figure 2.7), frequently referred to as hydroperoxide decomposers, decompose hydroperoxides into non-radical, non-reactive, and thermally stable products. They are often used in combination with primary antioxidants to yield synergistic stabilization effects.

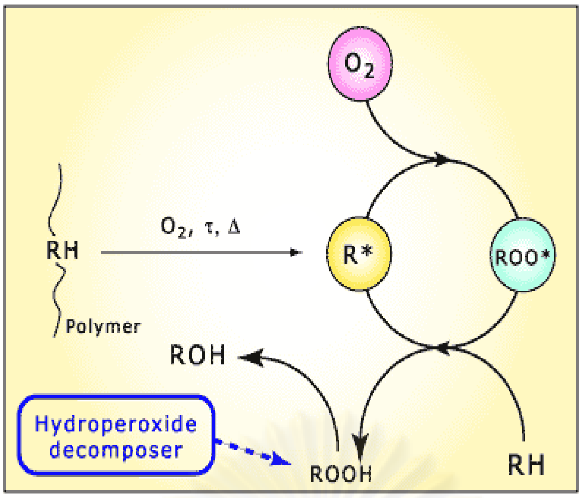

Figure 2.7 Mechanism of secondary antioxidants.

Hydroperoxide decomposers prevent the split of hydroperoxides into extremely reactive alkoxy and hydroxy radicals. Organophosphorus compounds are widely used hydroperoxide decomposers.

Multifunctional antioxidants

Multi-functional antioxidants have only recently become available. Due to their special molecular design, they optimally combine primary and secondary antioxidant functions in one compound. Having several stabilizing functions combined in the same molecule, multi-functional antioxidants eliminate the need for co-stabilizers, such as phosphites and thioethers (Figure 2.8). This not only simplifies the formulation, but it also simplifies the storage, handling, and use of the stabilizer.

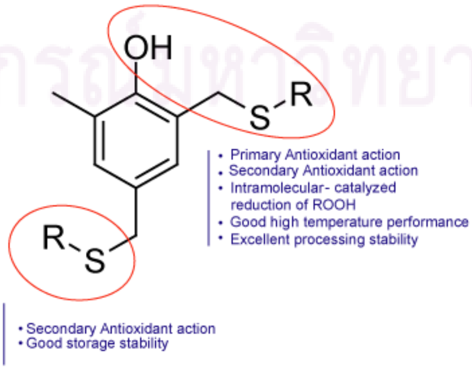

Figure 2.8 Structure of multifunctional antioxidants.

Radical scavengers

Radical scavengers (Figure 2.9) are antioxidants capable of trapping radicals. Scavenging of alkyl radicals would immediately inhibit the autoxidation cycle. Under oxygen deficient conditions alkyl radical scavengers contribute significantly to the stabilization of the polymer. Scavenging the extremely reactive alkoxy and hydroxy radicals is practically not possible.

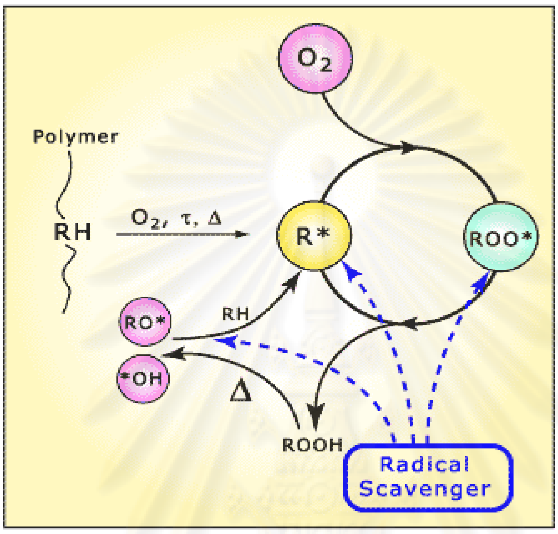

Figure 2.9 Mechanism of radical scavengers.

Carbon centered radical scavengers, such as lactones and acrylated bis-phenols, are extremely effective in oxygen deficient environments.

Benefits of antioxidants

During life cycle of lubricants, their components can undergo degradation. Any one of the factors in the life cycle leads to an undesirable change in physical properties of the unstabilized lubricants, creating manufacturing problems, poor product appearance. The role of antioxidants is to prevent or retard all these undesirable changes.

2.3 Electron spin resonance

Electron spin resonance (ESR) spectroscopy or electron paramagnetic resonance (EPR) or is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion. The basic physical concepts of ESR are analogous to those of nuclear magnetic resonance (NMR), but it is electron spins that are excited instead of spins of atomic nuclei. Because most stable molecules have all their electrons paired, the ESR technique is less widely used than NMR. However, this limitation to paramagnetic species also means that the ESR technique is one of great specificity, since ordinary chemical solvents and matrices do not give rise to ESR spectra.

Theory of an ESR signal

Every electron has a magnetic moment and spin quantum number s = 1/2, with magnetic components ms = +1/2 and ms = -1/2 (Figure 2.10). In the presence of an external magnetic field with strength B_0, the electron's magnetic moment aligns itself either parallel (ms = -1/2) or antiparallel (ms = +1/2) to the field, each alignment having a specific energy. In principle, ESR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant, or doing the reverse. In practice, it is usually the frequency which is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency. By increasing an external magnetic field, the gap between the ms = +1/2 and ms = −1/2 energy states is widened until it matches the energy of the microwaves, as represented by the double-arrow in the diagram above. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, there is a net absorption of energy, and it is this absorption which is monitored and converted into a spectrum as shown in Figure 2.11.

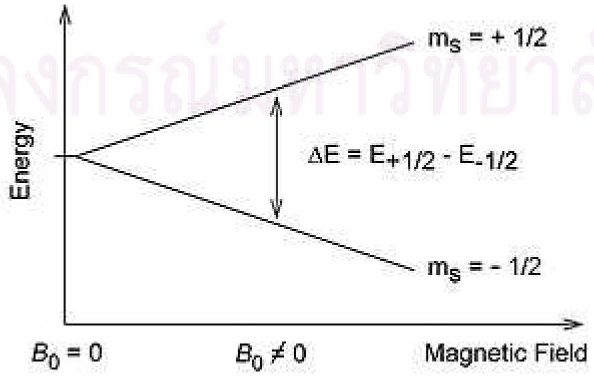

Figure 2.10 The splitting of the energy levels in an external magnetic field.

Figure 2.11 Illustration of ESR spectrum.

2.4 Oil’s properties assessment

In this work, many techniques which were chosen to characterize and test for the properties of lubricant samples will be explained in appendix B.

2.5 Literature reviews

The properties improvement of lubricants are the subject of interest in order to increase the performance of lubricant. Six research groups published works on preparation and analysis of several lubricants and antioxidant additives which are applied for industrial lubricating applications. The first group, Schmid, Bongardt and Wuest [11] prepared a low-viscosity lubricants which their composition stable to high and low temperatures. In their research, the ester oils which are the esterfication product of an aliphatic dicarboxylic acid having 8 or 9 carbon atoms and a branched Guerbet alcohol having from 12 to 20 carbon atoms are found to give good low viscosity at high and low temperatures. The second group, Murakami, Yoshizaki, Hiroshi [3] elucidated the role of dissolved oxygen in the synergistic lubrication mechanism of oils containing organic sulfurides by four ball tester. In their research it is found that in increasing temperature tests, high oxygen concentration with diphenyl disulfide and antioxidant additives exhibited superior load carrying capacity to reactive dibenzyl disulfide with the same antioxidant additives. On the contrary, in two step constant temperature tests, the oil containing antioxidant additives alone with high concentration of oxygen is shown to have better performance than oils containing diphenyl disulfide or dibenzyl disulfide. Weller, et al [12] investigated the effects of chemical structure of synthetic base fluids on friction and wear. They studied the type and number of ester linkages *via* alcohol structure, acid chain length and acid chain branching by using a four ball wear tester. Moreover, they studied properties of synthetic base fluids in the presence of extreme pressure (EP) and antiwear (AW) additives. It was found that the tendency of friction and wear increase when the number of ester linkages is increased. On the contrary, friction and wear decrease when acid chain length is increased. Furthermore, acid with chain branching has been found to increase friction and wear more than linear chain acid. The addition of additives can improve the performance of synthetic base fluids, but it does not overcome the effects from chemical structure. Moreover, Adhvaryu, et al [13] studied the effect of antioxidant to lithium grease microstructures. They found that at the presence of antimony dithiocarbamate used as antioxidant additive in grease produced a soap with looser network and lager fiber structure than similar grease which is not contained additive. Hu, et al [4] synthesized and evaluated performance of an oil soluble additive molybdate ester (ME) that was blended to dioctyldiphenylamine (DODPA) in poly alpha olefin (PAO) lubricants by differential scanning calometry (DSC) and hot oil oxidation (HOO) tester. Their results suggested that the ME is shown to have good oxidative synergism with DODPA antioxidant. Wei, et al [5] prepared and studied an oil soluble sulfur and phosphorus free organic molybdenum complex (MC). The antioxidant properties of MC and methylene bis(di-n-butyldithiocarbamate) (V 7723) containing PAO lubricants were evaluated by DSC and modified penn state micro oxidation test (PMOT). They found that oxidation induction time (OIT) of V 7723 containing PAO is improved and reduced the increase in weight loss by MC addition.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals were obtained from various suppliers as shown in Table 3.1 and they were used as received.

Table 3.1 Sources of chemicals

Number	Chemicals	Company
1	dioctyl sebacate (DOS)	Nye synthetic lubricant
2	octylated diphenylamine (ODPA)	Ciba Co, Ltd.
3	hindered bis-phenol (HP)	Ciba Co, Ltd.
4	tolutriazole (TZ)	Ciba Co, Ltd.
5	octylated phenyl-alpha-naphthylamine (OPANA)	Ciba Co, Ltd.
6	tricresyl phosphate (TCP)	Ciba Co, Ltd.
7	acetone	Merck
8	ethyl alcohol	Merck
9	AK-225	Nagase
10	potassium hydroxide	Merck
11	mixture of toluene-isopropyl alcohol-water	Kanto chemical
12	Hydanal-Coulomat AGH	Ridel-De-Haen
13	silicone oil	Shinetsu, Ltd.
14	hexane	Merck

3.2 Apparatus and instruments

All apparatus used in this experiment are listed in Table 3.2.

Table 3.2 Apparatus used in the experiment

Apparatus	Model	Manufacturer
Kinematic viscosity measurement	403-062	Rigosha Co.,Ltd.
Flash point tester	ACO-7	Tanaka scientific Limited.
Potentiometric auto titrator	APB-410	Kyoto electronics
Karl Fischer Titrator	ADP-611	Kyoto electronics
Pour point tester	RPP-02CML	Rigosha Co.,Ltd.
Density meter	35N	Anton Parr
Thermogravity analyzer (TGA)	TG/DTA220	SEIKO instrument
High-frequency linear-oscillation test machine (SRV)	SRV III	Optimal instruments Co.,Ltd.
Rotary Bomb Oxidation tester (RBOT)	RBOT-2BS	Yoshida Co.,Ltd.
Electron Spin Resonance (ESR)	JES-RE2X	JEOL Co.,Ltd.
Oven	DN410	Yamato scientific Co.,Ltd.
Ultrasonic	5510H	Branson
Analytical balance	GR202	AND

3.3 Finished lubricants preparation

The finished lubricants in the present study had a composition by mass as shown in Tables 3.3 - 3.5. For the purpose of comparison, the finished oils were separated into four groups according to the number of different antioxidant additives in the finished oils. Thus, forty samples of finished lubricants were obtained from twenty-four single, six double and six triple antioxidative compound additions that differed in their various antioxidant additive compositions. The best group of synergistic antioxidant candidates, evaluated from the results of this study as detailed below, were subsequentially blended with 0.5% (w/w) TCP (antiwear) in order to investigate the compatibility between antioxidant and antiwear.

3.3.1 Adding one type of antioxidant additive

Initially, base oil was blended with each type of antioxidant additives with variable percentage as shown in Table 3.3. These finished lubricants were sonicated for 30 minutes. Finally, a completed homogeneity of mixture would be checked by visual inspection.

The finished lubricants were designated as “Sample 1-1” to “Sample 1-24”, respectively.

Table 3.3 Combination of antioxidant in finished lubricants

Sample designation (Group 1)	Additive	
	Name	% amount in base oil (w/w)
1-1	ODPA	0.2
1-2		0.4
1-3		0.5
1-4		0.6
1-5		0.8
1-6		1.0
1-7	HP	0.2
1-8		0.4
1-9		0.5
1-10		0.6
1-11		0.8
1-12		1.0
1-13	OPANA	0.2
1-14		0.4
1-15		0.5
1-16		0.6
1-17		0.8
1-18		1.0
1-19	TZ	0.2
1-20		0.4
1-21		0.5
1-22		0.6
1-23		0.8
1-24		1.0

3.3.2 Adding two types of antioxidant additive

The same as above preparation, finished lubricants were prepared by blending base oil with antioxidant additives. However, in this step base oil was blended with two types of antioxidant additives at 0.5% w/w each.

The finished lubricants were designated as “Sample 2-1” to “Sample 2-6” as shown in Table 3.4.

Table 3.4 Combination of antioxidants in finished lubricants

Sample designation (Group 2)	0.5 wt% of each additive in base oil (Two additives)			
	ODPA	HP	OPANA	TZ
2-1	✓	✓	-	-
2-2	✓	-	✓	-
2-3	✓	-	-	✓
2-4	-	✓	✓	-
2-5	-	✓	-	✓
2-6	-	-	✓	✓

3.4 Investigation of antioxidant additive in finished lubricant on oxidation stability by RBOT instrument

Rotary bomb oxidation test was performed on a RBOT-2BS (Yoshida Company; Japan). The test oil, water and copper catalyst coil, contained in a covered glass container, were placed in a vessel equipped with a pressure gage. The vessel was charged with 99.5% (v/v) oxygen to a pressure gage of 620 kPa, placed in a constant temperature oil bath set at either 100 ^{o}C or 150 ^{o}C and rotated axially at 100 rpm at an angle of 30^{o} from the horizontal. The number of minutes required to reach a drop of 175 kPa in gauge pressure was taken as the OIT of the test sample, and this was used to denote the oxidation stability of the sample.

The finished lubricants *via* group of sample 1-1 to 1-24 and group of sample 2-1 to 2-6, were assessed for their performance of oxidation stability by RBOT.

After investigation on oxidation induction time (OIT) of each finished lubricant, the performance of oxidation stability was assessed using the finished lubricant samples 2-4, 2-5 and 2-6. Therefore, antioxidant additives such as HP, OPANA and TZ were used to blend together in finished lubricants for synergistic performance purpose. Therefore, these additives were selected as potential additive for finished lubricants as explanation in section 3.5.

3.5 Increasing synergistic performance of finished lubricants

3.5.1 Selection of types of antioxidant additives

The potential candidates of antioxidant additive were as follow.

- hindered bis-phenol (HP)
- octylated phenyl-alpha-naphthylamine (OPANA)
- tolutriazole (TZ)

3.5.2 Preparation of finished lubricants:three types of antioxidant additives

Finished lubricants were prepared by mixing HP, OPANA and TZ at various ratio. The total percentage of additive was 1% w/w in DOS base oil. These samples were prepared in the same way as the above method by sonication for 30 minutes and visual inspection to check for completed homogeneity.

The finished lubricant samples were designated as “Sample 3-1” to “Sample 3-6”, respectively.

Table 3.5 Combination of antioxidants in finished lubricants

Sample designation (Group 3)	Ratio with blending in base oil total antioxidant at 1 wt% (Three additives)		
	HP	OPANA	TZ
3-1	0.33	0.33	0.33
3-2	0.25	0.25	0.50
3-3	0.20	0.40	0.40
3-4	0.50	0.25	0.25
3-5	0.40	0.20	0.40
3-6	0.40	0.40	0.20

3.5.3 Properties assessment for finished lubricants

The physicochemical properties of the selected finished lubricants were determined according to the following standard test methods: viscosity-ASTM D445, flash point-ASTM D92, total acid number-ASTM D664, moisture content-D6304, specific gravity-ASTM D4052, pour point-ASTM D97, corrosion test by copper plate method -ASTM D130.

3.5.4 Oxidation stability assessment of finished lubricants

In this step, finished lubricants that blended with three types of antioxidant additives were investigated for their antioxidant property by RBOT instrument at extreme conditions.

Additionally, these synergistic lubricants were investigated for their compatibility with TCP as antiwear additive on OIT by RBOT in a constant temperature oil bath. The effect of TCP additive on oxidation stability of each antioxidant was also observed (Table 3.6).

Moreover, the lubricants with TCP were also investigated for their physicochemical properties using the same test as shown in section 3.5.3. Furthermore, the finished lubricants were investigated for their thermal stability and tribological properties using the following test methods. The properties of synergistic lubricants were compared with the commercial lubricant.

Table 3.6 Combination of TCP and antioxidants in finished lubricants

Sample designation (Group 4)	1 wt% of antioxidant and 0.5 wt% of TCP (Two additives)				
	ODPA	HP	OPANA	TZ	TCP
4-1	✓	-	-	-	✓
4-2	-	✓	-	-	✓
4-3	-	-	✓	-	✓
4-4	-	-	-	✓	✓

Thermal stability

The thermal stability of oil samples under an air atmosphere was investigated by monitoring the incipient oxidation temperature (IOT) by thermogravimetric analyses (TGA) over a temperature range from ambient to about 600 ^{o}C, at a rate of 10 ^{o}C/min using a SEIKO (model TG/DTA220) thermal analyzer.

Tribological properties

Friction and wear tests were carried out on a high-frequency linear-oscillation test machine (SRV), model SRV III made by Optimal Instruments, Germany. This test method, for determining the friction coefficient of the oil-antioxidant mixture with TCP, was used to investigate the ability of the oil to protect the test samples against wear when subjected to a high-frequency linear-oscillation motion. This was carried out using an SRV test machine with a test load of 200 N, a frequency of 50 Hz, a stroke amplitude of 1.00 millimeters, a duration of two hours and a temperature of 50 ^{o}C . The test pieces were 10.3 millimeters of diameter ball, and 24 millimeters x 8.1 millimeters of flat disk which both of them are stainless steel materials (series AISI52100).

The list of test methods for properties assessment of finished lubricants is shown in Table 3.8.

3.6 Half life expectancy of radical by ESR

The half life of radical in the synergistic lubricants was studied by electron spinning resonance (ESR). Samples were prepared by blending the original synthetic ester oil with 0.1 % t-butyl hydroperoxide (initiator) and synergistic additive as shown in Table 3.7. The half life of radical at 150°C was investigated. The condition of experiment was shown below.

1) Microwave unit is X band and frequency is 8.8-9.6 GHz.
2) Type of resonator is cylindrical.
3) Mn^{2+}/MgO is used for calibration. The g-factor of the fourth signal from the lowest magnetic field is known as 1.981 and g-factor of third signal is 2.034.
4) g-factor = 0.071448 x microwave frequency (GHz) / magnetic field (tesla)

Table 3.7 Samples designation for ESR test

Sample	Base oil	Initiator	ODPA	HP	TZ	OPANA	TCP
a	✓	✓					
b	✓	✓	✓				
c	✓	✓		✓			
d	✓	✓			✓		
e	✓	✓				✓	
f	✓	✓	✓	✓			
g	✓	✓	✓		✓		
h	✓	✓	✓			✓	
i	✓	✓		✓	✓		
j	✓	✓		✓		✓	
k	✓	✓			✓	✓	
l	✓	✓		✓	✓	✓	
m	✓	✓		✓	✓	✓	✓

Table 3.8 Test methods for finished lubricants

Test methods	ASTM no.	Appendices
Kinematic viscosity [14]	ASTM D-445	B1
Flash point [15]	ASTM D-92	B2
Total acid number [16]	ASTM D-664	B3
Moisture content [17]	ASTM D-1744	B4
Specific gravity [18]	ASTM D-4052	B5
Pour point [19]	ASTM D-5950	B6
High-frequency linear-oscillation test machine (SRV) [20]	ASTM D-5707	B7
Corrosion test by copper plate method [21]	ASTM D-130	B8
Thermal stability by TGA	-	B9
Oxidation induction time by RBOT [22]	ASTM D-2272	B10

CHAPTER IV

RESULTS AND DISSCUSSION

This research involved the investigation of the synergistic and antagonistic effects of several antioxidant additives with synthetic ester base oil. As proposed in the previous chapter, the results would be shown and discussed in each part, respectively.

4.1 Properties assessment of raw materials

In this research, dioctyl sebacate (DOS) was selected as base oil because it was used to prepare the lubricant for use in FDB spindle motors of hard disk drive (HDD) manufacturing. Therefore, initially the properties of DOS base oil were assessed in several items as represent in Table 4.1. Additionally, the properties of antioxidants and antiwear were also assessed in several items as represent in Table 4.2.

Table 4.1 Properties of DOS base oil

Items	Unit	DOS (CAS no.122-62-3)
Kinematic viscosity at 40°C	mm^2/s	11.84
Total acid number	mgKOH/g	0.05
Flash point	°C	242
Pour point	°C	below -60
Moisture content	ppm	225
Specific gravity	-	0.914
Oxidation induction time by RBOT	minute	50
Corrosion by copper plate test	-	1b

Table 4.2 The characteristics of the four currently available antioxidants (ODPA, HP, TZ and OPANA) and the antiwear (TCP).

Items	Kinematic viscosity at 40^{o}C [mm^{2}/s]	Flash point [^{o}C]	Melting point [^{o}C]	Density at 25^{o}C [g/cm^{3}]
ODPA	280	> 185	-	0.97
HP	-	280	105	1.08
OPANA	-	186	> 75	-
TZ	80	> 150	-	0.95
TCP	> 18	> 225	-	1.16

All properties are representative of at least 2 repeat measurements.

4.2 Investigation of antioxidant additives in finished lubricant on oxidation stability by RBOT instrument

The base oil was tested first without antioxidant and then with one or more antioxidants to a total antioxidant level at 1% (w/w). The DOS base oil without antioxidants performed poorly at both 100 ^{o}C (generally, a normal operating condition is less than 100 ^{o}C) and 150 ^{o}C (ASTM specification), with an OIT of less than 185 and 50 minutes, respectively (Table 4.4). The addition of any of the four antioxidants alone at either 0.5% or 1% to the DOS oil resulted in a significant improvement in the OIT level at 100 ^{o}C, and comparison of the magnitude of the enhanced OIT level revealed the trend of ODPA>>TZ > OPANA > HP at 100 ^{o}C. Significant lower OIT values were obtained at 150 ^{o}C rather than at 100 ^{o}C for all four antioxidants, with only a slight increase in stability afforded by HP or TZ over the base oil alone. However, a significant increase in stability was obtained from the addition of ODPA and OPANA. Thus, from a pure performance standpoint, HP was a fairly good primary antioxidant at low (< 100 ^{o}C) temperature conditions, presumably stabilized through steric hindrance and resonance structure as shown in Figure 4.1 [1, 8].

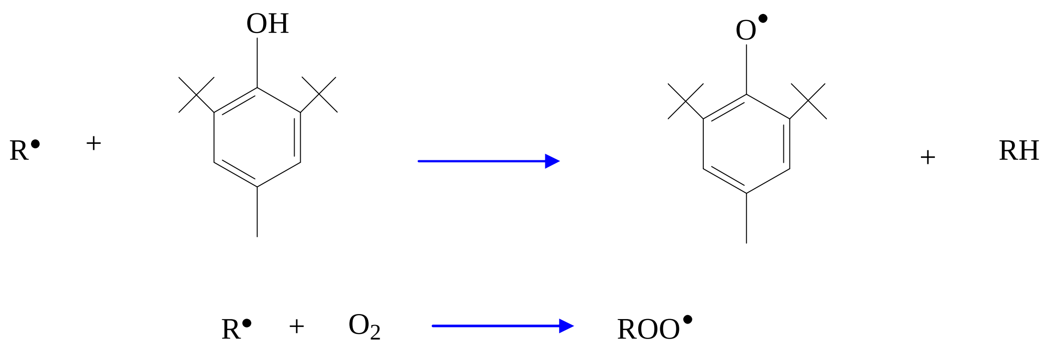

Figure 4.1 Reactivity of hindered phenolic (HP) with alkyl radical.

In contrast, the alkylated diphenylamines, OPANA and especially ODPA, were relatively excellent primary antioxidants at both 100 ^{o}C and 150 ^{o}C, exceeding the OIT level attained with HP by almost threefold because ODPA had a good reactivity with free radical (Figure 4.2). The oxidation inhibition mechanism was started with aminyl radical attacking a second alkyl peroxy radical to form a nitroxyl radical and alkoxy radical. The nitroxyl radical was stabilized through three possible resonance structures (Figure 4.3). Next, a third alkyl peroxy radical reacted with the nitroxyl radical to form a nitroxyl peroxide complex, which could further eliminate an ether molecule. Finally, it was dissociated to 1,4-benzoquinone and an alkylated nitrosobenzene. However, TZ, a metal deactivator was good at 100 ^{o}C but performed poorly at 150 ^{o}C (samples 8 and 9).

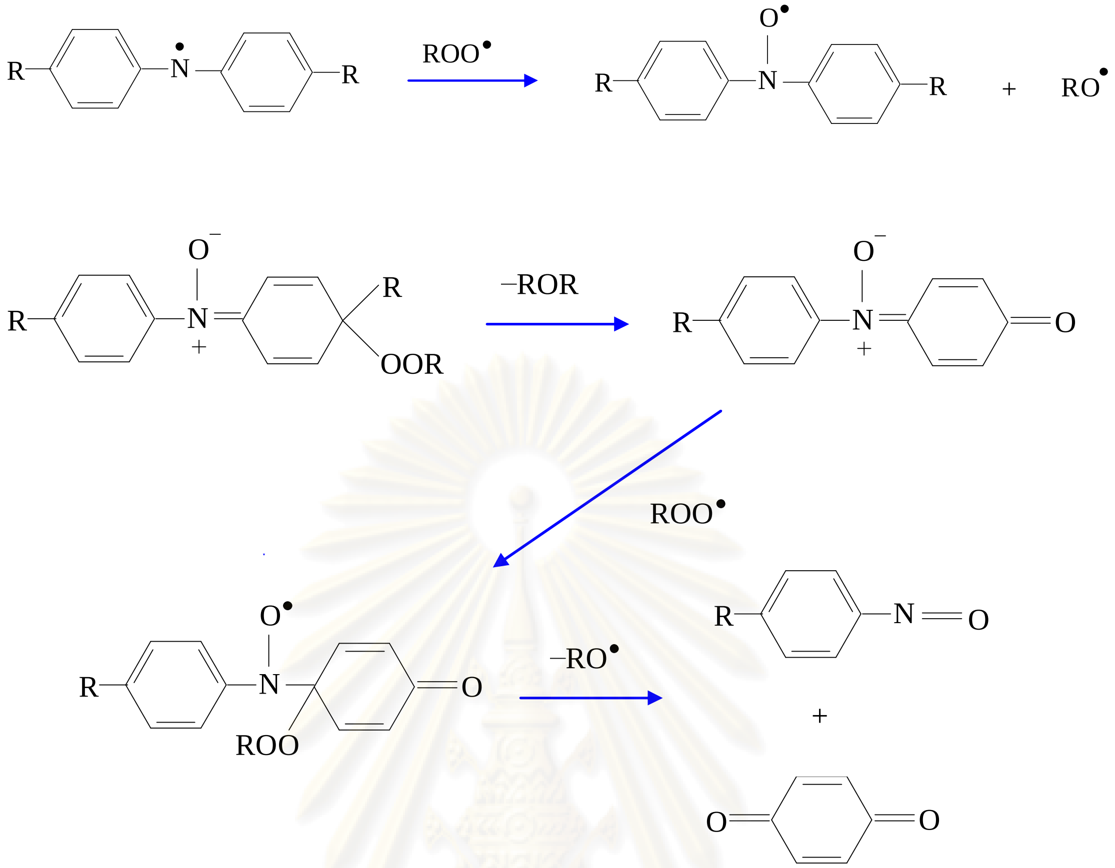

Figure 4.2 Octylated diphenylamine (ODPA) reactivity.

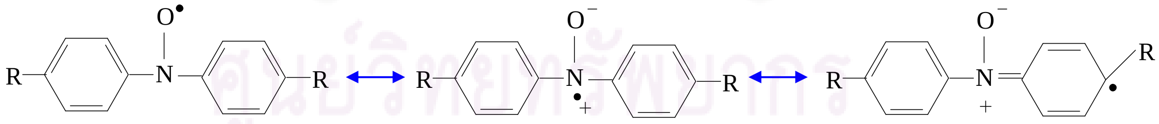

Figure 4.3 Resonance structures of nitroxyl radical.

Table 4.3. The oxidation induction time of each antioxidant at variable percentage in base oil

Sample designation (Group 1)	Additive		OIT [minutes]	
	Name	% amount in base oil (w/w)	100 ^oC	150 ^oC
1-1	ODPA	0.2	1200	980
1-2		0.4	1520	1000
1-3		0.5	1860	1240
1-4		0.6	1800	1300
1-5		0.8	1900	1350
1-6		1.0	2040	1455
1-7	HP	0.2	600	80
1-8		0.4	630	80
1-9		0.5	650	94
1-10		0.6	700	110
1-11		0.8	712	125
1-12		1.0	738	138
1-13	OPANA	0.2	650	550
1-14		0.4	750	650
1-15		0.5	945	755
1-16		0.6	985	870
1-17		0.8	1000	952
1-18		1.0	1135	980
1-19	TZ	0.2	700	60
1-20		0.4	982	75
1-21		0.5	1020	75
1-22		0.6	1125	70
1-23		0.8	1150	80
1-24		1.0	1247	89

To ascertain if the mixtures of these antioxidants were synergistic, they were added in pairs at 0.5% (w/w) of each (Table 4.4). The three-paired mixtures of ODPA with HP, OPANA or TZ all provided lower oxidative protection times (OITs) at both 100 ^{o}C and 150 ^{o}C than that observed with just ODPA at 1% (w/w). Because ODPA was reactive at low and high temperatures, therefore nitroxyl radical from ODPA was reacted with free radical of another antioxidant instead of a free radical from base oil. Therefore, the remaining free radical from base oil could change to acidic compounds. Finally, base oil was degraded. In contrast, the two paired-mixtures of (HP + OPANA) (sample no. 11) and (TZ + OPANA) (sample no. 15) both revealed a clear synergy at 100 ^{o}C, but not at 150 ^{o}C. Likewise, the combination of HP + TZ (sample no. 12) revealed a strong synergy in the OIT attained at 100 ^{o}C (about 74% increase from just the sum of both additives), and indeed was the highest observed OIT of all tested combinations. This paired combination also revealed some degree of synergy at 150 ^{o}C. However, under these conditions by far the largest OIT at 150 ^{o}C was observed with ODPA alone (sample no. 7).

Using OIT from commercial available oil as a reference (sample no. 22), the addition of ODPA alone at 1.0 % (W/W) (sample no. 7) would serve the purpose of extending the antioxidation stability of DOS base oil. However, the combination of ODPA and TZ, resulted in a poor performance at 150 ^{o}C (sample 14). Thus, the three additive components of HP+OPANA+TZ were brought into consideration. The combinations that gave better performance at 100 ^{o}C and 150 ^{o}C than those from the commercial oil were sample no. 16 (HP+OPANA+TZ at 0.33:0.33:0.33) and sample no. 17 (HP+OPANA+TZ at 0.20:0.40:0.40). The best performance at 100 ^{o}C was sample no. 21 (HP+OPANA+TZ at 0.50:0.25:0.25), however, this combination performed poorly at 150 ^{o}C. This could be explained by realizing that both combinations of HP+OPANA (sample no. 11) and HP+TZ (sample no. 12) gave synergistic effect at 100 ^{o}C but gave antagonistic effect at 150 ^{o}C. Sample no. 21 was also influenced by high content of HP which performed well at low temperature. Moreover at 100 ^{o}C, copper catalyst was not so reactive in oxidation reaction. Thus, TZ as metal deactivator was not so important.

The best performance was sample no. 17 (HP+OPANA+TZ at 0.20:0.40:0.40) when it was tested at 150 ^{o}C because this combination contained high amount of OPANA which performs very well at high temperature.

The combination of ODPA with other three oxidants resulted in antagonistic effect. The explanation for this apparent antagonism between ODPA and the other antioxidants on mixing may be that it was not until after the other additive was consumed then the ODPA antioxidant began to be consumed, presumably by reaction with the alkyl peroxy radical or radicals from the other additives, such as the HP radical (Figure 4.4). ODPA was initially more reactive than HP in scavenging alkyl peroxy radicals. As illustrated in Figure 4.4, the amine was first converted to an aminyl radical, which was relatively less stable and accepted a hydrogen atom from the HP to regenerate the alkylated amine. In consequence, the HP was converted to a phenoxy radical. On the other hand, the synergistic mixture of HP + TZ + OPANA all together, which showed an excellent primary antioxidant property, indicated that they could provide a better level of maximal protection than the synergistic mixture of any of the two additives due to the stabilization of different species in the oxidation mechanism and different functional temperature ranges.

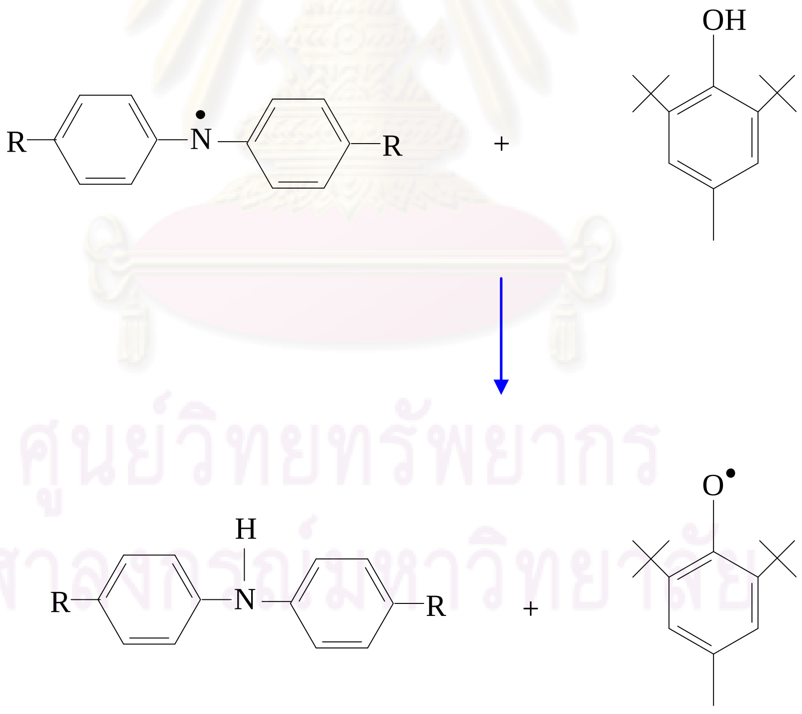

Figure 4.4 Mechanism of antagonism between ODPA and HP.

Table 4.4. The synergistic or antagonistic effect of additives in oil samples by RBOT. The numbers in parenthesis are percent by weight.

Sample number	Sample designation	OIT (minutes)	
		100 °C	150 °C
1	Base oil	185	50
2	HP (0.5)	650	94
3	HP (1.0)	738	138
4	OPANA (0.5)	945	755
5	OPANA (1.0)	1135	980
6	ODPA (0.5)	1860	1240
7	ODPA (1.0)	2040	1455
8	TZ (0.5)	1020	75
9	TZ (1.0)	1247	89
10	HP + ODPA (0.5 : 0.5)	1374	1018
11	HP + OPANA (0.5 : 0.5)	2523	309
12	HP + TZ (0.5 : 0.5)	2900	396
13	ODPA + OPANA (0.5 : 0.5)	1377	1236
14	ODPA + TZ (0.5 : 0.5)	1753	439
15	OPANA + TZ (0.5 : 0.5)	2080	590
16	HP + OPANA + TZ (0.33 : 0.33 : 0.33)	2542	1102
17	HP + OPANA + TZ (0.20 : 0.40 : 0.40)	2401	1350
18	HP + OPANA + TZ (0.40 : 0.40 : 0.20)	1825	1007
19	HP + OPANA + TZ (0.40 : 0.20 : 0.40)	1659	866
20	HP + OPANA + TZ (0.25 : 0.25 : 0.50)	2387	888
21	HP + OPANA + TZ (0.50 : 0.25 : 0.25)	2970	390
22	Commercial oil	1955	980

All tests are representative of at least 2 repeats.

In the presence of the boundary testing conditions it was found that the suitable (w/w) ratio of the HP:OPANA:TZ mixture could be used to block multiple oxidation reactions. Therefore, the three samples, HP + OPANA, HP + TZ and OPANA + TZ as well as various combinations of HP:OPANA:TZ were used to investigate for their physicochemical properties by comparison with the commercial oil and the pure DOS base oil.

Additionally, the optimal (w/w) ratio of HP:OPANA:TZ compositions at 100 ^{o}C (0.50 : 0.25 : 0.25) and 150 ^{o}C (0.20 : 0.40 : 0.40) were further investigated for their compatibility with TCP antiwear on the IOT, thermal stability and tribological properties (see section 4.3 and 4.4).

4.3 Characterization of the synergistic antioxidant lubricants

4.3.1 Physicochemical properties

The basic physicochemical properties of the synergistic antioxidant additive mixtures in the finished lubricants are presented in Table 4.5.

It is noted that the presence of two or especially three antioxidant additives in the DOS oil composition significantly increased their thermal stability which is a clear advantage in most applications, and exceeded that of the commercial oil sample used as a comparative reference. The presence of TCP further enhanced the thermal stability of DOS oil composition, as could be seen in the combination of HP + OPANA + TZ (0.20:0.40:0.40)+TCP (0.50) which gave the highest thermal stability. On the other hand, the total acid number of the oil blend, as determined by potentiometric titration (Table 4.5), very much depended on the type of the antioxidant used. The TAN results of oil samples are also of interest and reveal that the mixture of the three antioxidants (HP, TZ and OPANA) could provide a significantly greater protection level against acid generation from oxidation reactions, and at a higher level than that seen from the commercial reference oil sample. This is of relevance as it is an important function of lubricant antioxidants to ensure an extended service lifetime.

The viscosity and moisture content of the finished oils increased slightly and significantly, respectively, with increasing amount of additives but never exceeded that of the commercial lubricant (Table 4.5). Importantly, the mixture of two or three of the antioxidants had no significant affect on the flash point and specific gravimetry of these blended oils, which made them ideal additives in this respect. Thus, it could be affirmed that a HP + OPANA + TZ combination was likely to be an appropriate additive to be used in industrial oils, or at least to those similar to the DOS base oil used here.

Table 4.5 The influence of the four additives on physicochemical properties and performance of the finished lubricants

Sample designation	Viscosity [mm^2/s]	Flash point [^{o}C]	Moisture content [ppm]	SG	Pour point [^{o}C]	Thermal stability [^{o}C]	TAN [mgKOH/g]	
							b/f RBOT	a/f RBOT [a]
base oil	11.84 ± 0.00	242 ± 2	225 ± 4	0.914 ± 0.000	below -60	227.6 ± 0.3	0.05 ± 0.01	59.89 ± 0.35
HP + OPANA (0.50 : 0.50)	11.85 ± 0.00	240 ± 3	239 ± 3	0.914 ± 0.000	below -60	259.5 ± 0.4	0.15 ± 0.02	30.39 ± 0.24
HP + TZ (0.50 : 0.50)	11.90 ± 0.00	244 ± 2	247 ± 3	0.914 ± 0.000	below -60	256.9 ± 0.2	0.22 ± 0.02	42.76 ± 0.28
OPANA + TZ (0.50 : 0.50)	11.86 ± 0.00	242 ± 2	252 ± 3	0.914 ± 0.000	below -60	260.6 ± 0.4	0.18 ± 0.02	38.66 ± 0.18
HP: OPANA: TZ (0.33 : 0.33 : 0.33)	11.95 ± 0.00	244 ± 2	258 ± 5	0.914 ± 0.000	below -60	265.7 ± 0.5	0.21 ± 0.02	5.34 ± 0.07
HP: OPANA: TZ (0.25 : 0.25 : 0.50)	11.91 ± 0.00	240 ± 3	267 ± 5	0.914 ± 0.000	below -60	266.0 ± 0.4	0.25 ± 0.02	10.72 ± 0.07
HP: OPANA: TZ (0.20 : 0.40 : 0.40)	11.92 ± 0.00	246 ± 3	258 ± 5	0.914 ± 0.000	below -60	269.2 ± 0.3	0.27 ± 0.02	2.23 ± 0.04
HP: OPANA: TZ (0.50 : 0.25 : 0.25)	11.97 ± 0.00	244 ± 3	260 ± 3	0.914 ± 0.000	below -60	267.6 ± 0.4	0.13 ± 0.00	6.54 ± 0.06
HP: OPANA: TZ (0.40 : 0.20 : 0.40)	11.94 ± 0.00	242 ± 2	263 ± 6	0.914 ± 0.000	below -60	265.4 ± 0.4	0.19 ± 0.01	9.20 ± 0.06
HP: OPANA: TZ (0.40 : 0.40 : 0.20)	11.98 ± 0.00	244 ± 2	265 ± 5	0.914 ± 0.000	below -60	263.3 ± 0.5	0.15 ± 0.01	4.80 ± 0.06

[a] after RBOT tested at 150 ^{o}C with Cu and water catalyst.

SG, b/f and a/f denote to specific gravity, before and after, respectively.

The numbers in parenthesis are percent by weight.

4.3.2 Thermal stability of the synergistic antioxidant lubricants

The TGA results of the finished lubricant under an air atmosphere are summarized in Table 4.5, where the mixtures of HP, OPANA and TZ were shown to possess excellent thermal stability via IOT at over 260 ^{o}C and improved the thermal stability of the DOS base oil.

4.4 Compatibility between the synergistic antioxidant and TCP

4.4.1 Investigation of antioxidant additive in finished lubricant on oxidation stability by RBOT instrument

The addition of TCP alone to the DOS base oil increased the OIT significantly at 100 ^{o}C but slightly at 150 ^{o}C. However it was still at levels below that observed for the respective optimal HP: OPANA: TZ additives (Table 4.6). The blending of the antioxidant mixtures of HP: OPANA: TZ at a (w/w) ratio of 0.50 : 0.25 : 0.25 and 0.20 : 0.40 : 0.40 with 0.5% (w/v) TCP further improved the oxidation stability performance at 150 ^{o}C. Moreover, in all cases the observed OIT of DOS oil supplemented with both combinations of antioxidants and TCP were greater than that of the commercial oil used as a reference sample.

Table 4.6. Effect of the four additives on OIT and tribological properties.

Sample designation	OIT at 150 ^{o}C by RBOT [minute]	Friction coefficient	WSD [mm.]
base oil	50 ± 8	0.283 ± 0.009	1.30 ± 0.02
TCP (0.5)	99 ± 6	0.129 ± 0.011	0.99 ± 0.02
HP + OPANA+ TZ (0.20 : 0.40 : 0.40)	1350 ± 8	0.131 ± 0.010	0.98 ± 0.03
HP + OPANA + TZ (0.20 : 0.40 : 0.40) + TCP (0.50)	2750 ± 8	0.125 ± 0.009	0.95 ± 0.01
HP + OPANA + TZ (0.50 : 0.25 : 0.25)	390 ± 6	0.139 ± 0.009	1.01 ± 0.02
HP + OPANA + TZ (0.50 : 0.25 : 0.25) + TCP (0.50)	1154 ± 8	0.125 ± 0.012	0.97 ± 0.02
Commercial	980 ± 7	0.136 ± 0.010	1.01 ± 0.02

All properties are representative of at least 2 repeats. The numbers in parenthesis are percent by weight.

4.4.2 Physicochemical properties

The mixture of three additives with TCP did not significantly increase viscosity, flash point, specific gravimetry and pour point of the synergistic antioxidant ‘s lubricants. According to this result, it could be affirmed that TCP antiwear when blended with HP, OPANA and TZ antioxidant was an appropriate additive to enhance properties of the synergistic antioxidant ‘s lubricants and the results are given in Table 4.7.

Table 4.7 The influence of TCP additive on physicochemical properties of the synergistic antioxidant ‘s lubricants

Sample designation	Viscosity [mm^2/s]	Flash point [^oC]	Moisture content [ppm]	SG	Pour point [^oC]	Thermal stability [^oC]	TAN [mgKOH/g]	
							b/f RBOT	a/f RBOT [a]
HP + OPANA + TZ (0.20 : 0.40 : 0.40) + TCP (0.50)	11.93 ± 0.00	246 ± 2	262 ± 4	0.914 ± 0.000	below -60	272.7 ± 0.5	0.32 ± 0.02	2.05 ± 0.03
HP + OPANA + TZ (0.50 : 0.25 : 0.25) + TCP (0.50)	11.98 ± 0.00	240 ± 2	275 ± 3	0.915 ± 0.000	below -60	269.6 ± 0.4	0.42 ± 0.01	15.53 ± 0.07
Commercial	12.52 ± 0.00	244 ± 3	350 ± 5	0.916 ± 0.000	below -60	264.7 ± 0.5	0.18 ± 0.01	32.50 ± 0.31

[a] after RBOT tested at 150^oC with Cu and water catalyst

SG, b/f and a/f denote to specific gravity, before and after, respectively.

4.4.3 Tribological properties

Wear scar dimension

The antiwear property of the finished lubricants are shown in Table 4.6 as the wear scar diameter (WSD), where, as with the friction coefficient, the inclusion of TCP alone reduced the WSD of the DOS base oil close to that seen with the addition of just the antioxidants. Likewise, the co-addition of TCP and antioxidants resulted in a slightly reduced WSD (Table 4.6 and Figure 4.5). Therefore, TCP also improved the tribological properties of the mixed antioxidant lubricants, as well as the improvement in the oxidation stability.

Friction performance by SRV

Table 4.6 showed the friction coefficient of each finished lubricant under a force of 200 N. The addition of TCP antiwear alone to the DOS oil greatly decreased the friction coefficient of the oil, attaining a level somewhat similar to that seen with the addition of just the antioxidants. However, the co-addition of TCP with the antioxidants slightly lowered the friction coefficient, and was below that of the commercial oil sample used as a comparative reference.

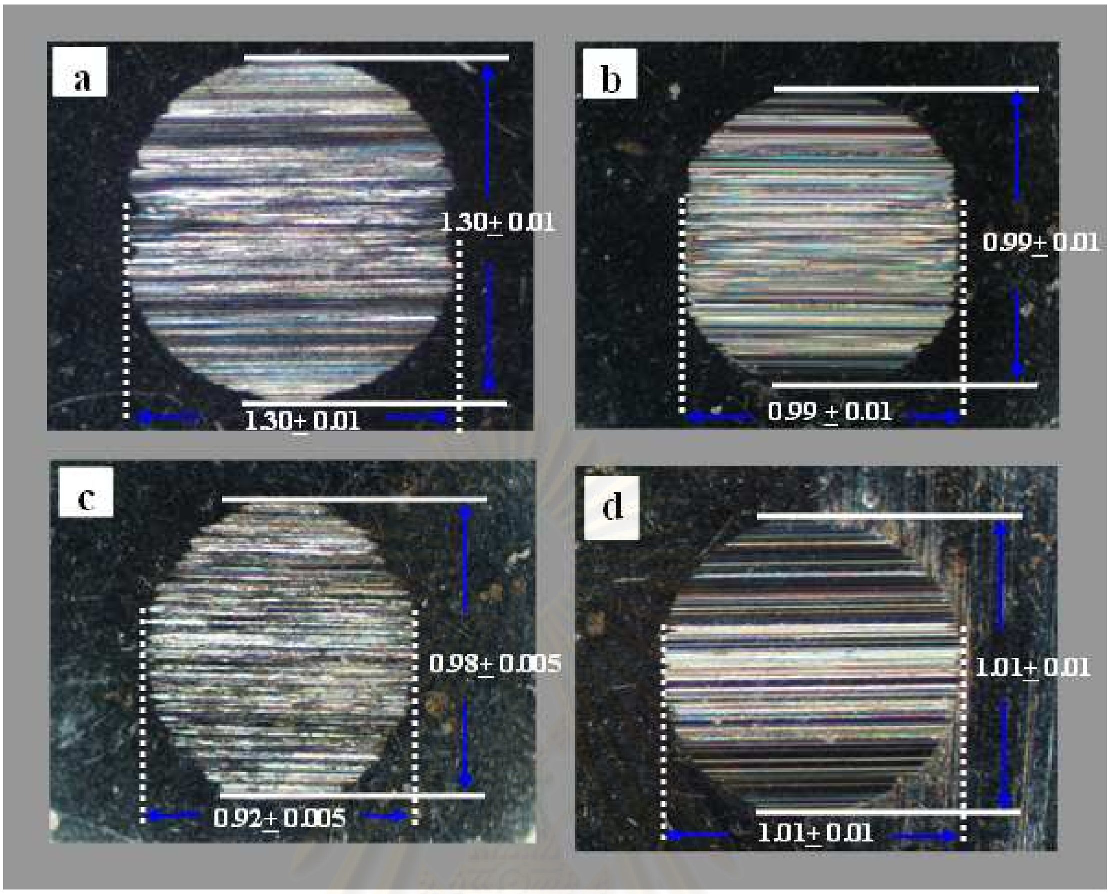

Figure 4.5 Photographs of wear scar lubricated with: (a) base oil, (b) base oil with a 0.20:0.40:0.40 (w/w) ratio of HP: OPANA: TZ, (c) base oil with a 0.20:0.40:0.40 (w/w) ratio of HP: OPANA: TZ plus 0.5% (w/w) TCP and (d) commercial oil. All photographs are at 80 x magnification and are representative of at least 2 repeats.

4.4.4 Thermal stability

The thermal stability, measured as the IOT, of the oil with the selected synergistic antioxidant mixtures was improved further by the addition of 0.5% (w/w) TCP (Figure 4.6). In contrast to the DOS base oil (227.6 ^{o}C), the thermal decomposition temperature of the HP: OPANA: TZ antioxidant supplemented oil was very high (269.2 ^{o}C) and this was elevated even further with the inclusion of TCP (272.7 ^{o}C).

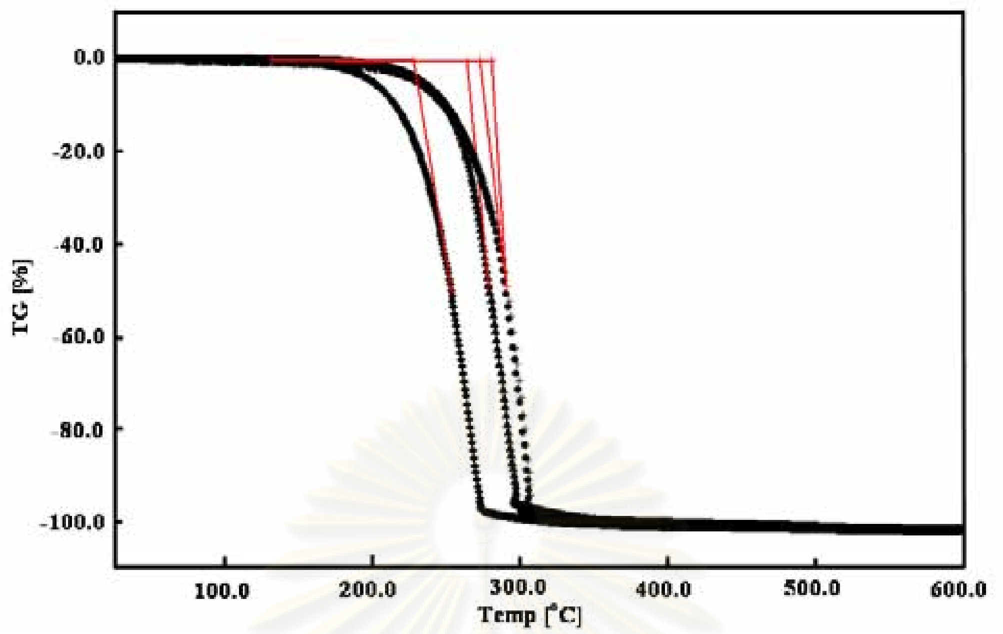

Figure 4.6 A typical TGA spectrum of oil under air atmosphere. The spectrum are representative of those from at least 2 independent repeats. The numbers in parenthesis are percent by weight. (◆) Base oil, IOT : 227.6°C, (▲) HP + OPANA, IOT : 259.5°C, (●) HP + OPANA + TZ (0.20 : 0.40 : 0.40), IOT : 269.2°C, (+) HP + OPANA + TZ (0.20 : 0.40 : 0.40) + TCP (0.50), IOT : 272.7°C.

4.4.5 Copper corrosion test

Copper corrosion test indicated that all the oil samples containing 1% (w/w) of total additives (DOS + antioxidant and DOS + antioxidant + TCP) were class 1B, compared to class 1A (Table C1) for the DOS base oil. The term "class" represents the property of copper corrosion, and it is judged according to the color of the copper strip. The lower the copper corrosion property the lower the "class" of the oil. Thus, the addition of these additives (HP, OPANA, TZ and TCP) into synthetic ester base oils improved their corrosion inhibition property.

Thus TCP improved oxidation stability through OIT, friction coefficient and wear scar size of the synergistic lubricants. Furthermore, its performance also was better than that of the current commercial oil.

4.5 Half life expectancy of radical by ESR

In the presence of the boundary testing conditions, the synergistic and antagonistic phenomena of each additive were found. Therefore the inhibitory activity of HP, OPANA, TZ combination in synthetic ester oil on the oxidation stability was investigated by ESR experiments.

The mechanism of inhibition by antioxidants (InH) was usually related to the reaction (1) and reaction (2) [25].

$$R^{\cdot}\ (\text{or } ROO^{\cdot}) + InH \longrightarrow RH\ (\text{or } ROOH) + In^{\cdot} \tag{1}$$

$$R^{\cdot}\ (\text{or } ROO^{\cdot}) + In^{\cdot} \longrightarrow \text{molecular products} \tag{2}$$

The radical $In^{\cdot}$ in inhibited oils can also be formed through the reaction (3)

$$2InH \longrightarrow 2In^{\cdot} + H_2 \tag{3}$$

Destruction of the $In^{\cdot}$ radicals may take place through reaction (2) and also through the reaction (4)

$$In^{\cdot} + In^{\cdot} \longrightarrow In-In \tag{4}$$

Since the activation energy for reaction (1) was far greater than that for (2), the probability of chain breaking by reaction (2) in the oxidation of inhibited oils was greater than the probability of breaking by reaction (1). Therefore, differences in oxidation stability of synthetic ester oil with these antioxidants must be related to differences in chemical activity of the $In^{\cdot}$ radicals and the kinetics of their accumulation in the oil.

At high temperature (150°C) with initiator, the contribution of reaction (1) to the kinetics of $^{\cdot}In_O$ as radical form of ODPA and OPANA (Figure. A1) become greater because both of them were excellent primary antioxidants under high temperature condition, but HP and TZ were poor performance. So, HP and TZ could not change to a stable $^{\cdot}In_P$ form as shown in Figure. A1. This result also agreed with that observed with RBOT testing.

The following results were obtained on the solutions of original synthetic ester oil with 0.1 % t-butyl hydroperoxide as initiator at 150°C. There were no ESR spectrum as shown in Figure 4.7a. However, the addition of 5% ODPA into the solution of synthetic ester oil with 0.1 % initiator could give an intense ESR spectrum (Figure 4.7b) with half life time at 387 minutes. ESR signal of the solution of 5%

OPANA in synthetic ester oil with 0.1 % initiator (Figure 4.7c) showed half life time at 66 minutes. According to ESR signal, the half life of radical was the time at the point on the falling part of peak where the peak height is dropped 50 % from the highest value. This result was consistent with the concept of formation of $^{\cdot}In_O$ radicals when ODPA or OPANA were dissolved in oil, in accordance with reaction (3).

The absence of the ESR spectrum of the $^{\cdot}In_O$ radicals could apparently be explained by the formation of a charge transfer complex with an original molecule of ODPA or OPANA as a second $^{\cdot}In_O$ radicals.

The same result was observed in the oxidation of the oil containing ODPA with other antioxidants (Figure 4.7f – Figure 4.7h), At high temperatures, the $^{\cdot}In_O$ radicals were formed primarily through reactions (1) and (2). In this case, destruction of the radicals may also occur through the reaction which resulted in the formation of a new molecule that was effective oxidation inhibitor. Therefore half life of ODPA solution with other antioxidants was less than that of ODPA alone (Table 4.8).

The same phenomena were observed from the mixture 5% OPANA with 5%HP (Figure 4.7i) or 5% OPANA with 5%TZ (Figure 4.7j) in synthetic ester oil with 0.1 % initiator. They showed an antagonistic effect as ESR signal exhibited shoter half life than that observed from OPANA alone.

The mixture of 5% HP in synthetic ester oil with 5%TZ and 0.1 % initiator could give synergistic ESR signal (Figure 4.7k). The half life was longer than that from 5%HP (Figure 4.7d) or 5%TZ (Figure 4.7e) alone. However, the addition of ODPA into other antioxidant (HP, OPANA or TZ) showed apparently the inhibiting effect.

The addition of TCP to the antioxidant showed the strong and long half life of ESR signal (Figure 4.7m and Table 4.8). Moreover, the TCP additive would be interacted vigorously with hydroperoxides which it was also a reinforcement of the inhibiting oxidation effect.

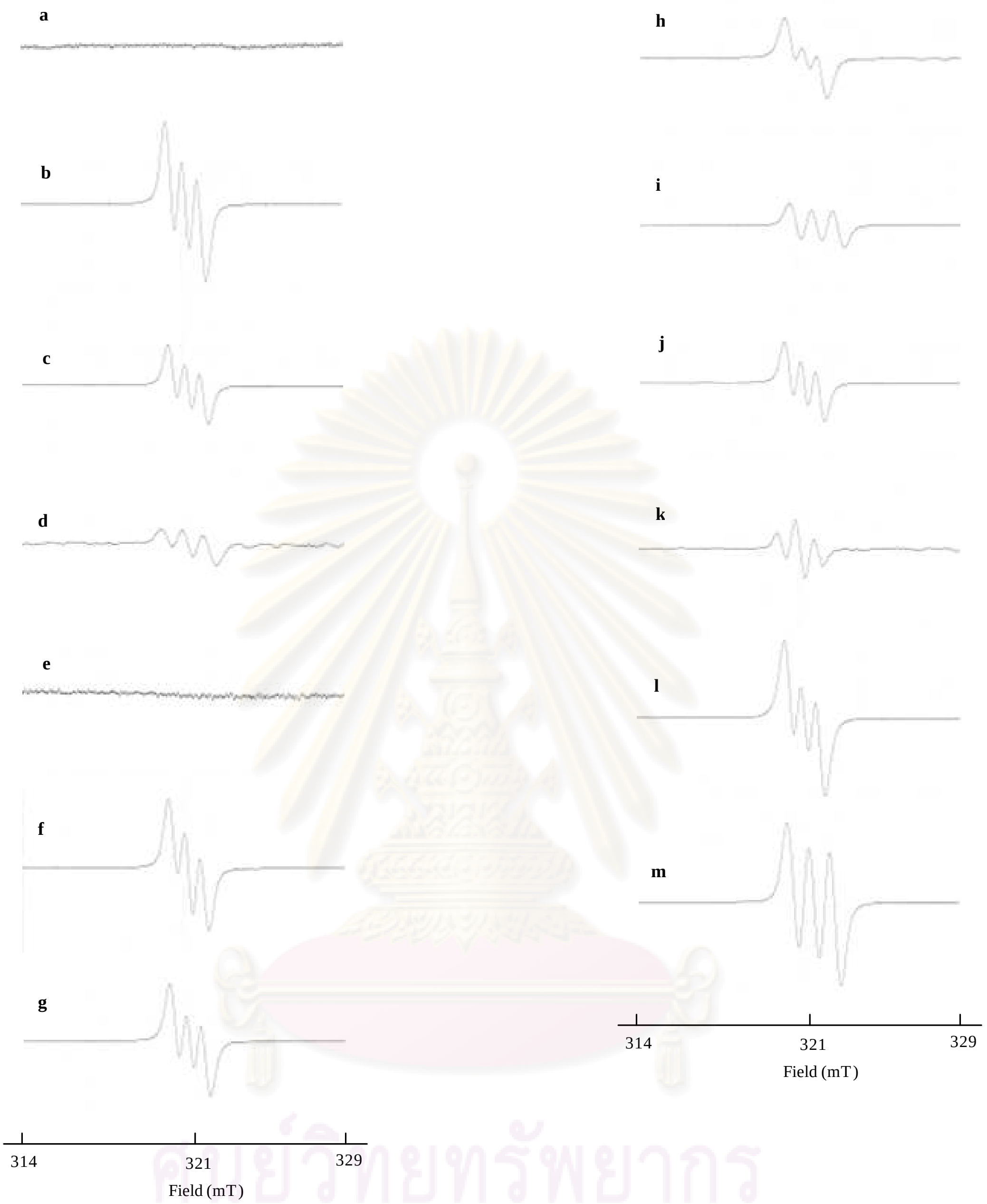

Figure 4.7 ESR spectra of synthetic ester oil + 0.1% initiator at 150^{o}C for 10 minutes a) without antioxidant b) with 5%ODPA c) with 5%OPANA d) with 5%HP e) with 5%TZ f) with 5% ODPA and 5% OPANA g) with 5%ODPA and 5%HP h) with 5%ODPA and 5%TZ i) with 5% OPANA and 5%HP j) with 5% OPANA and 5%TZ k) with 5% HP and 5%TZ l) with 5% OPANA, 5% HP and 5%TZ m) with 5% OPANA, 5% HP, 5%TZ and 5%TCP.

During ESR analysis, some samples such as OPANA (Figure 4.8) showed ESR pattern which was changed from initial pattern. It might be resulted from the interaction between various free radicals. Thus the mechanism of stabilization of antioxidant by ESR experiment should be studied in more detail.

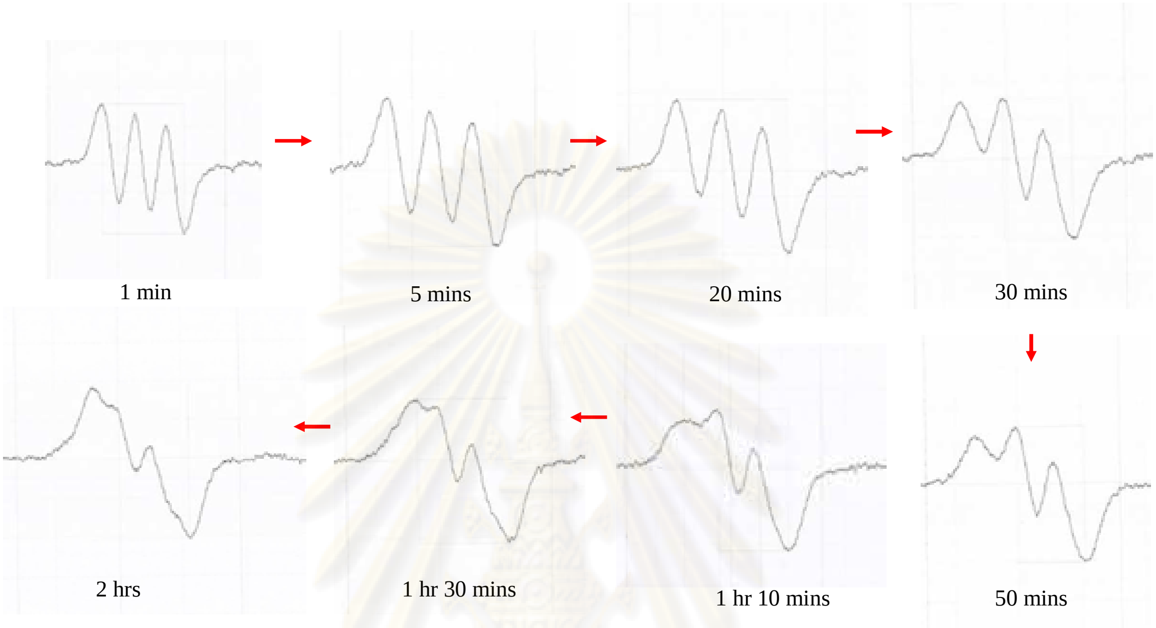

Figure 4.8 The ESR signal of OPANA at 150^{o}C.

Table 4.8 The synergistic or antagonistic effect of additives in oil samples on half life of radical at 150°C.

Sample designation	Half life of radical [minute]
base oil	no signal
ODPA (5)	387
OPANA (5)	66
HP (5)	2
TZ (5)	no signal
ODPA + OPANA (5 :5)	166
ODPA + HP (5 :5)	127
ODPA + TZ (5 :5)	31
OPANA + HP (5 :5)	30
OPANA + TZ (5 :5)	44
HP + TZ (5 :5)	32
HP + OPANA+ TZ (5 : 5 : 5)	486
HP + OPANA+ TZ (5 : 5 : 5) + TCP (5)	> 600

The numbers in parenthesis are percent by weight.

CHAPTER V

CONCLUSION

5.1 Conclusion

In isothermal and catalytic RBOT oxidation tests, ODPA showed an antagonistic effect on the OIT in all samples. The 0.50 : 0.25 : 0.25 (w/w) ratio mixture of HP: OPANA: TZ showed the best synergistic antioxidant activity in the DOS synthetic lubricant at mild (100 ^{o}C) conditions. However, at 150 ^{o}C, the 0.20 : 0.40 : 0.40 (w/w) ratio of HP: OPANA: TZ showed the best synergistic antioxidant activity. Thus, in this combination, the useful lifetime of the antioxidant additives could be extended beyond the expected performance of each additive if they were used separately. Antioxidant synergism was the effect of a combined use of two or more antioxidants being greater than that of any individual antioxidant. Synergistic antioxidant systems offer practical solutions to problems where using a single antioxidant was inadequated to provide satisfactory results. The factors which made antioxidant synergism are shown below.

1. Stabilization of different species in the oxidation mechanism.
2. Functions in a different temperature range.
3. Functions at different rate.

The results also indicated that the addition of 0.5% (w/w) TCP as antiwear additive to the antioxidant mixture in the lubricant could improve the antioxidation performance and the thermal stability of the lubricant as well as its tribological properties.

In the ESR experiments the synergistic antioxidant's lubricants containing HP and TZ showed longer half life of antioxidant's radicals than that observed from single antioxidant. On the other hand antagonistic mixture was indicated by the shorter half life of the radicals. These results showed the same tendency to those observed using RBOT testing.

5.2 Suggestion for future work

It is suggested that other additive such as conductive additive may be added into this synergistic finished lubricant to increase multi-performance such as long life, friction reduction and electric charge protection. Moreover, mechanism of stabilization of each antioxidant and combination by ESR experiment should be continued.

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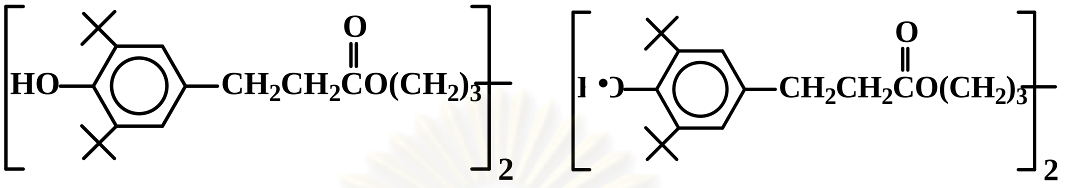
APPENDICES

APPENDIX A

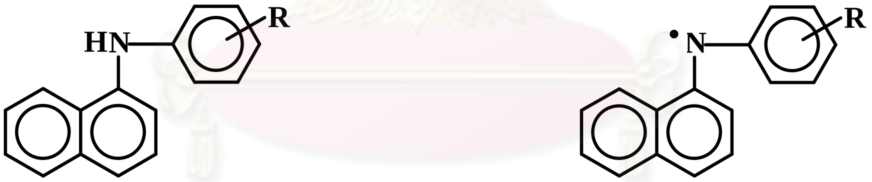
CHEMICAL STRUCTURES

Octylated diphenylamine (ODPA)

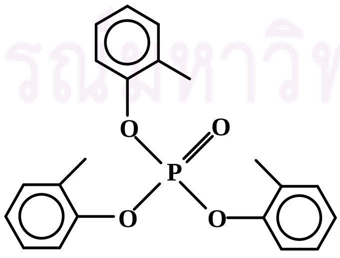


Hindered bis-phenolic (HP)

Tolutriazole (TZ)



Octylated phenyl-alpha-naphthylamine (OPANA)



Tricresyl phosphate (TCP)

Fig. A1. The chemical structures and the radical structures of currently available antioxidants and antiwear.

APPENDIX B

TEST METHOD

B1. Kinematic viscosity (ASTM D-445) [14]

Kinematic viscosity is the resistive flow of fluid, based on the time in seconds required for a fixed amount of fluid to flow through a calibrated capillary tube. The time is measured for a fixed volume of sample, contained in a glass viscometer to flow through a calibrated capillary at a closely controlled temperature.

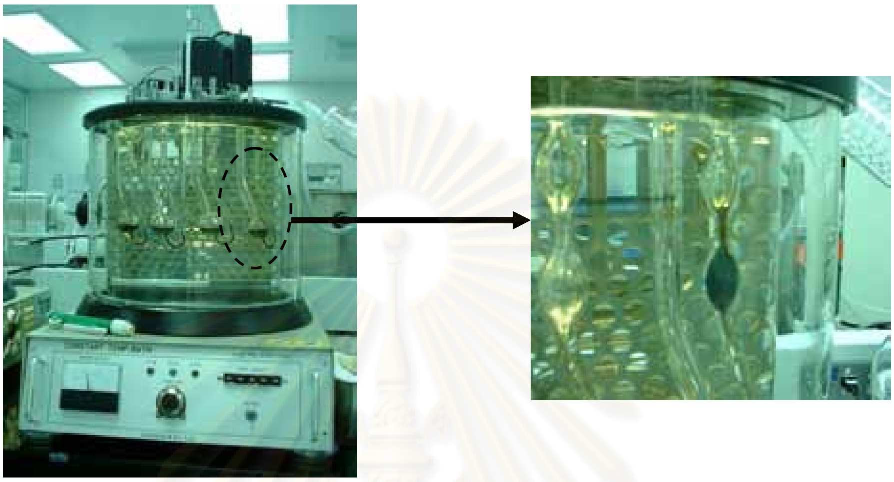


Figure B1 Kinematic viscosity instrument.

- Purpose

Kinematic viscosity are required for use in all bearing design calculations and used commercially throughout the world and applied in oil blending procedures.

- Definition

Kinematic viscosity is the resistance to flow of a fluid under gravity.

- Scope of test

1.1. This test method specified a procedure for determination of kinematic viscosity (ν) of liquid petroleum, transparent liquid, by measuring the time of a volume of liquid to flow under gravity through a calibrated glass capillary viscometer.
1.2. The range of kinematic viscosities covered by this test method is from 0.2 to 300,000 mm^2/s at all temperature.

- Test method

General procedure for kinematic Viscosity

1. Adjust and maintain the viscometer bath at the required test temperature. The temperature of the bath does not vary by more than +/- 0.05 ^{o}C of the selected temperature.
2. Thermometer shall be held in an upright position under the same condition of immersion when calibrated.
3. Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity.

Procedure for transparent liquids

1. Charge the viscometer with 7 ml of sample. If the sample contains solid particle, filtrate through Millipore filter (5 um or less than) before charging.
2. Allow the charged viscometer to retain in the bath long enough to reach the test temperature. Thirty minutes should be sufficient.
3. After the sample has reached temperature equilibrium, use suction to adjust the head level of test sample to a position in the capillary arm of the instrument above the first timing mark.
4. With the sample flow freely, measure in seconds to within 0.1s, the time required for the meniscus to pass from the first to the second timing mark.
5. Repeat to procedure describes in 6.2.4 to make a second measurement of flow time.
6. Calculate kinematic viscosity,ν, in mm^2/s from each measured flow time.
7. If the two determinations of kinematic viscosity, calculated from the flow time measurements, agree within the stated repeatability for product, use the average of these determinations to calculate the kinematic viscosity result to be reported.

- Calculation

Calculation of the kinematic viscosity is carried out using the equation B1.

$$\nu = c \times t \qquad \text{(B1)}$$

Where, ν = kinematic viscosity in mm^2/s

c = calibration constant of the viscometer in $(mm^2/s)/s$ unit

t = measured flow time in second unit

- Precision

Repeatability

The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in long run, in the normal and correct operation of this test method.

Base oil at 40 and 100 ^oC	$\pm$ 0.0011x
Formulated oil at 40 and 100 ^oC	$\pm$ 0.0026x

Where, x is the average of results being compared

B2. Flash point (ASTM D-92) [15]

The flash point of an oil is the lowest temperature at which it gives off vapors that will ignite when a small flame is periodically passed over the surface of the oil.

Figure B2 Flash point apparatus.

- Purpose

To determining the flash point of oil via petroleum product by Cleveland Open Cup apparatus (Fig. B2).

- Definition

Flash Point is the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a test specimen of sample to ignite under specified conditions of test.

- Scope of test

The Cleveland cup is filled with oil sample up to the specified filling mark. The bulb of the thermometer is immersed in the sample ¼ inch from the bottom of the cup. The oil is then heated at a constant rate. At every 2 ^{o}C rise in temperature a small flame is passed over the oil surface. When a flash occurs, the temperature reading is the flash point of the sample.

Remark : This test method is applicable to all lubricating oils with flash points above 70 ^{o}C and below 400 ^{o}C.

- Test method

<u>General Procedure for flash point</u>

1. Wash the test cup with solvent to remove any test specimen or traces of gum or residue remaining from a previous test. If any deposits of carbon are present, they should be removed with a material such as silicon carbide grit paper.
2. Ensure that the test cup is completely clean and dry before using again.
3. Ensure that the air ventilation by fume hood is stopped. The air flow can influence the vapors in the test cup and test flame.

<u>Procedure for Transparent Liquids</u>

1. Fill the test cup with approximately 70 ml of oil sample or reach to a level mark inside the cup, and place the test cup on the center of the heater. The temperature of the test cup and sample shall not be exceed 56 ^{o}C below the expected flash point.
2. Start the automated apparatus and adjust the test flame to a diameter of 3.2 to 4.8 mm or to the size of the comparison bead which is mounted on the apparatus.
3. Record data which shown on display when occurred flash point.

- Precision

Repeatability

The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical material, would in the long run, in the normal and correct operation of the test method.

Flash Point ± 8 °C

B3. Total acid number (ASTM D-664) [16]

This method determines the acidic constituents in a petroleum oil that are soluble in mixtures of isopropyl alcohol and toluene. It may be used to show relative changes occurring in an oil under oxidizing conditions.

Figure B3 Automatic potentiometric titrator apparatus.

- Purpose

To determine the total acid number in oil sample by use automatic potentiometric titrator (Fig. B3).

- Definition

Total acid number (TAN) is the quantity of base, expressed in milligram of potassium hydroxide, that is required to titrate all acidic constituents present in 1 g of samples.

Furthermore, total acid number is shown relative changes in an oil due to oxidation. Comparing the TAN with the values of a new oil will indicate the development of harmful products or the effect of additive depletion.

- Scope of test

This test method is the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and 2-propanol. By a weighed amount of sample in titration solvent is titrated with a standard alcoholic potassium hydroxide solution to a definite end point.

Remark : It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9}; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere.

- Test method

1. At first time of using machine should prepare for blank test by fresh titration solution 125 ml into titration beaker.
2. Drop magnetic bar into titration beaker and set up electrode. And then start machine to detect the end point.
3. When finished the test, remove mixture remained at electrode by soft wiper and rinse the electrode with alcoholic solvent and DI water then dip the electrode into DI water for 5 minutes before next sample.
4. Weighing sample about 20 ± 0.5 g into 250 ml titration beaker then mix with 125 ml of titration solution.
5. Record the result as total acid number.

- Calculation

Quantitative

The total acid number or acidity of hydro oil sample is determined by automatic calculation of machine when finished the titration.

Calculation formula

$$\text{Acid number (mg KOH/g)} = (A - B) \times M \times 56.1 / W \qquad \text{(B2)}$$

Where,
A = alcoholic KOH solution used to titrate sample to end point in ml unit
B = volume corresponding to A for blank titration in ml unit
M = concentration of alcoholic KOH solution in mol/l unit
W = sample mass in gram unit

B4. Moisture content (ASTM D-1744) [17]

The Moisture content or water content of petroleum products can be useful to predict quality and performance characteristics of the product.

Figure B4 Karl Fischer Titrator apparatus.

- Purpose

To analyze the moisture content by using Karl Fischer Titrator (Fig. B4).

- Definition

Moisture content of petroleum product can be useful to predict quality and performance characteristics of the products. The material to be analyzed is titrated with standard Karl Fischer reagent to an electrometric end point.

- Scope of test

This test method covers the determination of moisture content in liquid petroleum products.

- Test method

1. Should prepare for blank test by titration without sample injection.
2. Weighing 1 ml of oil sample with glass syringe and input weight to sample detail.
3. Inject sample to titration cell and push start to titrate.
4. After injected sample, weighing the remaining sample with glass syringe again and input weight to sample detail.
5. Record the result as the moisture content without any correction.

- Calculation

The moisture content result must be multiply to a constant that come from performance check by standard water solution as equation B3.

$$\text{moisture content} = (CF \times 1{,}000) / W \qquad \text{(B3)}$$

Where, C = milliliters of reagent required for tritration of the sample

F = water equivalence in ml unit

1,000 = factor for converting to parts per million

W = weight of sample used in grams unit

- Precision

Repeatability

The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical material, would in the long run, in the normal and correct operation of the test method.

Water content (ppm)	repeatability (ppm)
50 to 1,000	± 0.1 x

Where, x denotes average result

B5. Specific gravity (ASTM D-4052) [18]

The specific gravity is a fundamental physical property that can be used in conjunction with other properties to characterize both the light and heavy fractions of petroleum and petroleum products.

Figure B5 Digital density analyzer.

- Purpose

This test method covers the determination of specific gravity of petroleum distillates and viscous oils that can handed in a normal liquids at test temperatures between 15 and 35 ^{o}C by Digital density analyzer (Fig. B5). Its application is restricted to liquids with vapor pressure below 600 mm Hg (80 kPa) and viscosities below about 15,000 mm^2/s at temperature of test.

- Definition

Specific gravity is the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

- Scope of test

A small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of tube is used in conjunction with calibration data to determine the specific gravity of the samples.

- Test method

1. Flush the sample tube by the sample for 3 times then introduce a small amount of sample into sample tube of the instrument. Make sure that no bubbles are trapped in the tube.
2. After the instrument displays a steady reading to four significant figures for density, indicating that temperature equilibrium has been reached, record the density.

- Precision

Repeatability

The different between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty.

Range	Repeatability
0.68 – 0.64	± 0.0001

B6. Pour point (ASTM D-5950) [19]

The pour point of a petroleum oil is the lowest temperature at which the oil will pour or flow under prescribed conditions when it is chilled without disturbance at a fixed rate. Moreover, pour point is of importance in establishing the lowest temperature at which a diesel fuel is still sufficiently fluid to be pumped or transferred. However, many fuels can be pumped or transferred at temperatures below their pour point.

The pour point of petroleum product is an index of the lowest temperature of its utility for certain applications. Flow characteristics, like pour point, can be critical for the correct operation of lubricating oil system.

Figure B6 Automatic pour point apparatus.

- Purpose

This test method covers the determination of pour point of petroleum products by an automatic instrument that tilts the test jar during cooling and detects movement of the surface of the test specimen with and optical device as Fig. B6.

Remark : This test method includes the range of temperatures from -60 to +60 ^{o}C.

- Definition

Pour point is the lowest temperature at which movement of the test specimen is observed under the prescribed conditions of this test method.

- Scope of test

After preliminary heating, the test specimen is inserted into the automatic pour point apparatus. After starting the program, the specimen is cooled according to the cooling profiled. The lowest temperature at which movement of specimen is detected, by the automatic equipment, is displayed as the pour point.

- Test method

1. Pour the sample into the test specimen jar to the level mark. When necessary, heat the sample in a water bath or oven until it is just sufficiently fluid to pour the sample into the specimen jar.
2. Place the test jar in the selected test cell. Attach the detector head according to the manufacturer’s instruction.
3. Enter the expected pour point.
4. Start the test in accordance with the manufacturer’s instruction.
5. At this point, the instrument shall monitor the test specimen with the optical detector, adjusting the jacket temperature to the first temperature level and measuring the specimen temperature. When the pour point is determined, the instrument shall display the pour point result and start to reheat the test specimen.
6. Record the result as the pour point without any correction.

- Precision

Repeatability

The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed the following, only in one case in twenty.

$\pm$ 4.4 ^{o}C

B7. Friction coefficient analysis by SRV (ASTM D-5707) [20]

Figure B7 SRV instrument.

- Purpose

To analyze friction coefficient of lubricant by Oscillation Friction and Wear test machine (Fig. B7). Its ability to protect against wear when subject to high-frequency, linear-oscillation motion using.

- Definition

Coefficient of friction is the dimension less ratio of the friction force (F) between two bodies to the normal force (N) pressing these bodies together.

- Scope of test

This test method for determining a lubricating oil’s coefficient of friction and its ability to protect against wear when subjected to high-frequency, linear-oscillation motion using an SRV test machine at test load of 200N, frequency of 50 Hz, stroke amplitude of 1.00 mm, duration of 2 hours and temperature 50 ^{o}C.

- Test method

1. Clean the test pieces by sonicate with solvent for 5 minutes.
2. Set up test pieces as ball fix to holder and specimen base installed.
3. Use a spatula to place the sample on the test surface with a bit amount of oil.
4. Set load for 200 N and release load to ball to make sample touching on specimen surface.
5. Set up testing program as follow below parameter and start test.

Method for normal temperature

Test parameter

Load : 200 N
Temperature : 50 °C
Frequency : 50 Hz
Stroke : 1 mm
Time : 2 hours

- Acceptance Criteria

Acceptance Criteria of grease and oil‘s friction coefficient do not exceed 0.3.

- Precision

Repeatability

The difference between two test results, obtained by the same operator with same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty.

± 0.1 x

Where, x denotes average result

B8. Corrosion test by Copper plate method (ASTM D-130) [21]

It measures the corrosive attack of liquid petroleum products on copper by immersion under static laboratory conditions. The extent of damage is classified by comparing appearance with ASTM standards.

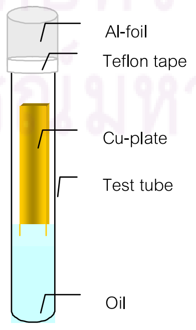


Figure B8 Illustration of sample preparation of corrosion test by copper plate method.

- Purpose

This test method to measure the corrosive attack of lubricating oil on copper plate under static laboratory conditions.

- Scope of test

A polished copper strip is immersed in oil and heat to 100 ^{o}C for 24 hours. The condition of the test strip is compared to ASTM corrosion standards (Fig. B9 and Table B1), provided by ASTM. The test serves as a measure of oil’s tendency to corrode copper under static conditions.

Figure B9 ASTM corrosion standards.

- Test method

Copper plate preparation

1. Remove all surface blemishes from all 6 sides of the copper plate with silicon carbide paper of such degrees of fineness as are needed to accomplish the desired results efficiently. Finish with 240-grit silicon carbide paper or cloth, removing all marks that may have been made by other grades of paper used previously.
2. Immerse the copper plate in Acetone which it can be withdrawn immediately for final preparation (polishing) and it can be stored for future use.

3. Remove a copper plate from the wash solvent. Subsequently handle only with stainless steel forceps; do not touch with the fingers and place it on clean paper.

Method

1. Pour 3 ml oil in test tube and dip copper plate in that tube then cover tube with Aluminum foil and seal with Teflon tape.
2. At the end of the test period, remove the sample from oven and allow them to cool to room temperature. Clean copper plate by slightly rub with clean room wipers.
3. Observed the discoloration of copper plate and interpret the corrosiveness of the sample accordingly as the appearance of the test strip agrees with one of the ASTM Copper Corrosion Standards.
4. When a copper plate is in the obvious transition state between that indicated by any two adjacent standard, judge the sample by the more tarnished standard. Should a copper plate appear to have a darker orange color than standard 1b, consider the observed plate as still belonging in classification 1; however, if any evidence of red color is observed, the observed plate belongs in classification 2.
5. A claret red plate in classification 2 can be mistaken for a magenta overcast on brassy plate in classification 3 if the brassy underlay of the latter is completely masked by a magenta overtone. To distinguish, immerse the plate in wash solvent; the former will appear as a dark orange plate while the latter will not change.
6. Take photo for discoloration of copper plate by microscope.

Table B1 Description of ASTM corrosion standards [21]

Classification	**Designation**	**Description**
1a	Slight tarnish	Light orange, nearly identical to freshly polished strip
1b	Slight tarnish	Dark orange
2a	Moderate tarnish	Claret red
2b	Moderate tarnish	Lavender
2c	Moderate tarnish	Multicolored with lavender blue or silver, or both, overlaid on claret red
2d	Moderate tarnish	Silver
2e	Moderate tarnish	Brass or gold
3a	Dark tarnish	Magenta overcast on brass strip
3b	Dark tarnish	Multicolored with red and green, but no gray
4a	Corrosion	Transparent black, dark gray or brown, with some green barely showing
4b	Corrosion	Graphite or lusterless black
4c	Corrosion	Glossy or jet black

B9. Thermal stability by TG/DTA instrument

Thermo gravimetric (TG) is the instrument for thermal analysis. Sample mass is gradually decreased when heating is applied to sample continuously. Measurements of changes in sample weight with temperature are using thermo balance. A thermo balance is a combination of a furnace, a temperature programmer and computer for control and data capture.

Figure B10 TG/DTA instrument.

- Purpose

Monitoring of the temperature difference between a sample and an inert reference as they are heated uniformly. Endothermic or exothermic changes in the sample lead to characteristic deviations in temperature.

- Scope of test

When sample weight changed, the optical position sensors detect changes in the position of slit and send the signal to balance circuit. The balance circuit feedback current for return the position of slit to balance. The current is detected and converted into weight signals.

- Test method

1. Turn on the power to the station.
2. Turn on the power to the TG/DTA module and wait a while, and then check that the liquid crystal displays shows "N Ready" (N is the channel no. it is connected to).
3. If gas flow during measurement is require, start the gas flow in advance.
4. Display the measurement screen for the Channel number connected to the TG/DTA module. Sample weighting is performed using the following as weight of sample about 10 mg into aluminum pan.
5. Pull the furnace to the front, turn off the fan switch, and place the containers that set program as bake at temperature 150 °C with rate 5.0 °C /min and hold 24 hours.

6. Close the furnace and wait for TG signal to stabilize. When it has stabilize, press zero key for the channel connected to the TG/DTA.
7. Check that the sample information of that channel read 0.0 mg.
8. Open the furnace again and place the samples in the respective pans, close the furnace.
9. Again wait for the TG signal to stabilize.
10. Go to the sample window. When the signal stabilize, move the cursor to AUTO WEIGHT and press enter.
11. Start run.
12. After finished testing, weight loss was record.

B10. Oxidation induction time of lubricant by RBOT (ASTM D-2272) [22]

The instrument use to utilizes an oxygen-pressured vessel to evaluate the oxidation stability of oil sample in the presence of water and copper catalyst coil at high temperature

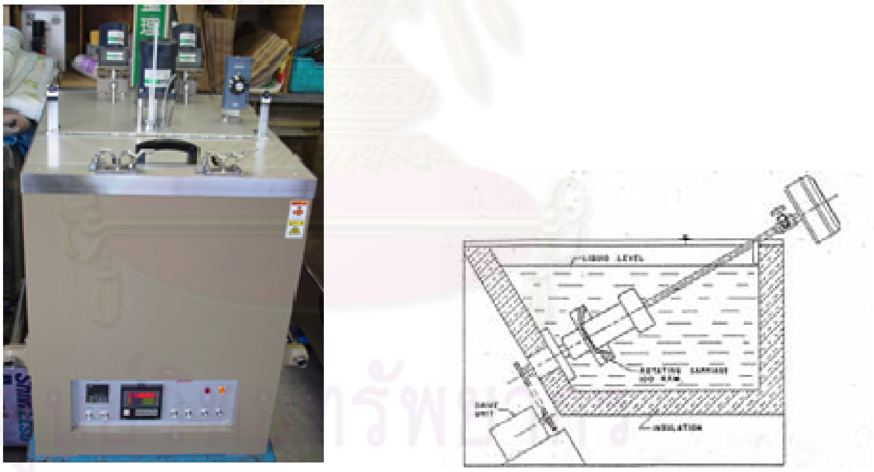


Figure B11 RBOT instrument.

- Purpose

The estimate of oxidation stability is useful in controlling the continuity of this property for batch acceptance of production lots having the same operation. Furthermore, it is also used to assess the remaining oxidation test life of in-service oils.

- Scope of test

The test oil, water and copper catalyst coil, contained in a covered glass container, are placed in a bomb equipped with pressure gauge. The bomb is charge with oxygen to pressure of 620 kPa, paced in a constant temperature oil bath set at 150 ^{o}C and rotated axially at 100 rpm at an angle 30 degrees from horizontal. The time for the test oil to react with given volume of oxygen is measured, completion of the time being indicated by a specific drop in pressure of 175 kPa.

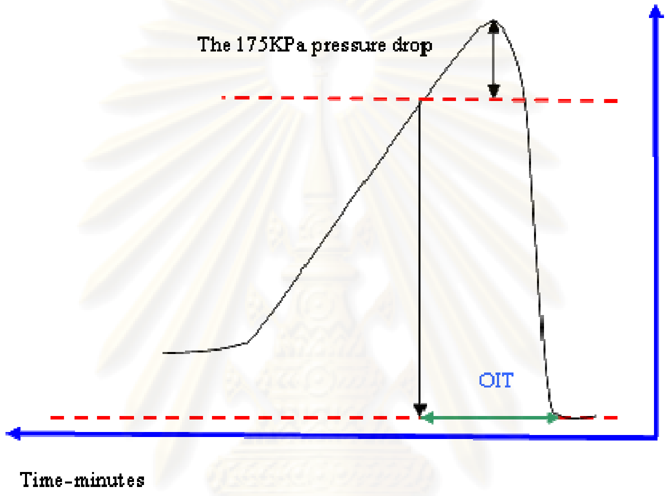


Figure B12 Oxidation induction time (OIT) by RBOT instrument.

From Fig. B12, observe the plot of the recorded pressure versus time and pressure. The result (Oxidation induction time) will be recorded the time at the point on the falling part of the curve where the pressure is drop 175 kPa from the highest pressure.

- Test method

Cu catalyst coil preparation

1. Before use, must be polish approximately 3 m of copper (Cu) wire with the silicone carbide abrasive cloth and wipe free from abrasive with the clean, dry cloth.
2. Wind the wire into a coil having an outside diameter 44 to 48 mm and stretched to a height of 40 mm to 42 mm.
3. Clean the coil thoroughly with solvent and make dry.

Sample preparation

1. Insert freshly cleaned catalyst coil inside the glass sample container by turning motion.
2. Set the weight of the glass sample container with a freshly cleaned catalyst coil to zero.
3. Weight 50 ± 0.5 g. of sample oil into the container; also add 5 ml of DI water.
4. Add another 5 ml of DI water to the vessel body.
5. Slide the sample container into vessel body.
6. Cover the glass container with 57.2 mm PTFE disk and place a PTFE ring on top of the PTFE disk .
7. Apply a thin coating of silicone grease to the O-ring vessel seal located in the gasket groove of the vessel cap to provide lubrication.
8. Insert the cap into the vessel body.
9. Tighten the closure ring. Cover the threads of the oxygen pressure sensor.
10. Attach the oxygen line with an inline pressure gage to the inlet valve on the vessel stem.
11. Slowly turn on the oxygen supply valve until the pressure has reached 620 kPa.
12. Turn off the oxygen supply valve. Slowly release pressure by purging process two more times; purge step should take approximately 3 minutes.
13. Adjust the regulating valve on the oxygen supply tank to 620 kPa at room temperature, 5 kPa shall be added or subtracted to attain the required initial pressure.
14. Fill the vessel to this required pressure and close the inlet valve securely by hand.

Method

1. Before testing, bring the heating bath to the test temperature while the stirrer is in operation.
2. Switch off stirrer, insert the vessel into the carriages and record the time.
3. Restart the stirrer.

4. The bath temperature shall stabilize at the test temperature within 15 minutes after the vessel is inserted. Maintain the test temperature within ± 0.1 °C.
5. Keep the vessel completely submerged and maintain continuous and uniform rotation throughout the test. A standard rotational speed of 100 ± 5 rpm is required.
6. The test is complete after the pressure drops more than 175 kPa below the maximum pressure.
7. After termination of the test, the vessel shall be removed from the oil bath and cooled to room temperature.

- Precision

Repeatability

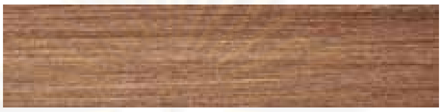
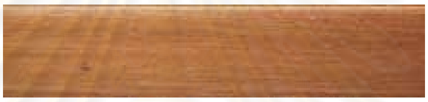
The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in long run, in the normal and correct operation of this test method.

± 30 minutes

APPENDIX C

PICTURES OF Cu CORROSION AND WEAR SCAR

Table C1 Pictures of Cu plate corrosive results of base oil samples

Sample	**Picture of Cu plate after tested**	**Corrosive level**
Blank		-
DOS		1a
TCP		1b
HP + OPANA (0.50 : 0.50)		1b
HP + TZ (0.50 : 0.50)		1b
OPANA + TZ (0.50 : 0.50)		1b
HP + OPANA+ TZ (0.33 : 0.33 : 0.33)		1b
HP + OPANA + TZ (0.25 : 0.25 : 0.50)		1b

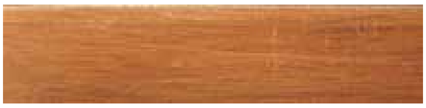
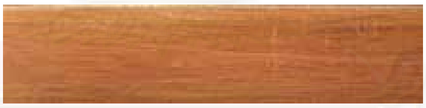
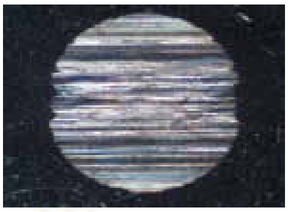
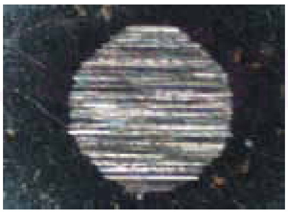
Sample	Picture of Cu plate after tested	Corrosive level
HP + OPANA + TZ (0.20 : 0.40 : 0.40)		1b
HP + OPANA + TZ (0.50 : 0.25 : 0.25)		1b
HP + OPANA + TZ (0.40 : 0.20 : 0.40)		1b
HP + OPANA + TZ (0.40 : 0.40 : 0.20)		1b
HP + OPANA + TZ (0.20 : 0.40 : 0.40) + TCP		1b
Commercial		1b

Table C2 Wear scar by SRV instrument

Sample	Wear scar	
	Scar picture	Scar size [mm.]
base oil		1.3
TCP		0.99
HP+ OPANA + TZ (0.20 : 0.40 : 0.40)		0.98
HP+ OPANA + TZ (0.50 : 0.25 : 0.25)		1.01
HP+ OPANA + TZ (0.20 : 0.40 : 0.40) + TCP (0.50)		0.95
HP+ OPANA + TZ (0.50 : 0.25 : 0.25) + TCP (0.50)		0.97
Commercial		1.01

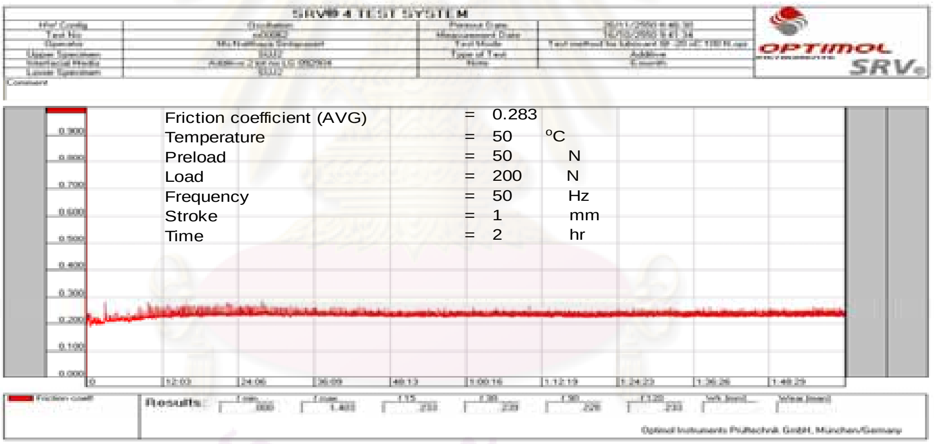
APPENDIX D

OXIDATION INDUCTION TIME AND FRICTION COEFFICIENT

Table D1 The oxidation induction time of oil samples

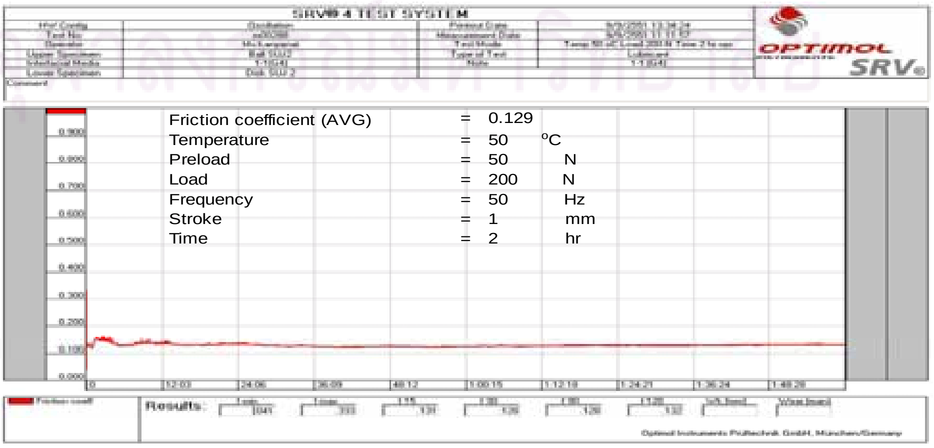
Sample designation	OIT (minutes)	
	100 °C	150 °C
HP + OPANA + TZ (0.30 : 0.35 : 0.35)	2495	1005
HP + OPANA + TZ (0.35 : 0.30 : 0.35)	2455	990
HP + OPANA + TZ (0.35 : 0.35 : 0.30)	2470	1020
HP + OPANA + TZ (0.45 : 0.45 : 0.10)	1840	981

Friction coefficient by SRV instrument



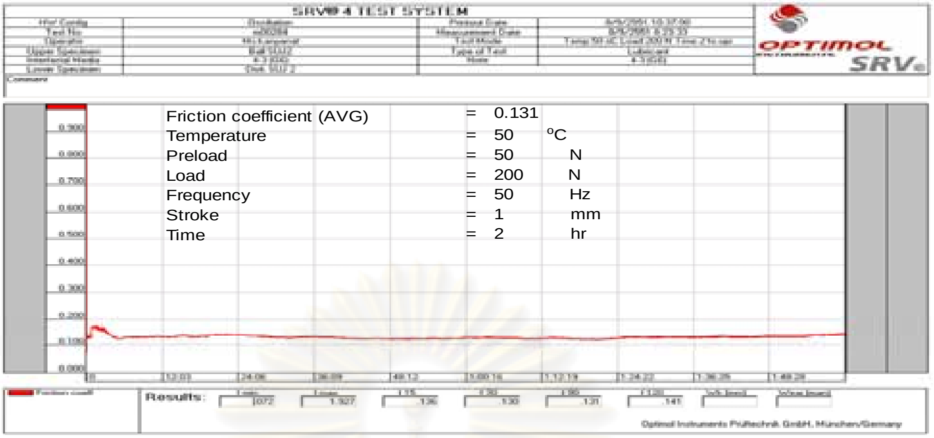
Friction coefficient (AVG) = 0.283
Temperature = 50 °C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D1 Graph of friction coefficient versus testing time at 50 ^{o}C of base oil.



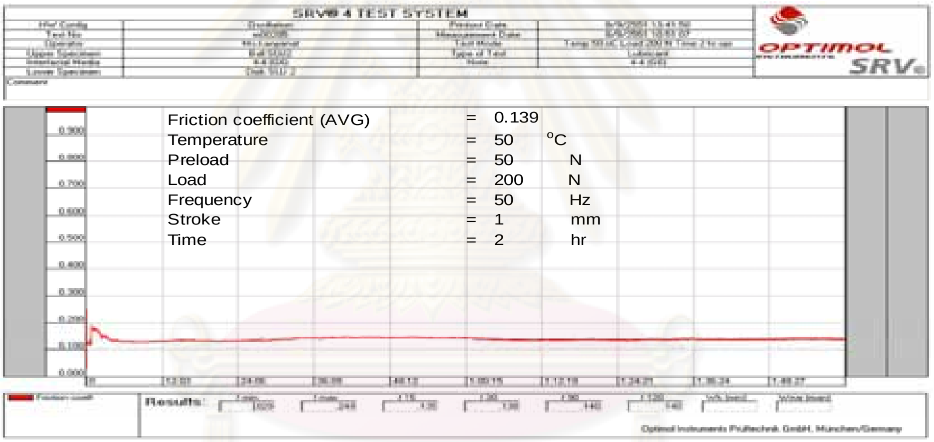
Friction coefficient (AVG) = 0.129
Temperature = 50 °C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D2 Graph of friction coefficient versus testing time at 50 °C of base oil with TCP.


SRV® 4 TEST SYSTEM

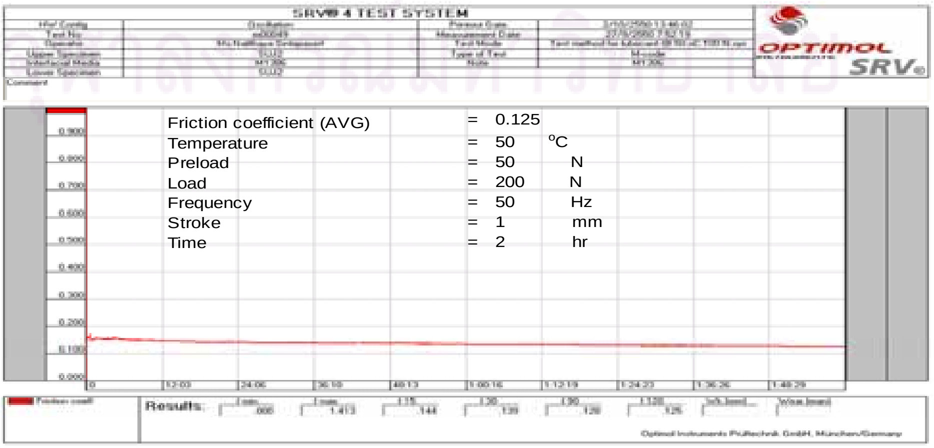
Friction coefficient (AVG) = 0.131
Temperature = 50 °C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D3 Graph of friction coefficient versus testing time at 50 °C of base oil with HP + OPANA+ TZ (0.20 : 0.40 : 0.40).


SRV® 4 TEST SYSTEM

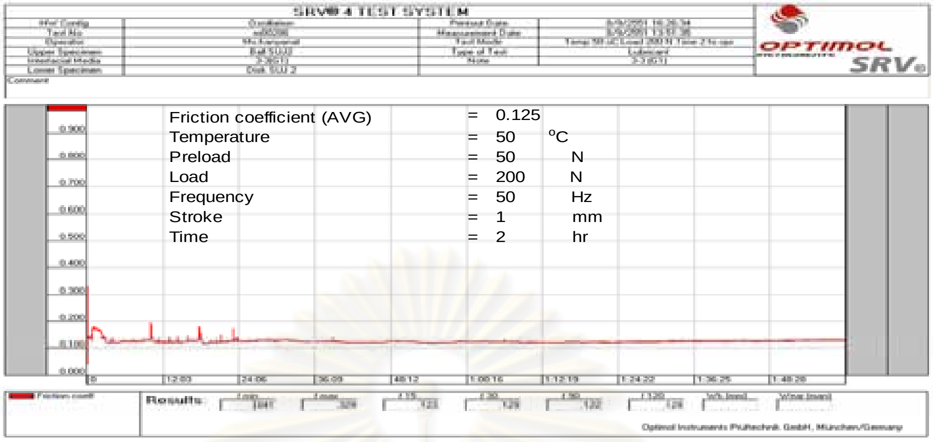
Friction coefficient (AVG) = 0.139
Temperature = 50 °C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D4 Graph of friction coefficient versus testing time at 50 °C of base oil with HP + OPANA + TZ (0.50 : 0.25 : 0.25).


SRV® 4 TEST SYSTEM

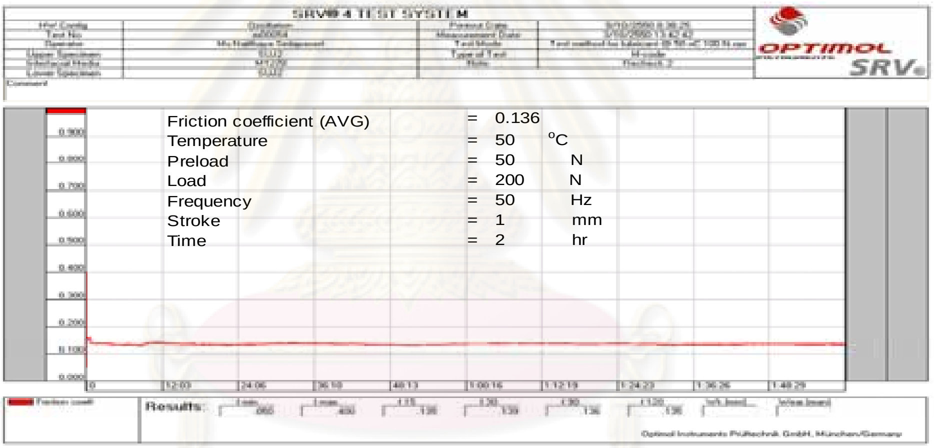
Friction coefficient (AVG) = 0.125
Temperature = 50 °C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D5 Graph of friction coefficient versus testing time at 50 ^{o}C of base oil with HP + OPANA + TZ (0.20 : 0.40 : 0.40) + TCP.



Friction coefficient (AVG) = 0.125
Temperature = 50 ^{o}C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D6 Graph of friction coefficient versus testing time at 50 ^{o}C of base oil with HP + OPANA + TZ (0.50 : 0.25 : 0.25) + TCP.



Friction coefficient (AVG) = 0.136
Temperature = 50 ^{o}C
Preload = 50 N
Load = 200 N
Frequency = 50 Hz
Stroke = 1 mm
Time = 2 hr

Figure D7 Graph of friction coefficient versus testing time at 50 ^{o}C of commercial oil.

VITA

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