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นายธนทัฐ พฤกษ์ไพบูลย์

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TRIBOLOGICAL CHARACTERISTICS OF MOLYBDATE ESTERS

Mr. Tanatath Pluekpaiboon

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By	Mr. Tanatath Pluekpaiboon
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Thesis Advisor	Assistant Professor Warinthorn Chavasiri, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

S. Hannongbua ..... Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

..... Chairman

(Professor Pattarapan Prasassarakich, Ph.D.)

Warinthorn Chavasiri ..... Thesis Advisor

(Assistant Professor Warinthorn Chavasiri, Ph.D.)

W. Trakarnpruk ..... Examiner

(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

Pongchart Buranaprasertsuk ..... External Examiner

(Pongchart Buranaprasertsuk, Ph.D.)

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งานนี้ได้ศึกษาผลของหมู่แอลคิลของสารเติมแต่งโมลิบเดตเอสเทอร์ต่อการต้านการสึกหรอ สารเติมแต่งนี้ได้สังเคราะห์จากการทำปฏิกิริยาระหว่างไดเอทานอลามีน เกลือของโมลิบดีนัมและกรดไขมันชนิดต่างๆ จากนั้นผสมสารเติมแต่งที่ได้กับน้ำมันพื้นฐานและทดสอบสมบัติการสึกหรอ สารสังเคราะห์โมลิบเดตเอสเทอร์มีปริมาณโมลิบดีนัมอยู่ประมาณ 2 %โดยน้ำหนัก ผลการทดสอบการสึกหรอด้วยเครื่อง Four-ball tester แสดงดังนี้ 0:0.76, 20:0.64, 60:0.64, 120:0.66 และ 200:0.44 (ppm ของ Mo:มม. ของ เส้นผ่านศูนย์กลางรอยสึกหรอ) แสดงถึงสมบัติต้านการสึกหรอได้ โดยมีแนวโน้มของเส้นผ่านศูนย์กลางรอยสึกหรอกลับกันกับสัดส่วนของปริมาณโมลิบดีนัมในน้ำมันผสม อย่างไรก็ตามน้ำมันผสมเกิดการแยกตัวเป็น 2 วัฏภาคภายใน 2-3 ชั่วโมง การเปลี่ยนสูตร ชนิดของน้ำมันพื้นฐานและเติมสารช่วยในการกระจายตัวพบว่าน้ำมันผสมมีความคงตัว เส้นผ่านศูนย์กลางรอยสึกหรอของน้ำมันผสมเพิ่มขึ้นเมื่อเติมสารช่วยในการกระจายตัวและสารสังเคราะห์โมลิบเดตเอสเทอร์

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This work explores the effect of the alkyl group of molybdenum ester additives on antiwear. The additives were synthesized by the reaction of diethanolamine, molybdenum salt and various fatty acids. The derived additive was then mixed with base oil and tested for wear property. The synthesized molybdate ester contained molybdenum about 2 wt%. The wear tests by Four-ball tester were as follows: 0:0.76, 20:0.64, 60:0.64, 120:0.66 and 200:0.44 (ppm of Mo:mm of wear scare diameter). The synthesized molybdenum esters exhibited antiwear property. The trend of wear scare diameter revealed the reversed proportional to the Mo content in blended oil. However the blended oil was split into 2 phases within few hours. By changing the formulations, base oil type, adding dispersant, the stability of blended oil could be maintained. The wear scare diameter of blended oils was increased with the addition of dispersants and synthesized molybdate esters.

Field of Study: Petrochemistry and Polymer Science
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Student's Signature Tanatath Pluekpaiboon
Advisor's Signature W. Chavasiri

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LIST OF ABBREVIATIONS

API	American Petroleum Institute
A_r	Atomic weight
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
DEA	Diethanolamine
DODPA	*p,p′*-dioctyl-diphenylamine
DSC	Differential scanning calorimeter
E-amine	Ethylenediamine
EP additive	Extreme pressure additive
EtOAc	Ethylacetate
FT-IR	Fourier transform infrared spectroscopy
HOO	Hot oil oxidation test
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
IOT	Incipient oxidation temperature
ME	Synthesized molybdate ester
Mo	Molybdenum
MoDTC	Molybdenum dialkyldithio-carbamate
NH_4Mo	Ammonium molybdate
OIT	Oxidation induction time
P-amine	Propylamine
PAO	Poly-α-olefin
PTFE	Polytetrafluoroethylene
T-amine	Triethylenetetramine
VI	Viscosity index
WSD	Wear scare diameter
ZDDP	Zinc dialkyldithiophosphate
ZnP4	Zinc di-n-butyldithiophosphate and zinc di-n-heptyldithiophosphate
ZnP8	Zinc di-n-octyldithiophosphate

ZnS4	Zinc di-iso-butyldithiophosphate and zinc di-iso-heptyldithiophosphate

CHAPTER I

INTRODUCTION

1.1 Purpose of investigation

In 2010, Thailand imported lubricant additives approximately 5.6 billion Baht [1]. If these kinds of additives are commercially available with similar properties inside the country, it is definitely reduced the imports. Molybdenum compound is one of the general additives used in lubricant for engines in industry and automobile to reduce friction and anti-wear. Some reports involve modifying the structures of molybdenum compounds to be of an anti-wear property and anti-oxidation which were similar to zinc dialkyldithiophosphate (ZDDP) [2]. However, according to the literature review, there has been the limitation of using allkylthiophosphate ligands which are harmful to health and environment. This research focuses on the synthesis of molybdenum ester of fatty acids which can be found easily and inexpensive. In addition, the performance of synthetic substances as an anti-wear and anti-oxidation was conducted.

1.2 Research objectives

The objective was to synthesize lubricant additives consisting of molybdenum ester of fatty acids with anti-wear property.

1.3 Scope of investigation

1. Literature review and in-depth study concerning this research work.
2. Synthesize molybdate oleate ester and adjust the reaction conditions to obtain good yield of target product.
3. Synthesize molybdate esters from stearic acid and octanoic acid.

4. Characterize the synthesized molybdate esters by FT-IR and determine the molybdenum content by ICP-AES.
5. Investigate wear and oxidation properties, and kinematic viscosity of blended oil containing synthesized products, dispersants and base oil.
6. Summarize data and report.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Tribology, friction, wear and lubrication [3-4]

Tribology is the science involving the study of friction, wear and lubrication of system. An object moving or rubbing on others produces the friction causing to energy lost and wear damage to the objects. The system was thus needed a lubricant to reduce friction and wear for better economic and efficiency of the system.

Friction is the force that resists or hinders of object movement on other surfaces calling an external friction. On the other hand, the internal friction is the friction between lubricant molecules such as viscosity.

“Wear” could be classified into 3 types depending on mechanisms as follows:

1. Adhesive wear occurs in rubbing of objects with similar in hardness and high load until adhesive force is larger than cohesive force of the objects then weld the contact surface and tear out the surface.

2. Abrasive wear occurs in rubbing of matters with different in hardness and loading not too high till adhesive force is larger than cohesive force of the matters. An object that has lower hardness will tear out by other.

3. Tribochemical reactions are the wear resulting from the chemical reaction in tribological condition.

Lubrication is the modified sliding surface by introducing lubricant between the surfaces. Lubricants could be classified into 3 types as solid, liquid lubricants, and grease.

Liquid lubricant normally inserts between the surfaces of object to prevent the surface contact and rubbing that the course of wear. Solid lubricant formed the thin, soft coating on the surface to reduce friction such as graphite, molybdenum disulfide, PTFE plastic or by a sulfur-, phosphorus-rich layer formed by adsorption of additives from a lubricating oil (Fig 2.1).

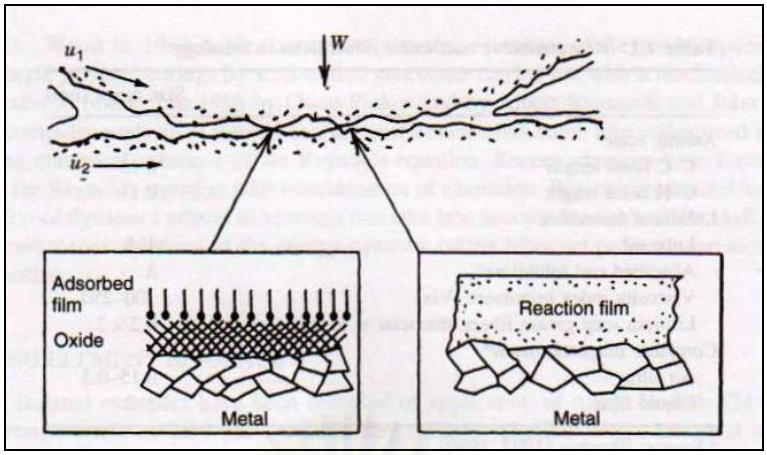


Fig 2.1 Surface films at asperity contacts between rubbing surfaces. [3]

Solid lubricant does not squeeze out when carrying high load which is different from liquid lubricant (Fig 2.2).

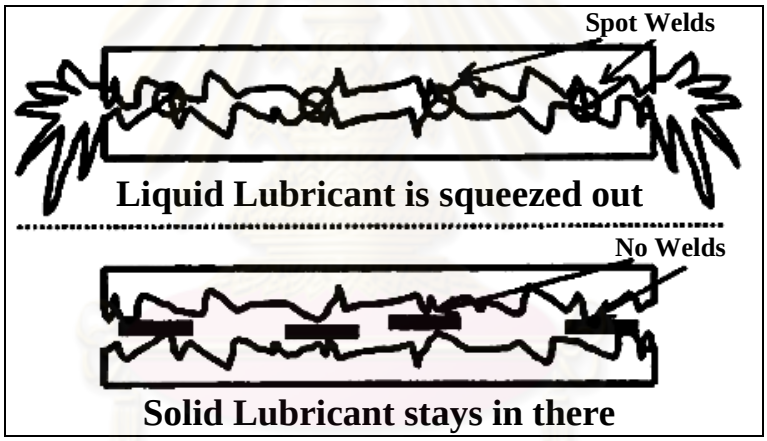


Fig 2.2 Comparison of liquid and solid lubricant carry high load. [4]

Grease is the mixture of oil and soap, sodium, calcium or lithium soap jelly. It forms gel-like so it can apply to the open box tools and gears such as ball bearing and open gear (Fig 2.3).

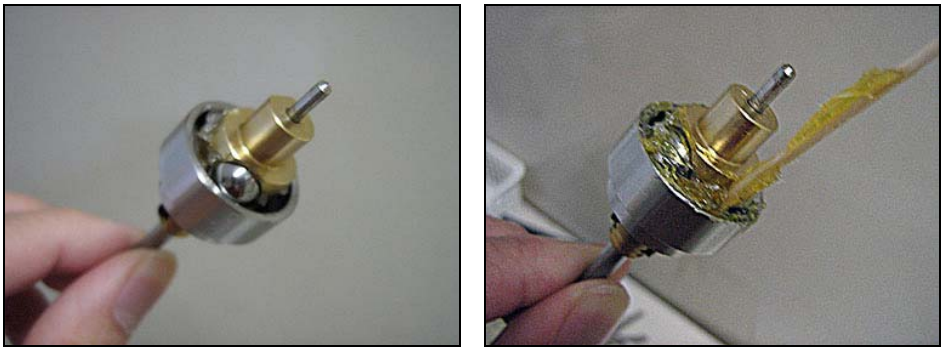


Fig 2.3 Grease application.

2.2 Application of molybdenum as lubricant additive [4]

Molybdenum was used in lubrication field since the early 19th century as dry lubricant of molybdenum disulfide powder with purity usually exceeds 98%. Hexagonal lattice structure of molybdenum disulfide is displayed in Fig 2.4. The weak van der Waal forces between sulfur atoms of hexagonal MoS_2 sheet act as easy shear sliding sheet between rubbing surface to reduce friction, while the strong covalent bond between molybdenum and sulfur atoms of crystal could carry high load to protect object from wear.

Many researchers synthesized oil soluble organomolybdenums and developed to other functional or multifunctional additives such as molybdenum dialkyldithio-carbamate (MoDTC) for friction modifier and anti-wear [5].

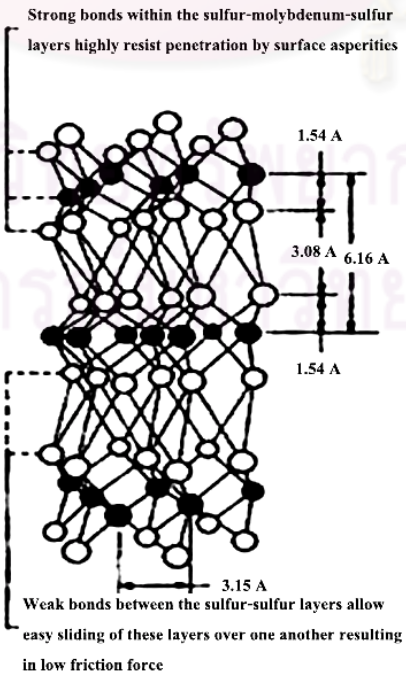
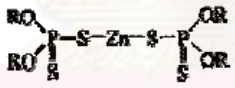
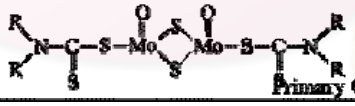


Fig 2.4 Lattice structure of molybdenum disulfide. [4]

2.3 Literature reviews

Muraki *et al*. [2] examined the effect of the alkyl group of zinc dialkyl-dithiophosphate (ZDDP) to friction coefficient of oils containing molybdenum dialkyldithiocarbamate (MoDTC) and ZDDP with a reciprocating roller-on-disk tester. The blended oils composed of base oil with viscosity of 20.74 mm^2/s at 40°C and 4.19 mm^2/s at 100°C, and ZDDP and MoDTC at different extents. The chemical structure and properties are presented in Table 2.1. The effect of molybdenum content to the friction coefficient in blended oils containing Zn at 1000 ppm revealed that the content of molybdenum reduced the coefficient of friction. The effect of alkyl group in ZDDP compared with blended oil containing Zn at 1000 ppm and Mo at 50 ppm was examined. ZDDP with *n*-octyl group provided the lowest friction coefficient. When the Mo/Zn ratio at concentration of molybdenum being higher than 50 ppm, the small effect of alkyl group in ZDDP was observed. The coefficient of friction curves are exhibited in Fig 2.5.

Table 2.1 The chemical structures and properties of additives. [2]

Additive	Content (mass%)				Chemical structure	Alkyl chain	Pyrolysis temperature[a] (°C)
	Zn	P	S	Mo			
ZnP8	7.6	6.6	11.6	–		Primary C8	280
ZnP4	8.9	8.0	16.8	–		Primary C4, C5	240
ZnS4	7.8	7.2	15.2	–		Secondary C4, C5	200
MoDTC	–	–	5.7	4.5		Primary C8 C13	360

Huang and co-workers [6] investigated tribological properties of magnesium alloy using compounds containing nitrogen as the additive by a block-on-ring wear tester with a similar configuration to a Timken tester in test condition as follows: sliding speed at 1.54 ms^{-1} at room temperature and load of 200 - 1000N with sample feed rate at 0.7 mL/min for 30 min. The block sample was made of an AZ91D magnesium alloy at a Vicker hardness of 96 and the ring sample was made of bearing steel (AISI52100) at a Vicker hardness of between 653 and 746.

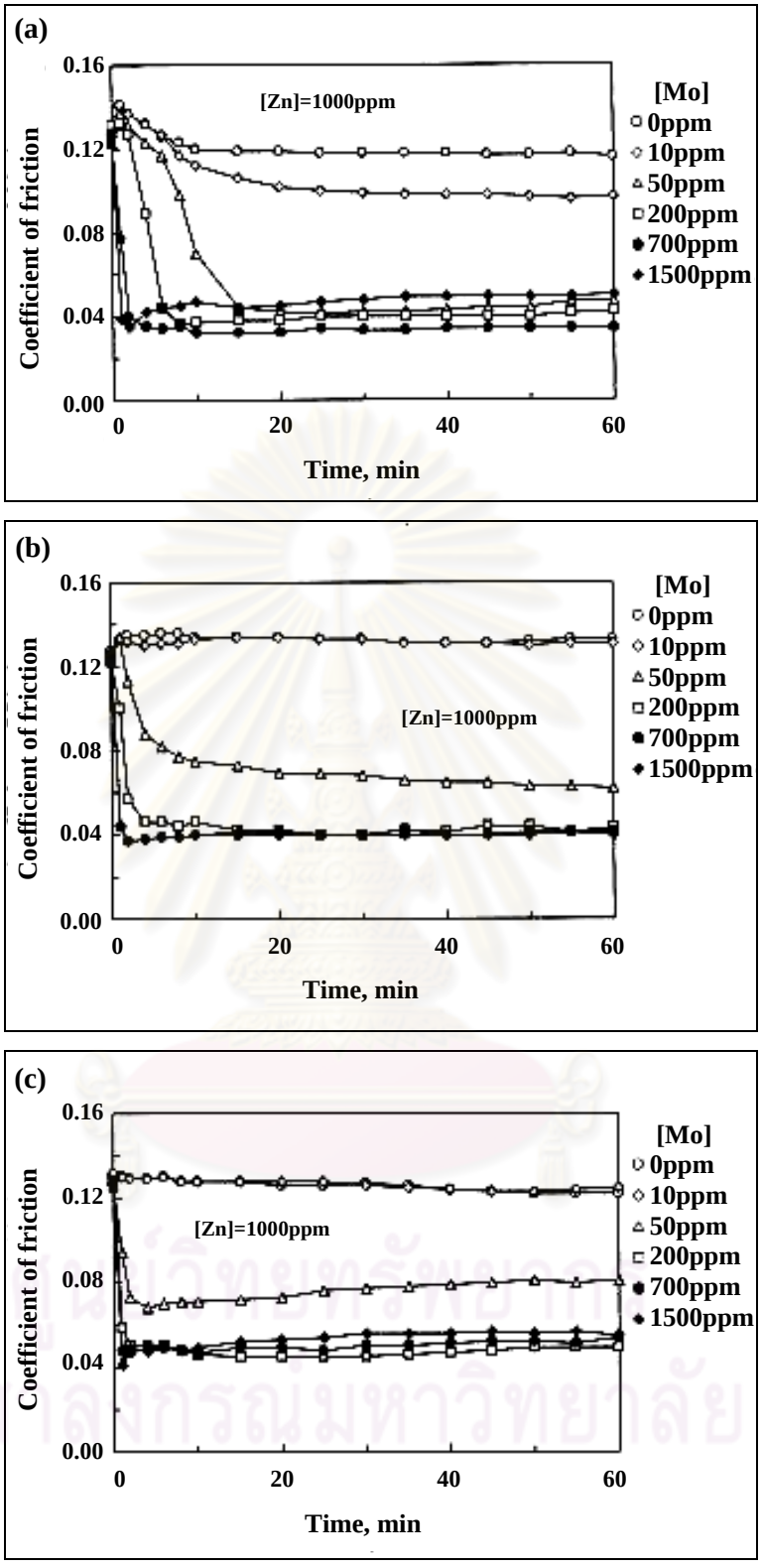


Fig 2.5 Coefficient of friction curves of blended oils.

(a) ZnP8+MoDTC, (b) ZnP4+MoDTC and (c) ZnS4+MoDTC [2]

The specimens were prepared by mixing together of 0-5 wt%. of additive in liquid paraffin, viscosity at 21.49 mm^2/s at 40°C and 4.42 mm^2/s at 100°C. The formulas and molecular weights of the additives showed in Table 2.2. The effect of number of amidogen group and different amides on wear, friction and load-carrying capacity were studied at 200 – 1000N of load. With 3 wt% of additive concentration, the wear, friction and load-carrying capacity of specimens were improved (Fig 2.6) The length of alkyl group of amides was found to improve wear, friction coefficient and load-carrying capacity of specimens (Fig 2.7). The effects of concentration on friction and wear were investigated at load of 400N and additive concentrations of 0-5 wt%. The results revealed the concentration of additives affecting the reduction of wear and friction of specimens and the optimum concentration at 3 wt% (Fig 2.8).

Table 2.2 Formulas and molecular weights of the additives. [2]

Additives	**Formulas**	**Molecular weight**
Propylamine (P-amine)	$CH_3CH_2CH_2NH_2$	59
Ethylenediamine (E-amine)	$H_2NCH_2CH_2NH_2$	60
Triethylenetetramine (T-amine)	$H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$	146
Acetamide	CH_3CONH_2	59
Acrylamide	$CH_2CHCONH_2$	71

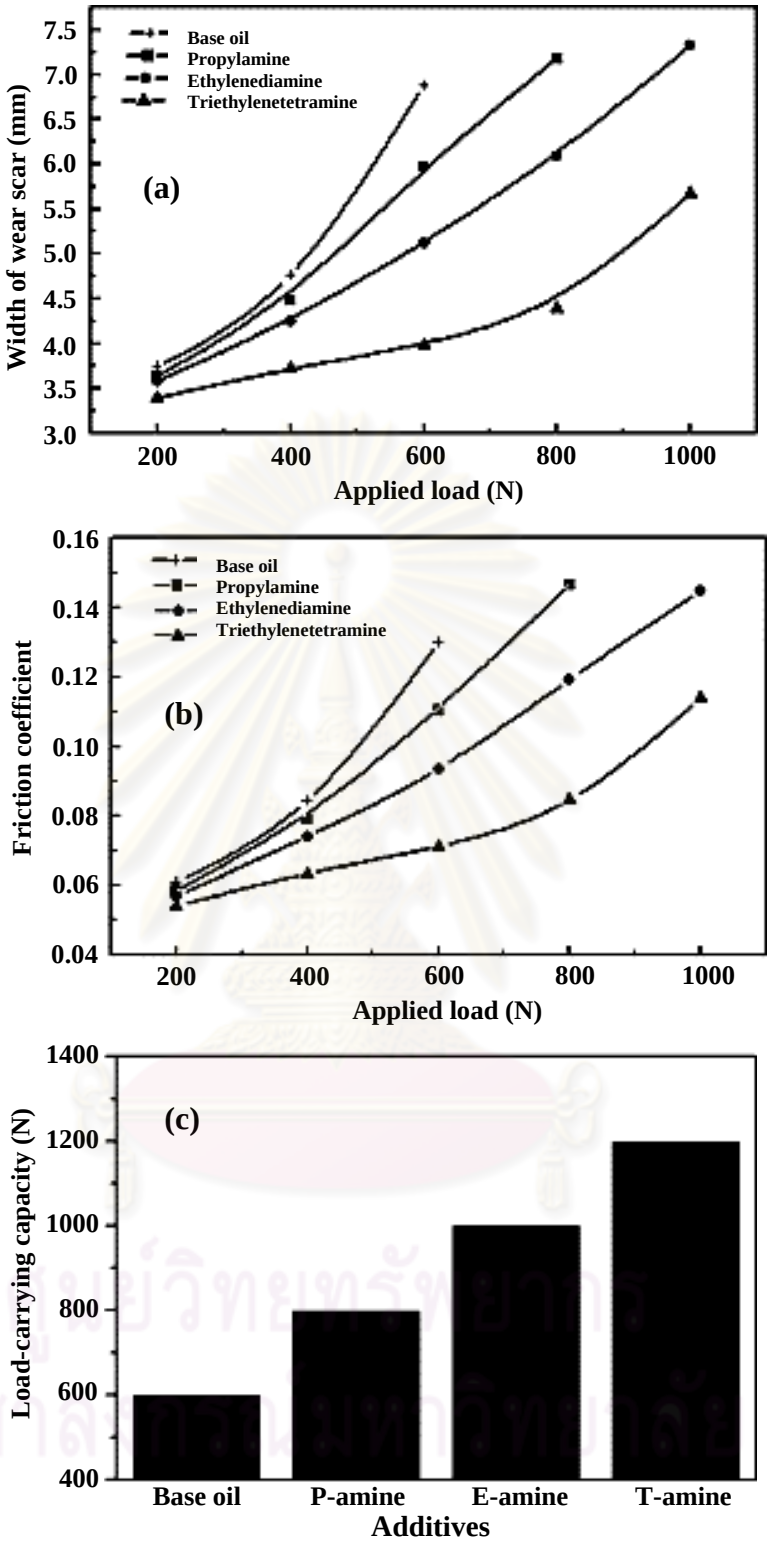


Fig 2.6 The effect of amidogen group on lubrication properties of specimens. (a) wear property, (b) friction coefficient property and (c) load-carrying capacity property. [2]

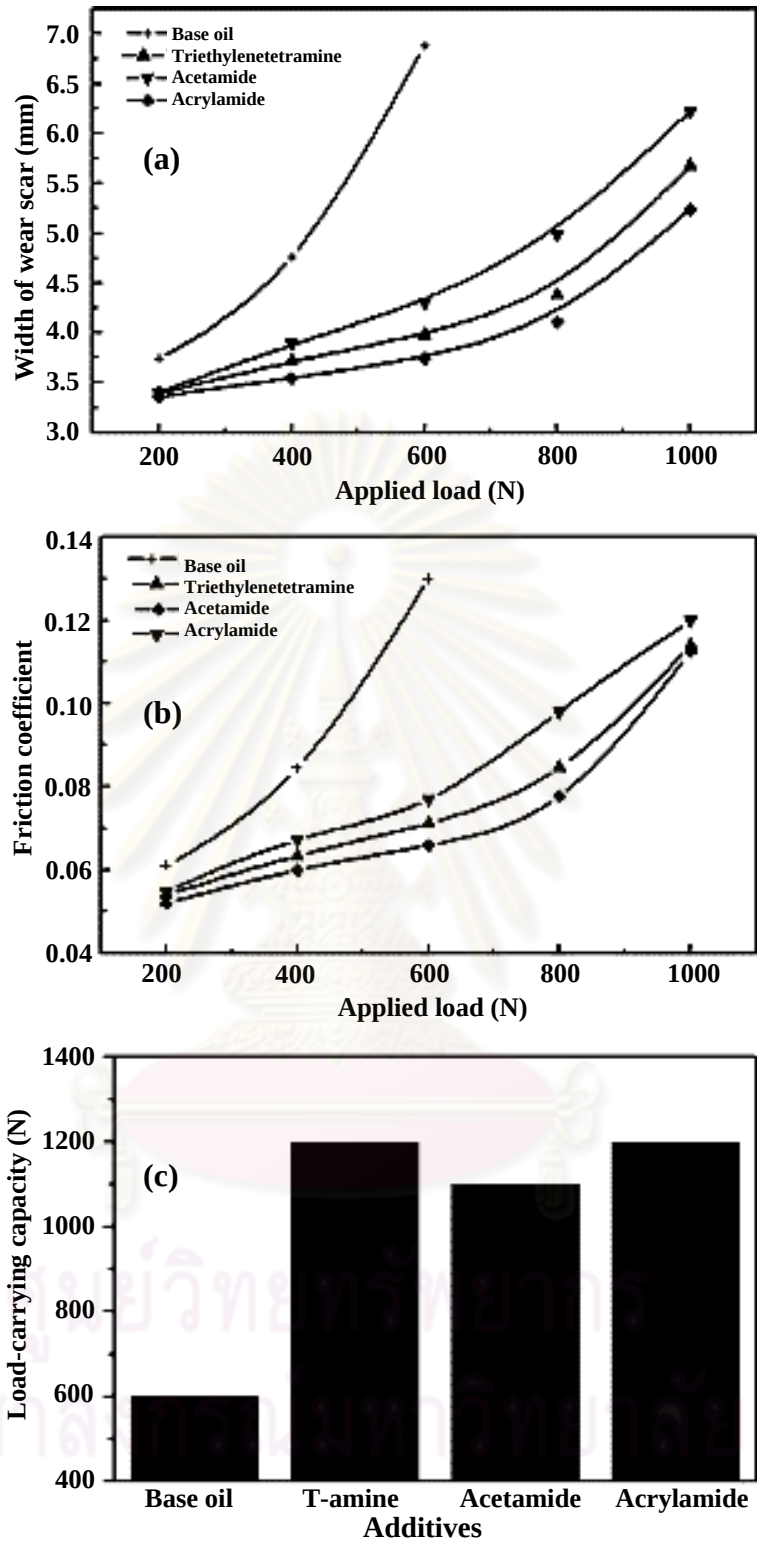


Fig 2.7 The effect of different amide on lubrication properties of specimens. (a) wear property, (b) friction coefficient property and (c) load-carrying capacity property. [2]

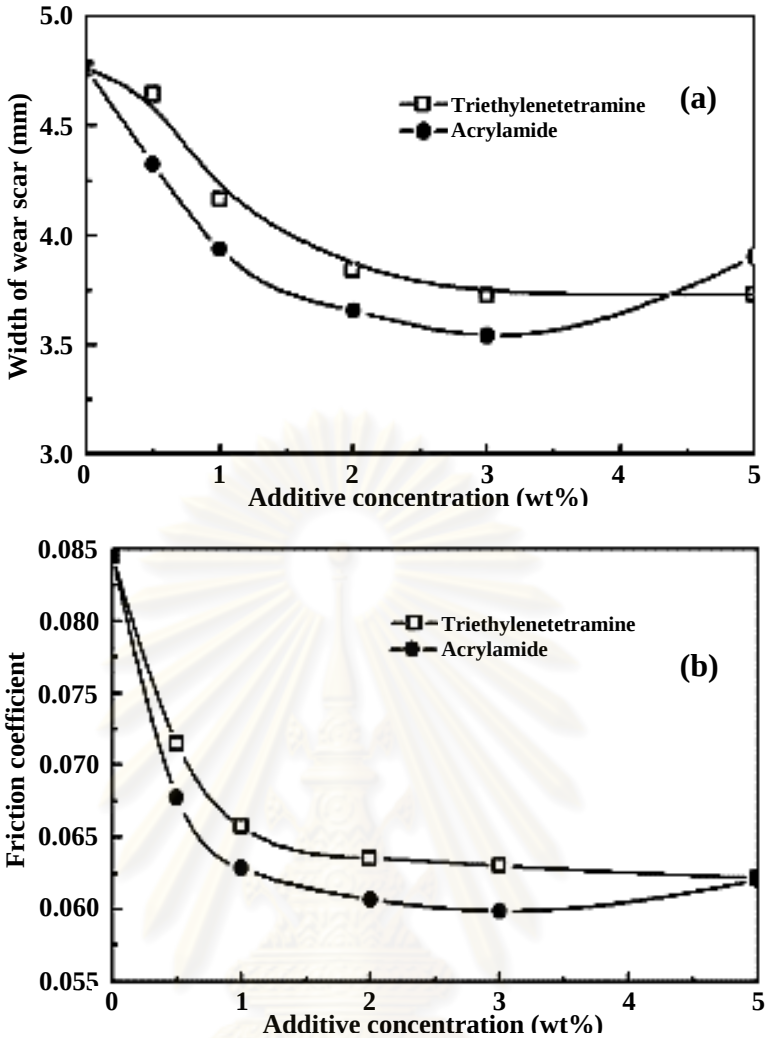


Fig 2.8 Effect of additive concentrations on wear and friction.
(a) wear curve and (b) friction coefficient curve. [2]

Hua and co-workers [7] synthesized molybdate ester (ME) of oleic acid by two-step reaction. First, the mixture of 28.3 g of oleic acid and 12.0 g of diethanolamine (DEA) was refluxed at 145°C for 1.5 h, and then 2.0 g of ammonium heptamolybdate in water was added and heated at 110°C for 1 h. The mixture was distilled under reduced pressure at 110°C and then filtered inorganic specimen to obtain brown liquid of ME. The structure of ME was confirmed by FT-IR (Fig 2.9). The oxidation property of mixed ME with poly-α-olefin 150 SN (PAO) and *p,p′*-dioctyl-diphenylamine (DODPA) was evaluated by differential scanning calorimeter (DSC) and hot oil oxidation test (HOO).

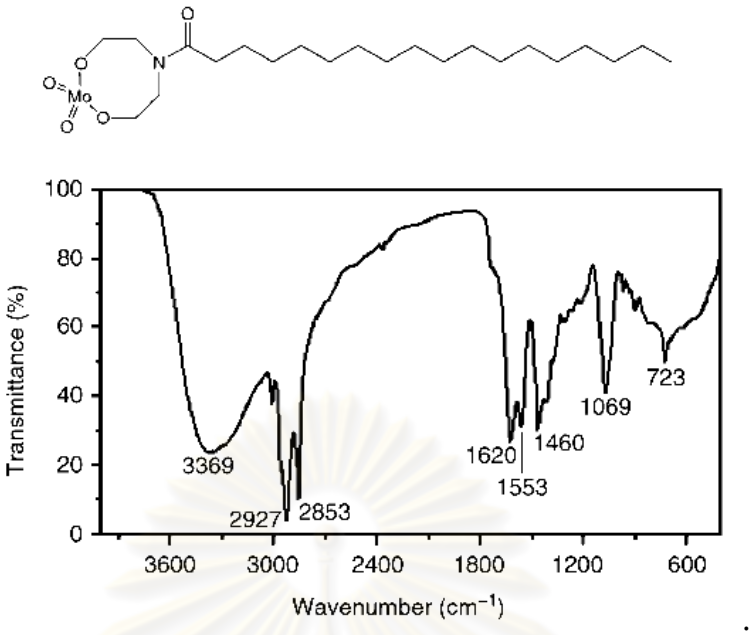


Fig 2.9 FT-IR spectrum and structure of ME [7]

Blended PAO, DODPA with and without ME were evaluated by DSC. The results of DSC in incipient oxidation temperature (IOT) and oxidation induction time (OIT) were displayed in exothermic and isothermal modes as shown in Figs 2.10-2.12.

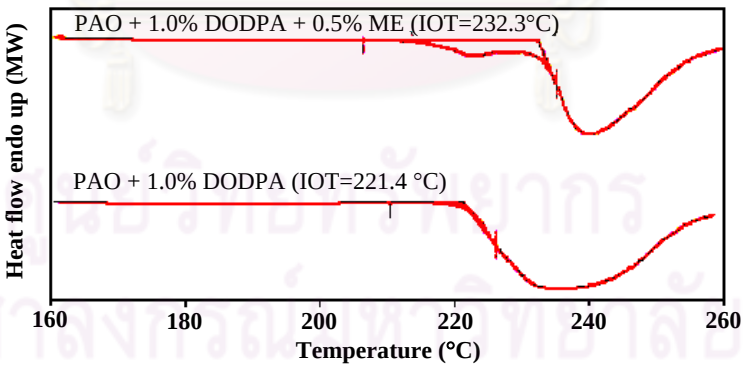


Fig 2.10 Temperature programmed DSC test of PAO oxidation in the presence of DODPA with and without ME at 10 °C/min [7]

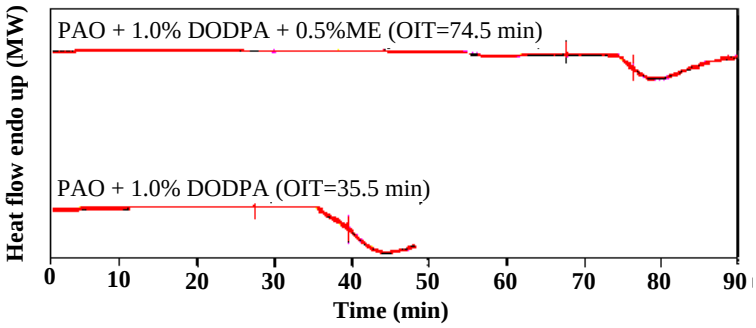


Fig 2.11 Isothermal DSC test of PAO oxidation in the presence of DODPA with and without ME at 180°C [7]

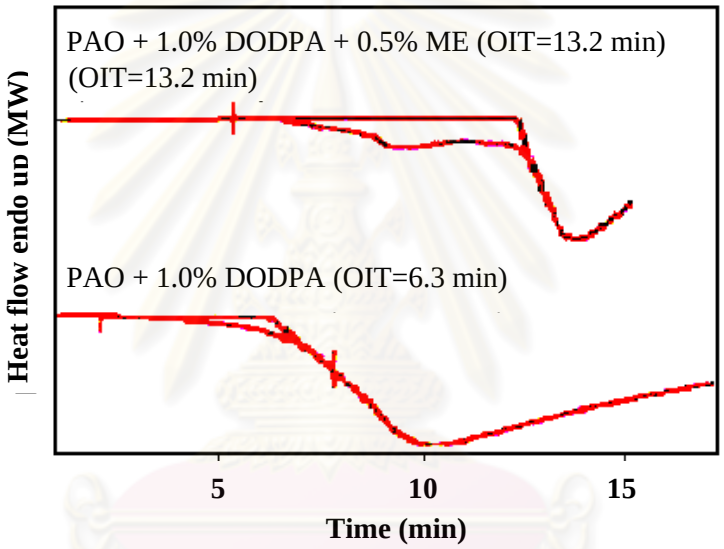


Fig 2.12 Isothermal DSC test of PAO oxidation in the presence of DODPA with and without ME at 200°C [7]

The IOT and OIT of blended oil with ME were higher than those without ME. The HOO test was carried out for blended oil of PAO, DODPA with ME and the blended oil without ME at 160°C and blew dry air through the oil at 10 L/h. The viscosity at 40°C was then measured at 24, 48, 72 and 96 h (Fig 2.13). The viscosity increasing of blended oil with ME was lower than blended oil without ME. The results of DSC and HOO exhibited that the antioxidation property of blended oil, PAO, DODPA and ME was better than that without ME.

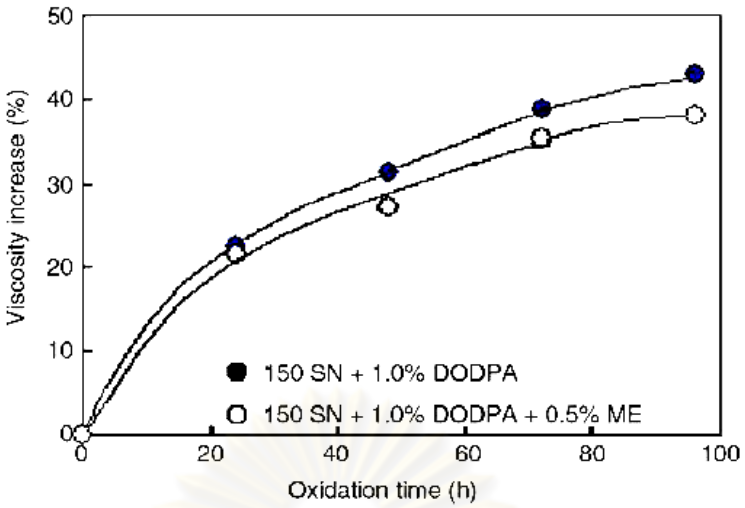
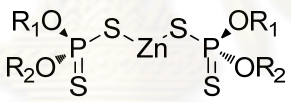


Fig 2.13 Time profile of viscosity increase for 1.0% DODPA-containing 150 SN oil with and without ME. [7]

Hua and co-workers [8] inspected tribological properties as wear and friction of oil containing ME of oleic acid and with ZDDP.



Structure of ZDDP

The friction and wear properties of blended oils were investigated by Four-ball machine with rotating speed 1450 rpm for 30 min and load of 392, 588 and 686 N at room temperature as presented in Figs 2.14-2.17. Figs 2.14-2.15 showed the optimal concentration of ME at 2.0% with the lowest WSD and the lowest friction coefficient. At high concentration of ME, above 2.0%, the friction coefficient was slightly increased. In Figs 2.16 and 2.17, good WSD and friction coefficient in blended oil were detected in range of 0.50% - 1.25% of ZDDP. With the concentration of ZDDP over 1.25%, the WSD and friction coefficient were increased at load of 686N. With the WSD and friction coefficient increased at high load and high concentration of ZDDP because corrosive wear occurred while high load and oil contained high sulfur and phosphorus decomposing from ZDDP.

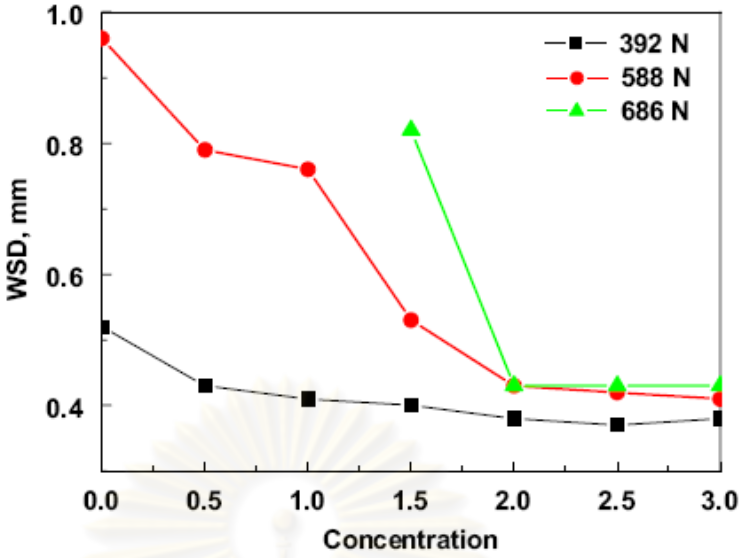


Fig 2.14 Effect of ME concentration on WSD with 1.0% ZDDP [8]

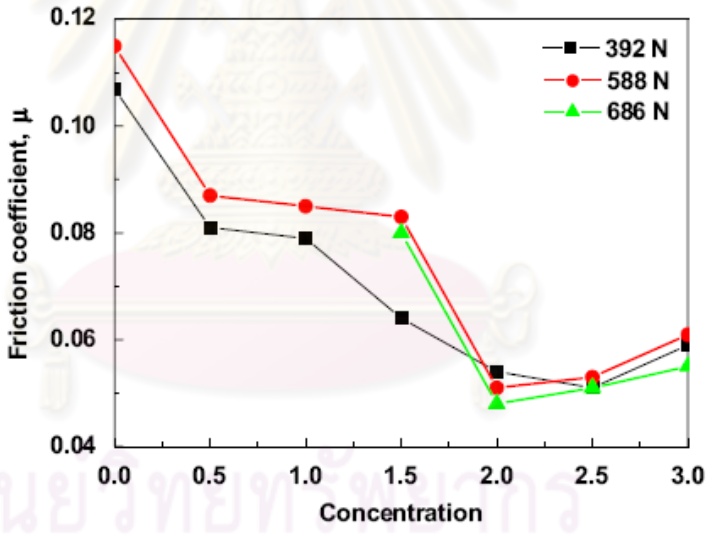


Fig 2.15 Effect of ME on friction coefficient with 1.0% ZDDP [8]

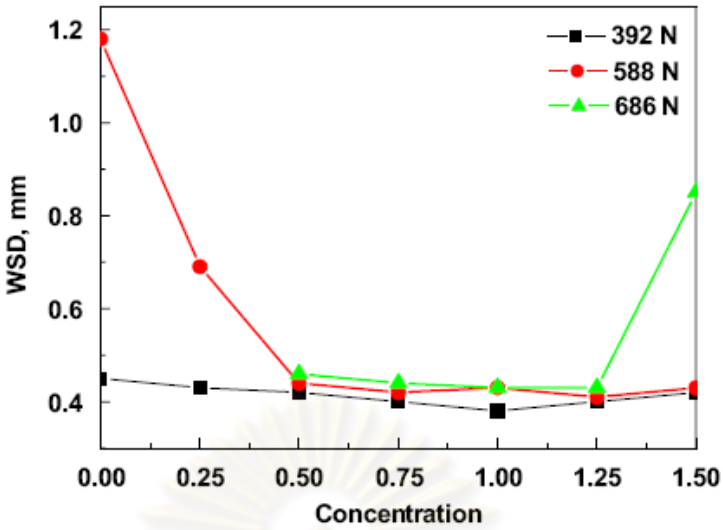


Fig 2.16 Effect of ZDDP concentration on WSD with 2.0% ME [8]

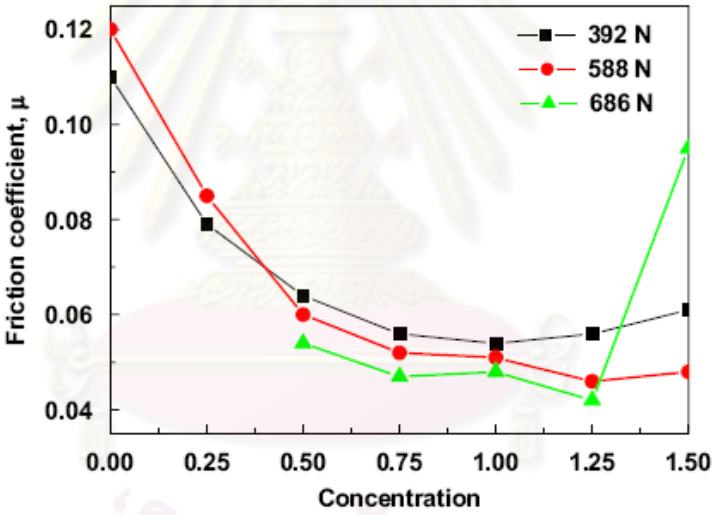


Fig 2.17 Effect of ZDDP on friction coefficient with 2.0% ME [8]

Both friction and wear properties of blended oil containing ME, ZDDP and base oil 150SN were better than those blended oils with either ME or ZDDP with base oil 150SN only.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

A list of chemicals used are as follows: Ammonium molybdate tetrahydrate, ACS reagent, purity ≥99.0% obtained from Riedel-de Haen, diethanolamine, ACS reagent, purity ≥ 99.0 % obtained from Fluka, oleic acid purity 90% and 1-octanoic acid, purity ≥98% purchased form Aldrich and stearic acid purity 95% purchased from Sigma-Aldrich.

Dispersants: Lubrizol 6404, Lubrizol 6420, Viscoplex 1-330 and base oil 150SN, 150J, 500SN, Yubase-4 were obtained from BP-castrol (Thailand) Ltd.

3.2 Synthesis of molybdate esters [7]

The molybdate ester was prepared by reacting the designed fatty acid: oleic acid, octanoic acid or stearic acid, and diethanolamine in the round bottom flask at 145°C for 1.5 h. The reaction mixture was cooled down to 110°C, and then ammonium molybdate solution was added. The reaction was continuously stirred at 110°C for 1 h. The mixer was dried by rotary evaporator. EtOAc was added into the mixture, then filtered inorganic matter out the filtrate was evaporated at 65°C to achieve the synthesized product. The reaction recipe is listed in Table 3.1.

Table 3.1 List of chemicals used in the reactions.

Reaction nos	Chemicals (eq)				
	Oleic acid	Stearic acid	Octanoic acid	DEA[1]	NH_4Mo[2]
1	1	-	-	1.14	0.113
2	1	-	-	1.14	0.565
3[3]	1	-	-	1.14	0.113
4	1	-	-	1.5	0.113
5	1	-	-	2	0.113
6	-	1	-	2	0.113
7	-	-	1	2	0.113

[1] diethanolamine

[2] ammonium molybdate (solution)

[3] ammonium molybdate (solid)

3.3 Properties of synthesized molybdate esters.

3.3.1 The appearance of synthesized molybdate esters

The synthesized molybdate esters were stored at ambient temperature for a week then observe their appearance.

3.3.2 Structure of synthesized molybdate esters

Perkin-Elmer Paragon 1000PC FT-IR operated in the range of 4000-550 cm^{-1} was used to proof the structure of the synthesized molybdate esters.

3.3.3 Determination of molybdenum content in synthesized molybdate esters

The molybdenum content in MEs was determined by ICP-AES technique according to ASTM D 5185 “Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES)” with Perkin-Elmer Optima 5300V. The dilution solvent prepared by diluted Conostand standard containing cobalt 5000 ppm in Exxol D 80 to final concentration about 10 ppm. The calibration curve was prepared by diluted Conostand S-21 multi-elements containing 500 ppm each with baseoil (Yubase-4) and

dilution solvent. The synthesized specimens were prepared in the same way with working standard about 10 folds of dilution.

3.4 Tribology and kinematic viscosity of blended oil

3.4.1 Tribology of blended oil

The ME containing 1 eq of oleic acid, 2 eq of diethanolamine and 0.133 eq of ammonium molybdate aqueous solution (reaction no **5**) was used to test in this study. The weight ratio of ME to base oil Yubase-4 was 0.1, 0.3, 0.6 and 1.0 respectively. The tribology was investigated by Four-ball wear tester (19800-5 Seta-Shell Four-ball lubricant tester) at a rate of 1200 rpm, load 40 kgf, ambient temperature and operated time 1 h. This experiment was carried out at Shell of Thailand Company limited.

3.4.2 Kinematic viscosity

The blended oils were investigated the kinematic viscosity at 40 and 100°C by Cannon CAV2100F automatic viscometer that complied with ASTM D 445 “Standard test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity)”

3.4.3 Improvement of the solubility of synthesized molybdate ester in blended oil

The solubility improvement of ME in blended oil was carried out by adjusting the formulation of blended oil with dispersants and changing base oil types (Table 3.2), then investigated by visual at ambient temperature for a week.

Table 3.2 The chemical list used in the formulations.

Formulation nos	Chemicals								
	Rx5	**Rx6**	**Rx7**	**150SN**	**150J**	**Yubase-4**	**Lubrizol 6420**	**Viscoplex 1-330**	**Lubrizol 6404**
1	1			99					
2	1				99				
3	1					99			
4		1		99					
5		1			99				
6		1				99			
7			1	99					
8			1		99				
9			1			99			
10	1			96.8			2	0.2	
11	1			96.3			2.5	0.2	
12	1			95.8			3	0.2	
13	1			94.8			4	0.2	
14		1		96.8			2	0.2	
15		1		96.3			2.5	0.2	
16		1		95.8			3	0.2	
17		1		94.8			4	0.2	
18			1	96.8			2	0.2	
19			1	96.3			2.5	0.2	
20			1	95.8			3	0.2	
21			1	94.8			4	0.2	
22	1			93.8			5	0.2	
23	1			93.7			5	0.3	
24	1			93.6			5	0.4	
25	1			93.5			5	0.5	
26		1		93.8			5	0.2	
27		1		93.7			5	0.3	
28		1		93.6			5	0.4	
29		1		93.5			5	0.5	
30			1	93.8			5	0.2	
31			1	93.7			5	0.3	
32			1	93.6			5	0.4	
33			1	93.5			5	0.5	
34	1			95.7				0.3	3
35	1			92.7				0.3	6
36	1			88.7				0.3	10
37		1		95.7				0.3	3
38		1		92.7				0.3	6
39		1		88.7				0.3	10
40			1	95.7				0.3	3
41			1	92.7				0.3	6
42			1	88.7				0.3	10

3.4.4 Tribology of blended oil of formulation nos 36, 39 and 42

The selected formulations nos 36, 39 and 42, with various amount of MEs as 0, 0.1, 0.3, 0.6 and 1.0%wt were used to investigate tribology by Four-ball wear tester at a rate of 1200 rpm, load 40 kgf, ambient temperature and operated time 1 h.

CHAPTER IV

RESULTS AND DISCUSSION

In the field of lubricant field, molybdenum compounds have been widely used as a multifunction lubricant for reducing friction, antiwear, EP additive and antioxidant. Molybdenum compounds with rich phosphorus and sulfur ligands as organometallics are generally toxic. In this research, the use of fatty acids coordinating with molybdenum is a choice to solve this problem. The alkyl group of ME may affect on lubricity properties, therefore alkyl groups of ME were investigated by varying fatty acid and tested wear properties of blended oil to obtain new antiwear additive from ME.

4.1 The synthesis and structure of synthesized molybdate esters

The desirable ME in this research as antiwear additives should be oil soluble. The synthesis of ME was carried out in one-pot reaction [7]. Firstly, reflux the mixture of DEA and fatty acid at 145°C for 1.5 h. Three fatty acids: oleic acid, octanoic acid and stearic acid were selected to explore the effect of alkyl group in fatty acid chain on tribology of blended oil. Secondly, ammonium molybdate was added and the mixture was refluxed at 110°C for another one hour. The mixture was evaporated until dried, and then EtOAc was added. The inorganic matter was filtered out and the filtrate was evaporated to achieve the ME. Seven reactions were conducted by variation types of fatty acids, the ratio of fatty acid, DEA and ammonium molybdate. The results are summarized as presented in Table 4.1.

Table 4.1 %Yield, appearance and molybdenum content of synthesized molybdate esters.

Test	Reaction nos						
	1	**2**	**3**	**4**	**5**	**6**	**7**
%Yield	8.2	3.9	3.3	3.0	10.8	10.9	10.1
Appearance after 1 week storage	P	H	P	P	C	W	C
Mo content (%wt)	1.6	0.75	0.64	0.59	2.1	2.1	2.7

C – Clear liquid, H – Hazy liquid, P – Precipitate, W - Wax

The ideal ME should be a clear liquid since it is able to blend homogeneously with the base oil. With the ratio of oleic acid: DEA: ammonium molybdate as 1:1.14:0.113 (reaction no **1**), the precipitated ME was observed after storage for 1 week with Mo content 1.6 %wt. When more ammonium molybdate solution was added in order to change the ratio of oleic acid: DEA: ammonium molybdate to 1:1.14:0.565 (reaction no **2**), the hazy ME was formed and Mo content decreased to 0.75 %wt. To observe the effect of adding solid ammonium molybdate into the reaction instead of as solution with the same ratio (reaction no **3**), the ME was precipitated after 1 week storage with Mo content of 0.64 %wt. This was clearly seen that the amount and matter of ammonium molybdate could not increase the Mo content, %yield and appearance of ME. In reaction no **4**, the quantity of diethanolamine was adjusted as the ratio of oleic acid: DEA: ammonium molybdate as 1:1.5:0.113, the attained ME was still precipitated within a week of storage with low Mo content of 0.59 %wt. With the ratio of oleic acid: DEA: ammonium molybdate as 1:2.0:0.113 (reaction no **5**), a clear liquid with high Mo content of 2.1 %wt was achieved. As a result, the appropriate quantity of diethanolamine needed to be adjusted to stabilize the ME. Therefore the conditions of reaction no **5** were designed for further synthesis of other MEs. Fig 4.1 shows the appearance of MEs.

The variation of different fatty acids was conducted under the optimal conditions with the ratio of fatty acid/DEA/Mo of 1:2:0.133. The other fatty acids experimented were stearic acid (reaction no **6**) and octanoic acid (reaction no **7**).

While the former system gave the Mo content 2.1%wt with wax appearance at ambient temperature, the latter provided the ME with clear liquid and higher Mo content of 2.7%wt as that obtained from reaction no **5**.

Fig 4.1 Appearance of synthesized molybdate esters after 1 week storage

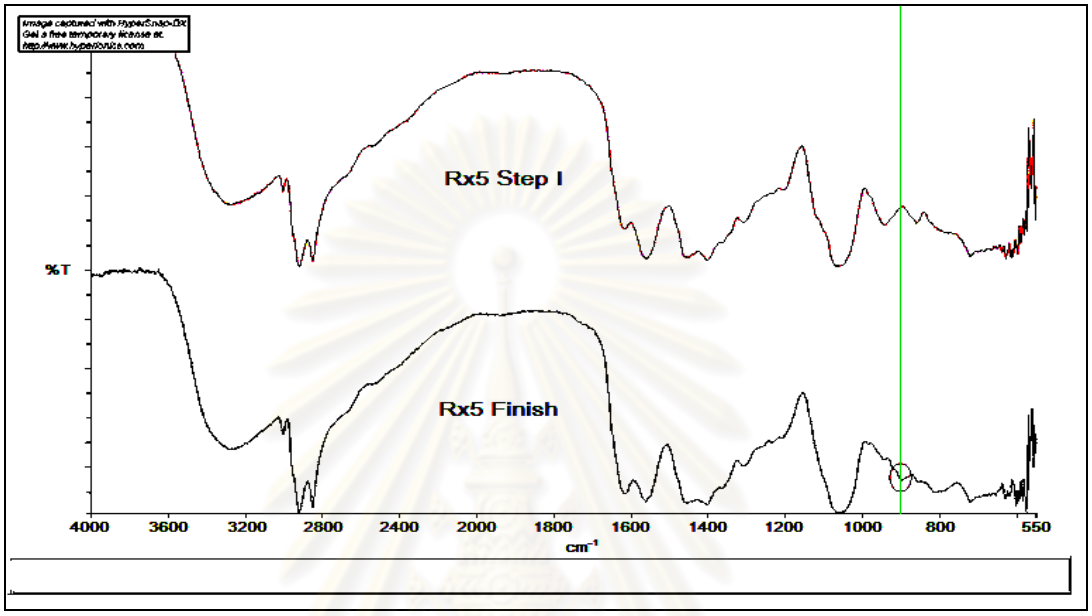
The structures of MEs were confirmed by FT-IR with ATR cell as presented in Fig 4.2. The assignments were summarized in Table 4.2.

Table 4.2 The assignments of synthesized molybdate esters

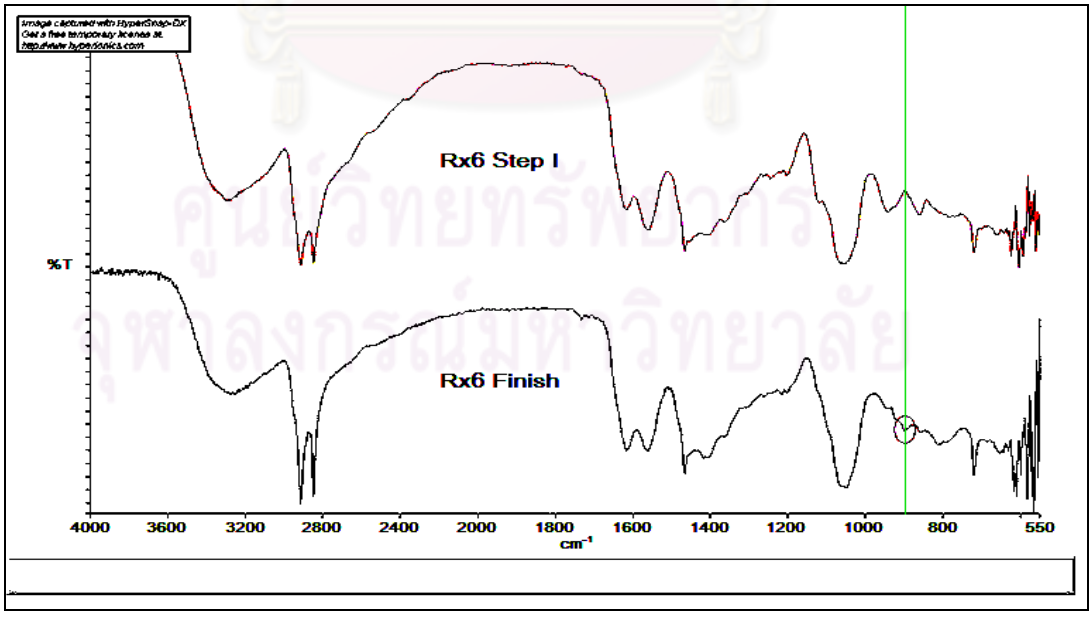
Wavenumber (cm^{-1})	**Assignment**
3280	O-H stretching
2910	C-H asymmetrical stretching
2840	C-H symmetrical stretching
1620	Amide carbonyl band C=O stretching
1560	Secondary amine N-H bending
1450	C-H bending
1060	Secondary amide C-N stretching
900	Mo-O stretching
720	$(CH_2)_n$ rocking

Fig 4.2 shows FT-IR spectra of a) reaction no **5**, b) reaction no **6** and c) reaction no **7**. In general, the characteristic broad band responsible for molybdate in MEs could be observed around 900 cm^{-1}[9]. This characteristic peaks were different

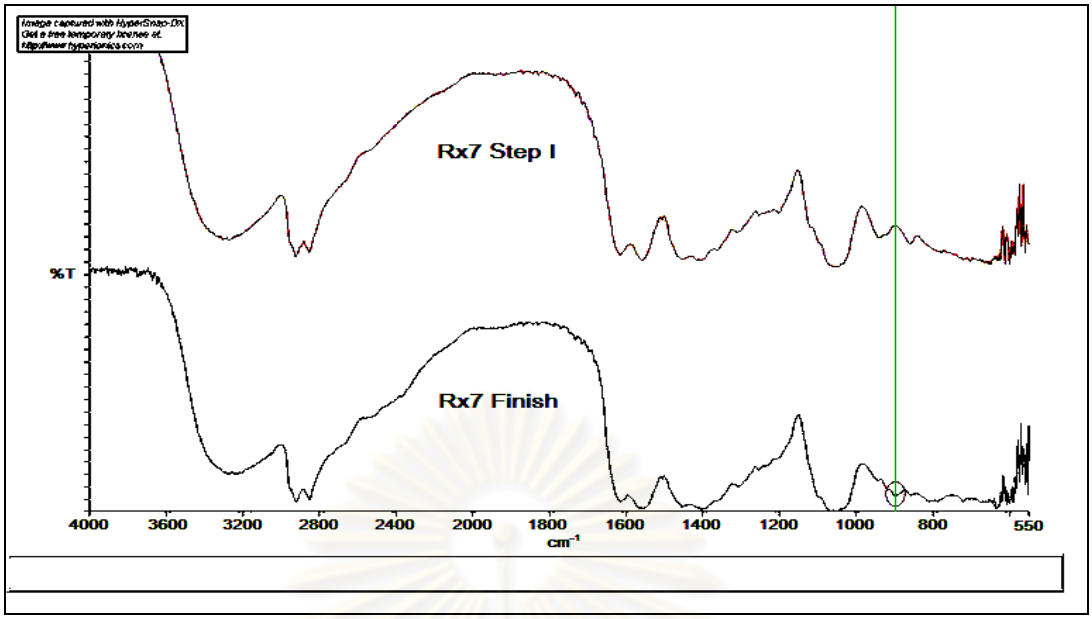
from those observed in step I from each reaction before adding ammonium molybdate solution. The secondary amide band and the amide carbonyl absorption peak could be detected around 1060 and 1620 cm^{-1}, respectively. These typical absorption bands normally use to verify the MEs.



a) FT-IR spectra of reaction no **5**



b) FT-IR spectrum of reaction no **6**



c) FT-IR spectrum of reaction no **7**

Fig 4.2 FT-IR spectra of synthesized molybdate ester from reactions nos **5-7**.

4.2 Properties of based oil and synthesized molybdate esters

4.2.1 Base oil selection

The essential parameters of three different base oils: 150SN, 500SN and Yubase-4 were carried out: kinematic viscosity at 40 and 100°C, viscosity index and Four-ball wear, parameter as rate of 1200 rpm, load at 40 kgf, at ambient temperature and ran time for 1 h. The results are shown in Table 4.3.

Table 4.3 Kinematic viscosity, viscosity index and WSD of selected base oils

Base oil	Test			
	KV @ 40 c cSt	KV @ 100 c cSt	VI -	WSD mm
150 SN	30.10	5.176	100	0.77
500 SN	96.59	10.85	97	0.69
Yubase-4	19.38	4.240	127	0.76

Among three selected base oils, Yubase-4 displayed high wear scare diameter (WSD) 0.76 m.m. and the highest viscosity index as 127, lowest temperature impact to viscosity. Thus, this base oil was selected to blend with MEs and tested the tribology.

4.2.2 Tribology of blended oil of synthesized molybdate ester (reaction no 5) and Yubase-4 base oil

The MEs from the reactions nos **5**, **6** and **7** are appropriate to test of tribology by Four-ball wear tester with parameters at rotation speed of 1200 rpm, load at 40 kgf, ambient temperature and tested time for 1 h. The results of Four-ball wear test of base oil (Yubase-4) and blended oils are shown in Table 4.4 and Fig 4.3. The base oil without ME revealed wear scare diameter (WSD) 0.76 mm, while that with various amounts of ME (reaction no **5**) of 0.1, 0.3, 0.6 and 1.0 %wt showed WSD of 0.64, 0.64, 0.66 and 0.44 mm, respectively. The MEs from reaction nos **6** and **7** were not soluble in this base oil, so they could not be tested. The trend of WSD was reversed to the amount of ME. Those results demonstrated that the ME from reaction no **5** could improve antiwear property of the blended oil. However, the stability of that blended oil was not excellent since it was split into two phases within a few hours.

Table 4.4 Four-ball wear test of the blended oil with the synthesized molybdate ester from reaction no **5**.

Content of ME from reaction no **5** (w/w %)	0	0.1	0.3	0.6	1.0
WSD (mm)	0.76	0.64	0.64	0.66	0.44

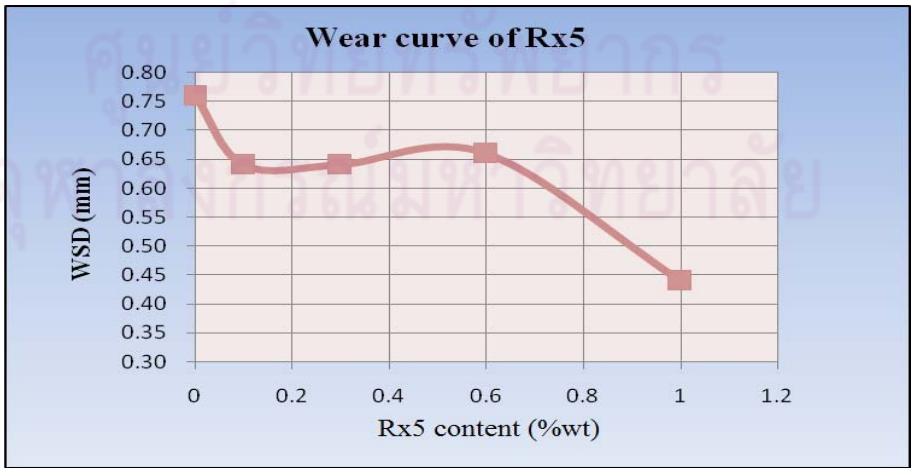
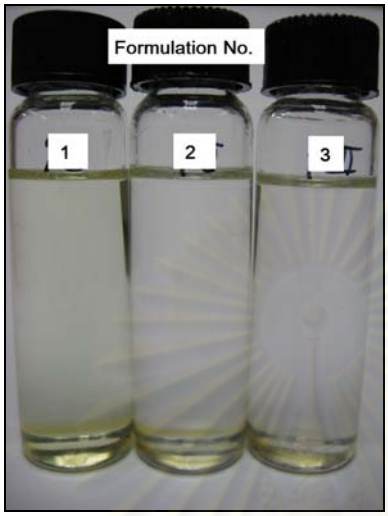


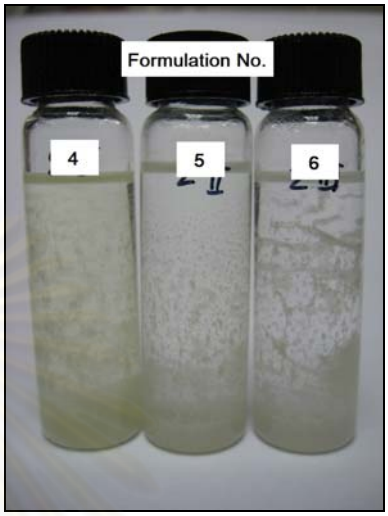
Fig 4.3 Wear curve of the blended oil with the synthesized molybdate ester from reaction no **5**.

4.2.3 Improvement of the solubility of synthesized molybdate ester in blended oil

The blended oil containing MEs with Yubase-4 was not exceptional stable, therefore it should improve the solubility and stability by changing based oil type and/or adding dispersant. The solubility and stability enhancement formulations were conducted by varying amount and category of dispersants (see Chapter III). Nearly all formulations still found the precipitation or phase separation, except for the formulation nos **36, 39** and **42**. The only variation of base oil in API group as 150SN (group I), 150J (group II) and Yubase-4 (group III) as presented in formulation nos **1-9** did not improve the solubility and stability of blended oils. The MEs were dropped and in some cases precipitated within an hour (Fig 4.4). The addition of dispersant Lubrizol 6420 and Viscoplex 1-330 could improve solubility, but still poor stability of blended oils. The MEs were completed soluble, but still precipitated and dropped within a week, as formulation nos **10-33** (Fig 4.5). The blended oils (formulation nos **36**, **39** and **42**) possessed good solubility and stability, the MEs did not precipitated and separated out with the ratio of 1%wt of MEs, 10%wt of Lubrizol 6404, 0.3 %wt of Viscoplex 1-330 and 88.7 %wt of base oil 150SN (Fig 4.6).



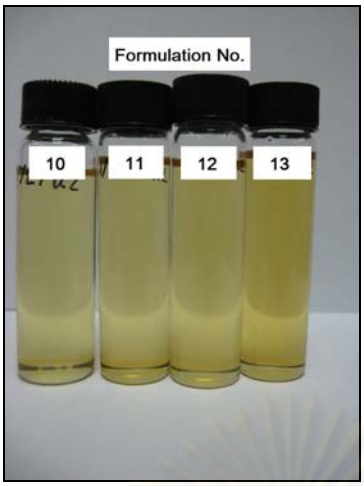
a) Formulation nos **1-3**



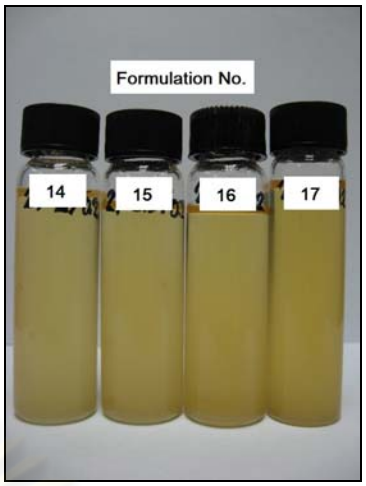
b) Formulation nos **4-6**

c) Formulation nos **7-9**

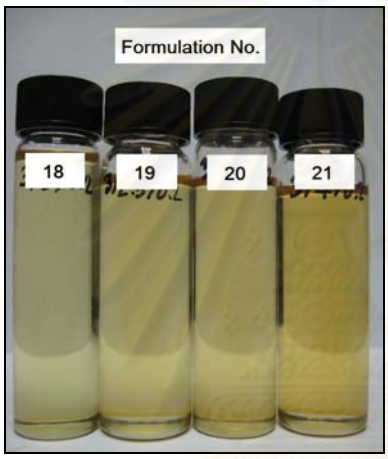
Fig 4.4 Appearance of blended oils of formulation nos **1-9** after storage for 1 week at ambient condition.



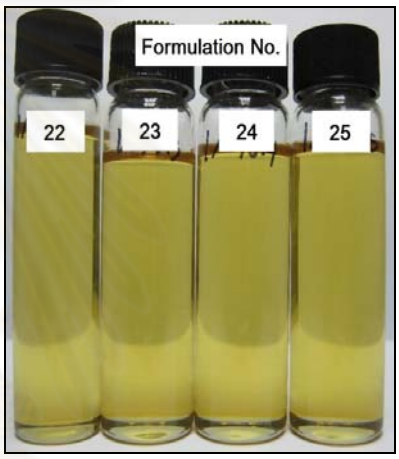
a) Formulation nos **10-13**



b) Formulation nos **14-17**



c) Formulation nos **18-21**

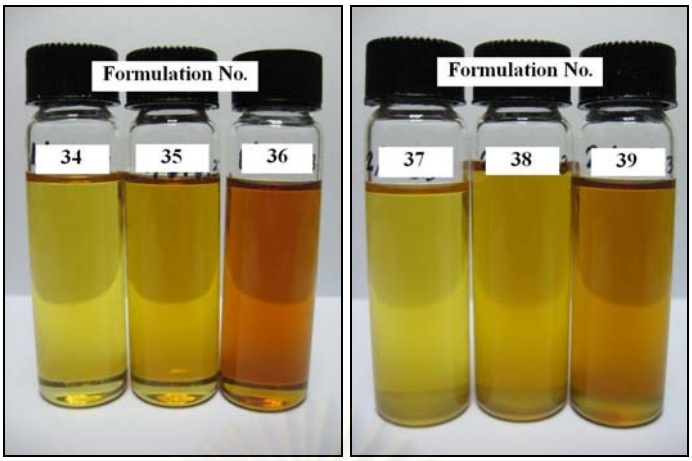


d) Formulation nos **22-25**

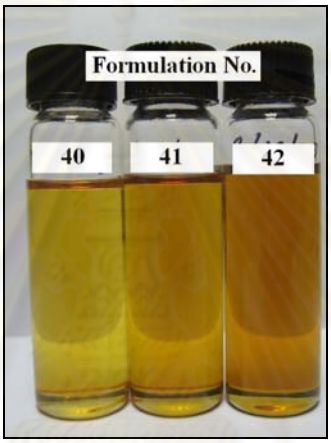
e) Formulation nos **26-29**

f) Formulation nos **30-33**

Fig 4.5 Appearance of blended oils formulation nos **10-33** after storage for 1 week at ambient condition.



a) Formulation nos **34-36** b) Formulation nos **37-39**



c) Formulation nos **40-42**

Fig 4.6 Appearance of blended oils formulation nos **34-42** after storage for 1 week at ambient condition.

4.2.4 Tribology of blended oil formulation nos 36, 39 and 42

The selected formulations were used to test for wear, kinematic viscosity, viscosity index and molybdenum content. The blended oil formulation nos **36, 39** and **42** were mixed with various amounts of MEs in the range as follows: 0.0, 0.1, 0.3, 0.6 and 1.0%wt. Then determined to test kinematic viscosity at 40 and 100°C by automatic viscometer Cannon CAV2100F, viscosity index by calculation, wear property by Four-ball wear tester at spin rate 1200 rpm, load of 40 kgf, ambient temperature and operated time for 1 h and molybdenum content by ICP-AES technique with Perkin-Elmer 5300V. The results showed slightly increase of kinematic viscosity and viscosity index from blended oil without MEs. The wear scare diameter of blended oils with MEs was larger than the blended oil without MEs

(Tables 4.5-4.7 and Fig 4.7). Increasing of wear scare diameter may cause of dispersants which were added into the blended oil and competed with the ME to adsorb on the metal surface. Therefore, the dispersant acted interfered the adsorption of MEs.

Table 4.5 The test results for wear, kinematic viscosity, viscosity index and molybdenum content of blended oils formulation no **36**

formulation no	36				
content of the ME from reaction no **5** (%wt)	0.0	0.1	0.3	0.6	1.0
Mo content (ppm)	0	22	65	128	213
KV @ 40°C (mm^2/s)	38.84	40.28	40.19	40.01	39.91
KV @ 100°C (mm^2/s)	6.477	6.639	6.639	6.673	6.633
VI	119	119	120	122	121
WSD (mm)	0.45	0.55	0.53	1.16	0.51

Table 4.6 The test results for wear, kinematic viscosity, viscosity index and molybdenum content of blended oils formulation no **39**

formulation No.	39				
content of the ME from reaction no **6** (%wt)	0.0	0.1	0.3	0.6	1.0
Mo content (ppm)	0	23	67	131	221
KV @ 40°C (mm^2/s)	38.84	40.10	40.08	40.02	39.83
KV @ 100°C (mm^2/s)	6.477	6.670	6.641	6.659	6.618
VI	119	122	120	121	121
WSD (mm)	0.45	0.49	0.51	0.52	0.48

Table 4.7 The test results for wear, kinematic viscosity, viscosity index and molybdenum content of blended oils formulation no **42**

formulation No.	42				
content of the ME from reaction no **7** (%wt)	0.0	0.1	0.3	0.6	1.0
Mo content (ppm)	0	24	79	155	233
KV @ 40°C (mm^2/s)	38.84	41.38	40.53	40.87	40.36
KV @ 100°C (mm^2/s)	6.477	6.752	6.695	6.728	6.684
VI	119	119	121	120	121
WSD (mm)	0.45	0.59	0.68	0.68	0.52

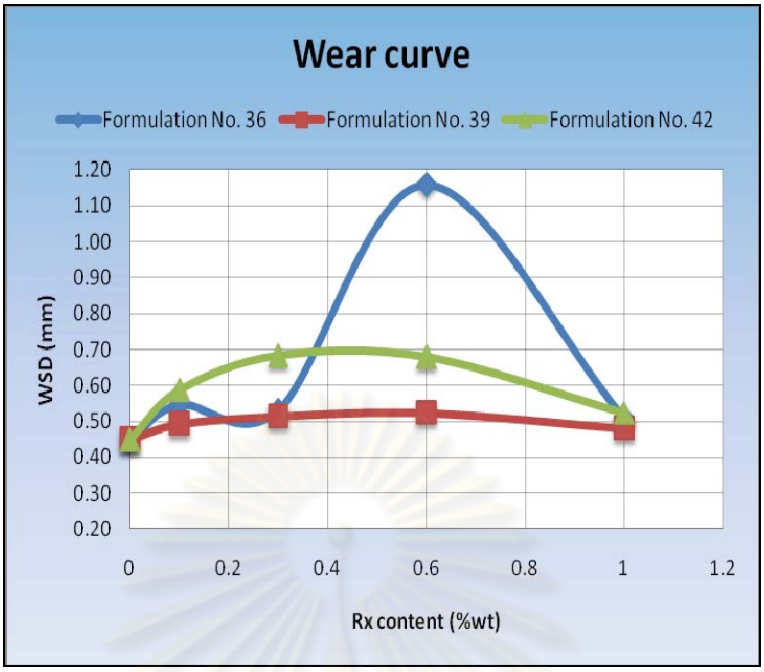


Fig 4.7 Wear curve of blended oil formulation nos **36**, **39** and **42**

Fig 4.7 showed that the double bond of the alkyl group of MEs was not significant on wear property, whereas the length of alkyl group was slightly affected on wear property of MEs. ME with C18 alkyl group displayed lower WSD than ME with C8 alkyl group.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The ME at the ratio of oleic acid/DEA/NH_4Mo as 1/2/0.133 eq was successfully achieved with the stabilized liquid more than that with other ratios at ambient atmosphere. The band responsible for molybdate is observed around 900 cm^{-1}. The blended oil containing base oil (Yubase-4) and the ME from reaction no **5** provided satisfied antiwear property with reduced WSD *via* Four-ball wear test. However, the blended oil was inhomogeneous within an hour. The dispersants added to blended oil could improve stability of blended oil. The ratio of ME/Lubrizol 6404/ Viscoplex 1-330/base oil 150SN as 1/10/0.3/88.7 showed homogeneous solution after a week at ambient condition. This formulation behaves a good wear trend increasing with amount of ME. This is perhaps the dispersants are interfere with the ME to adsorb on metal surface. The double bond of alkyl group of ME was not significant on wear property. The length of alkyl group of ME was slightly affected on wear property, ME with C18 alkyl group showed lower WSD than that containing C8 alkyl group.

5.2 Recommendation

For the future work, the varieties of alkyl chain of MEs may be examined. The ideal ME should be homogenized in base oil, thus decrease the content of dispersants in blended oil.

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APPENDICES

Appendix A

The appearance of synthesized molybdate esters

Table A-1 The appearance of synthesized molybdate esters

Reaction nos	Initial	Step I	Step II	Step II evaporated	Finished
1					
2					
3					
4					

5					
6					
7					

Appendix B

API base oil categories

Table B-1 API base oil categories [10]

Base oil	% Saturates	% Sulfur	VI
Group I	<90	>0.03	80-119
Group II	≥90	≤0.03	80-119
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAO)		
Group V	Not included in Group I, II, III, or IV.		

Appendix C

Four-ball wear data

Table C-1 Four-ball wear of formulation no **39**

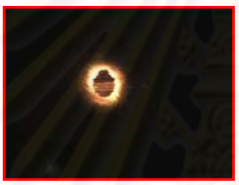
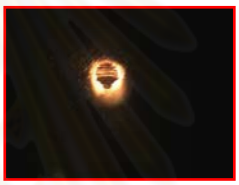
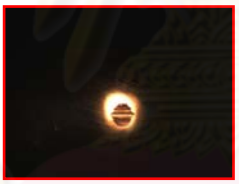
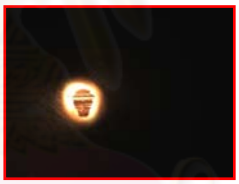
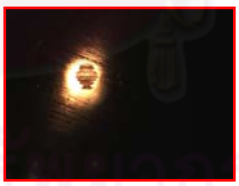
Sample	ME content (%wt)	Replication no	Ball nos		
			1	**2**	**3**
Formulation no **39**	0.1	**1**			
	0.3	**1**			
	0.6	**1**			
	1.0	**1**			

Table C-2 Four-ball wear of 150SN stock and formulation no **36**

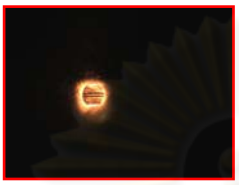
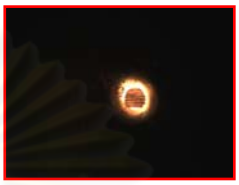
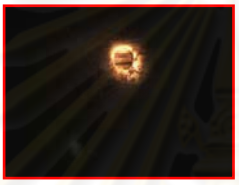
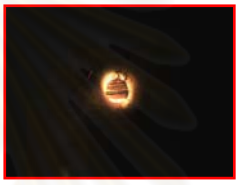
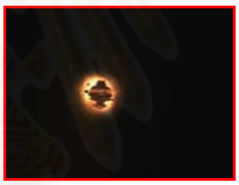
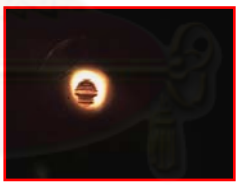
Sample	ME content (%wt)	Replication no	Ball nos		
			1	**2**	**3**
150SN Stock	0.0	**1**			
	0.0	**2**			
Formulation no **36**	0.1	**1**			
	0.3	**1**			
	0.6	**1**			
	1.0	**1**			

Table C-3 Four-ball wear of formulation no **42** replication no **1**

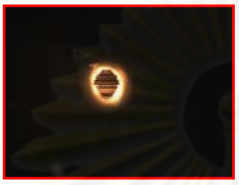
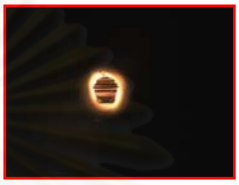
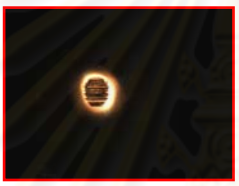
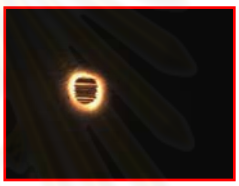
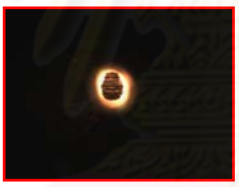
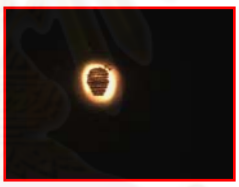
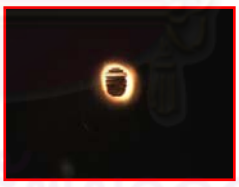
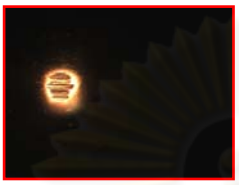
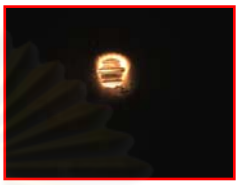
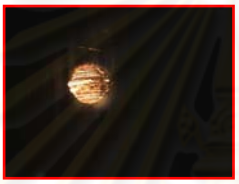
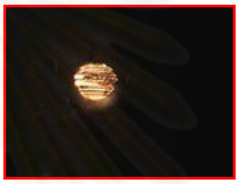
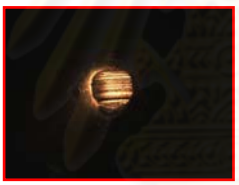
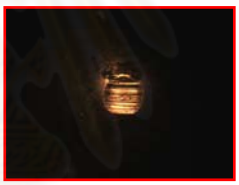
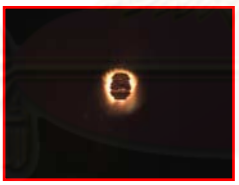
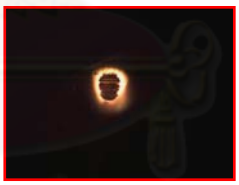
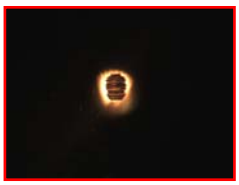
Sample	ME content (%wt)	Replication no	Ball nos		
			1	**2**	**3**
Formulation no **42**	0.1	**1**			
	0.3	**1**			
	0.6	**1**			
	1.0	**1**			

Table C-4 Four-ball wear of formulation no **42** replication no **2**

Sample	Synthesized content (%wt)	Replication no	Ball nos		
			1	**2**	**3**
Formulation no **42**	0.1	**2**			
	0.3	**2**			
	0.6	**2**			
	1.0	**2**			

Appendix D

% Yield calculation

Table D-1 Molecular weight of chemicals

Chemical	Molecular weight g/mol
DEA	105.14
Oleic acid	282.46
Stearic acid	284.48
Octanoic acid	144.21
NH_4Mo	1235.86
ME reaction no **5**	495.56
ME reaction no **6**	497.58
ME reaction no **7**	357.31
Molybdenum	95.96

Formulation D-1 %Yield calculation formulation.

$$\%Yield = (\%Mo \times MW \text{ of ME}) / A_r \text{ of Mo}$$

Formulation D-2 Theoretical of molybdenum content in the synthesized molybdate esters.

$$\%Mo = \frac{(Ar \text{ of Mo} \times eq \text{ of Mo}) \times 100\%}{[(MW \text{ of DEA} \times eq \text{ of DEA}) + (MW \text{ of fatty acid} \times eq \text{ of fatty acid}) + (Ar \text{ of Mo} \times eq \text{ of Mo})]}$$

Appendix E

ICP data

Table E-1 ICP data of synthesized product and blended oil.

Mean Data

ID: Calib Blank 1 Seq. No.: 6 A/S 1

Sample Qty g Prep. Vol.: Dilution: : Date: 2009/07/29

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample	RSD
Ag 328.068	1,328.3	[0.00]	124.65	ppm				9.38 %
Al 396.153	13,295.6	[0.00]	90.18	ppm				0.68 %
B 249.677	1,519.0	[0.00]	124.51	ppm				8.20 %
Ba 233.527	236.8	[0.00]	3.71	ppm				1.57 %
Ca 317.933	3,027.2	[0.00]	31.90	ppm				1.05 %
Cd 228.802	83.6	[0.00]	8.85	ppm				10.59 %
Cr 267.716	5.7	[0.00]	16.71	ppm				293.56 %
Cu 327.393	459.1	[0.00]	29.12	ppm				6.34 %
Fe 238.204	61.9	[0.00]	11.39	ppm				18.41 %
Mg 285.213	396.5	[0.00]	23.18	ppm				5.85 %
Mn 257.610	528.2	[0.00]	43.41	ppm				8.22 %
Mo 202.031	-68.0	[0.00]	4.73	ppm				6.95 %
Na 589.592	70,073.4	[0.00]	825.38	ppm				1.18 %
Ni 231.604	1,378.1	[0.00]	21.02	ppm				1.53 %
P 213.617	11.7	[0.00]	4.39	ppm				37.53 %
Pb 220.353	10.0	[0.00]	8.78	ppm				87.46 %
Si 251.611	1,555.8	[0.00]	19.30	ppm				1.24 %
Sn 189.927	-32.7	[0.00]	7.39	ppm				22.56 %
Ti 334.940	-73.1	[0.00]	91.38	ppm				124.98 %
V 290.880	6.5	[0.00]	17.38	ppm				266.56 %
Zn 206.200	20.6	[0.00]	1.05	ppm				5.09 %

Mean Data

ID: STD Seq. No.: 7 A/S 2

Sample Qty g Prep. Vol.: Dilution: : Date: 2009/07/29

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample	RSD
Co 228.616	25,328.5	14.84	34.90	mg/L				0.14 %
Ag 328.068	988,537.7	[20.3674]	1,369.13	ppm				0.14 %
Al 396.153	325,106.4	[20.3674]	993.54	ppm				0.31 %
B 249.677	110,183.3	[20.3674]	358.91	ppm				0.33 %
Ba 233.527	102,778.5	[20.3674]	519.04	ppm				0.51 %
Ca 317.933	594,010.3	[20.3674]	3,553.05	ppm				0.60 %
Cd 228.802	60,040.3	[20.3674]	119.87	ppm				0.20 %
Cr 267.716	275,996.2	[20.3674]	1,898.91	ppm				0.69 %
Cu 327.393	738,687.2	[20.3674]	1,724.50	ppm				0.23 %
Fe 238.204	114,492.7	[20.3674]	540.13	ppm				0.47 %
Mg 285.213	1,187,564.2	[20.3674]	2,322.41	ppm				0.20 %
Mn 257.610	1,256,084.2	[20.3674]	4,252.10	ppm				0.34 %
Mo 202.031	6,332.2	[20.3674]	26.79	ppm				0.42 %
Na 589.592	788,103.2	[20.3674]	6,004.88	ppm				0.76 %
Ni 231.604	36,561.9	[20.3674]	147.43	ppm				0.40 %
P 213.617	2,721.1	[20.3674]	7.14	ppm				0.26 %
Pb 220.353	2,801.2	[20.3674]	2.52	ppm				0.09 %
Si 251.611	155,304.6	[20.3674]	205.70	ppm				0.13 %
Sn 189.927	853.8	[20.3674]	4.45	ppm				0.52 %
Ti 334.940	3,746,656.5	[20.3674]	6,217.65	ppm				0.17 %
V 290.880	389,786.1	[20.3674]	923.30	ppm				0.24 %
Zn 206.200	14,537.5	[20.3674]	32.22	ppm				0.22 %

Mean Data
ID: STD

Seq. No.: 8

A/S

Sample Qty 1.23 g Prep. Vol.: 30.08 Dilution: : Date: 2009/07/29

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample	RSD
Co 228.616	24,807.2	14.54	0.077	mg/L			mg/L	0.53 %
Ag 328.068	1,003,616.4	20.68	0.126	ppm	507.6	3.09	ppm	0.61 %
Al 396.153	329,045.0	20.61	0.153	ppm	506.1	3.75	ppm	0.74 %
B 249.677	111,040.0	20.53	0.181	ppm	503.9	4.45	ppm	0.88 %
Ba 233.527	103,273.9	20.47	0.080	ppm	502.4	1.95	ppm	0.39 %
Ca 317.933	595,898.5	20.43	0.107	ppm	501.6	2.63	ppm	0.52 %
Cd 228.802	60,693.2	20.59	0.042	ppm	505.4	1.03	ppm	0.20 %
Cr 267.716	276,832.1	20.43	0.108	ppm	501.5	2.65	ppm	0.53 %
Cu 327.393	750,578.4	20.70	0.136	ppm	508.1	3.34	ppm	0.66 %
Fe 238.204	115,544.2	20.55	0.069	ppm	504.6	1.70	ppm	0.34 %
Mg 285.213	1,196,298.2	20.52	0.107	ppm	503.7	2.62	ppm	0.52 %
Mn 257.610	1,267,575.0	20.55	0.066	ppm	504.6	1.62	ppm	0.32 %
Mo 202.031	6,363.3	20.47	0.050	ppm	502.5	1.22	ppm	0.24 %
Na 589.592	797,777.9	20.62	0.257	ppm	506.1	6.31	ppm	1.25 %
Ni 231.604	36,853.7	20.53	0.106	ppm	504.0	2.60	ppm	0.52 %
P 213.617	2,762.3	20.68	0.013	ppm	507.6	0.32	ppm	0.06 %
Pb 220.353	2,801.7	20.37	0.095	ppm	500.1	2.32	ppm	0.46 %
Si 251.611	157,182.6	20.61	0.074	ppm	506.0	1.81	ppm	0.36 %
Sn 189.927	844.8	20.15	0.167	ppm	494.7	4.09	ppm	0.83 %
Ti 334.940	3,787,389.6	20.59	0.085	ppm	505.4	2.08	ppm	0.41 %
V 290.880	393,918.0	20.58	0.072	ppm	505.3	1.76	ppm	0.35 %
Zn 206.200	14,517.1	20.34	0.063	ppm	499.3	1.54	ppm	0.31 %

Mean Data

ID: Rx1 Seq. No.: 13 A/S

Sample Qty 0.13 g Prep. Vol.: 11.79 Dilution: : Date: 2009/07/29

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample	RSD
Co 228.616	26,397.5	15.47	0.078	mg/L			mg/L	0.51 %
Ag 328.068	-1,096.9	-0.023	0.0010	ppm	-2.054	0.0915	ppm	4.45 %
Al 396.153	55,021.1	3.447	0.0060	ppm	313.3	0.55	ppm	0.18 %
B 249.677	-2,937.3	-0.543	0.0131	ppm	-49.35	1.195	ppm	2.42 %
Ba 233.527	-64.7	-0.013	0.0010	ppm	-1.165	0.0929	ppm	7.97 %
Ca 317.933	5,310.1	0.182	0.0024	ppm	16.55	0.218	ppm	1.32 %
Cd 228.802	-449.3	-0.152	0.0022	ppm	-13.85	0.203	ppm	1.46 %
Cr 267.716	38.5	0.003	0.0015	ppm	0.258	0.1405	ppm	54.36 %
Cu 327.393	-1,325.1	-0.037	0.0008	ppm	-3.321	0.0741	ppm	2.23 %
Fe 238.204	-1,561.8	-0.278	0.0041	ppm	-25.25	0.373	ppm	1.48 %
Mg 285.213	2,059.5	0.035	0.0006	ppm	3.211	0.0512	ppm	1.59 %
Mn 257.610	-598.2	-0.010	0.0001	ppm	-0.882	0.0066	ppm	0.75 %
Mo 202.031	55,211.2	177.6	0.43	ppm	16140	38.8	ppm	0.24 %
Na 589.592	21,521.6	0.556	0.0218	ppm	50.56	1.978	ppm	3.91 %
Ni 231.604	-349.1	-0.194	0.0140	ppm	-17.67	1.272	ppm	7.20 %
P 213.617	176.4	1.320	0.0356	ppm	120.0	3.24	ppm	2.70 %
Pb 220.353	-87.2	-0.634	0.0627	ppm	-57.62	5.696	ppm	9.89 %
Si 251.611	7,042.3	0.924	0.0022	ppm	83.95	0.203	ppm	0.24 %
Sn 189.927	-5.9	-0.140	0.2140	ppm	-12.71	19.456	ppm	153.03 %
Ti 334.940	859.9	0.005	0.0001	ppm	0.425	0.0105	ppm	2.48 %
V 290.880	-931.5	-0.049	0.0009	ppm	-4.424	0.0854	ppm	1.93 %
Zn 206.200	-21.2	-0.030	0.0038	ppm	-2.696	0.3488	ppm	12.94 %

Mean Data
ID: STD Seq. No.: 15 A/S

Sample Qty 1.23 g Prep. Vol.: 30.08 Dilution: : Date: 2009/07/29

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample	RSD
Co 228.616	23,245.8	13.62	0.071	mg/L			mg/L	0.52 %
Ag 328.068	1,066,091.6	21.97	0.128	ppm	539.2	3.14	ppm	0.58 %
Al 396.153	357,692.4	22.41	0.117	ppm	550.1	2.86	ppm	0.52 %
B 249.677	73,427.0	13.57	0.206	ppm	333.2	5.07	ppm	1.52 %
Ba 233.527	103,191.2	20.45	0.043	ppm	502.0	1.05	ppm	0.21 %
Ca 317.933	598,041.0	20.51	0.180	ppm	503.4	4.41	ppm	0.88 %
Cd 228.802	62,677.2	21.26	0.060	ppm	522.0	1.47	ppm	0.28 %
Cr 267.716	280,093.4	20.67	0.083	ppm	507.4	2.04	ppm	0.40 %
Cu 327.393	808,691.3	22.30	0.126	ppm	547.4	3.08	ppm	0.56 %
Fe 238.204	117,227.2	20.85	0.026	ppm	511.9	0.63	ppm	0.12 %
Mg 285.213	1,259,574.9	21.60	0.078	ppm	530.3	1.91	ppm	0.36 %
Mn 257.610	1,296,581.0	21.02	0.101	ppm	516.1	2.48	ppm	0.48 %
Mo 202.031	6,465.2	20.80	0.113	ppm	510.5	2.77	ppm	0.54 %
Na 589.592	903,671.9	23.35	0.245	ppm	573.3	6.01	ppm	1.05 %
Ni 231.604	36,920.3	20.57	0.019	ppm	504.9	0.48	ppm	0.09 %
P 213.617	2,806.6	21.01	0.081	ppm	515.7	1.98	ppm	0.38 %
Pb 220.353	2,752.6	20.01	0.104	ppm	491.3	2.56	ppm	0.52 %
Si 251.611	165,400.1	21.69	0.089	ppm	532.5	2.19	ppm	0.41 %
Sn 189.927	822.6	19.62	0.268	ppm	481.7	6.57	ppm	1.36 %
Ti 334.940	3,957,779.8	21.52	0.048	ppm	528.2	1.18	ppm	0.22 %
V 290.880	405,162.6	21.17	0.009	ppm	519.7	0.21	ppm	0.04 %
Zn 206.200	14,319.6	20.06	0.094	ppm	492.5	2.30	ppm	0.47 %

VITA

Mr. Tanatath Pluekpaiboon was born on December 21st, 1981 in Bangkok, Thailand. He was graduated with a high school's degree from Chan Pradittharam Witthayakhom School and a Bachelor's degree from department of chemistry, Faculty of Science, Silpakorn University. He has his study in Master Degree in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2007 and finished his study in 2011. He presented a part of his research work at the 21st National Graduate Research Conference at Rangsit University on May 26th, 2011.