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เพื่อใช้เป็นสารต้านออกซิเดชันในสารหล่อลื่น

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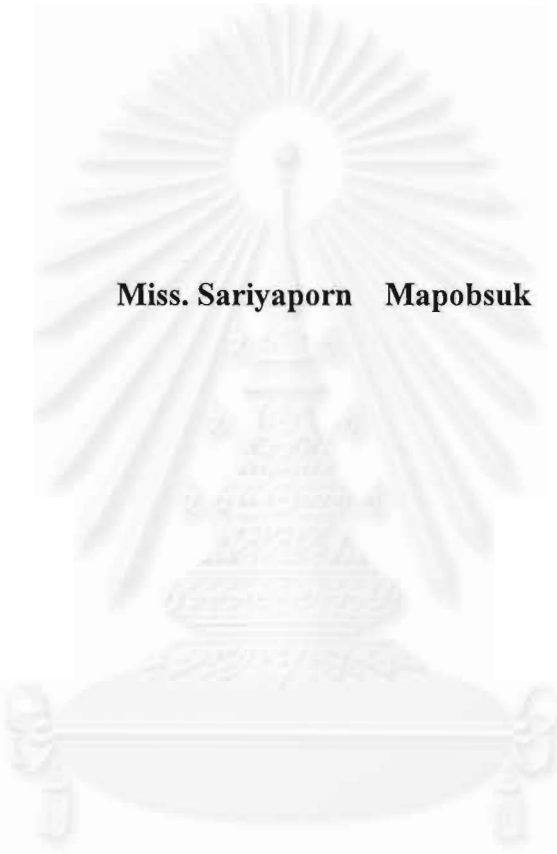
SYNTHESIS OF METAL DIISOAMYL DITHIOPHOSPHATE

FROM METAL SALTS AS LUBRICANT ANTIOXIDANTS

Miss. Sariyaporn   Mapobsuk

A Thesis Submitted in Partial Fulfillment of the Requirements

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

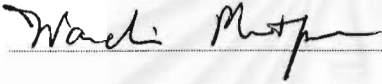Program of Petrochemistry and Polymer Science

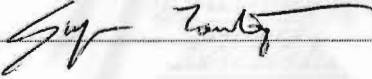Faculty of Science

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Thesis title   SYSTHESIS OF METAL DIISOAMYLDITHIOPHOSPHATE

FROM METAL SALTS AS ANTIOXIDANT LUBRICANTS

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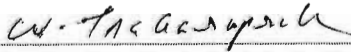
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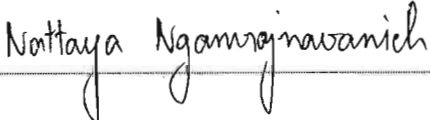
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สริยาภรณ์ มาพบสุข : การสังเคราะห์โลหะไดไอโซเอมิลไดไทโอฟอสเฟตจากเกลือโลหะ เพื่อใช้เป็นสารต้านออกซิเดชันในสารหล่อลื่น (Synthesis of Metal diisoamyl dithiophosphate from metal salts as lubricant antioxidants) อาจารย์ที่ปรึกษา : รศ.ดร.โสภณ เริงสำราญ; 76 หน้า. ISBN 974-334-064-5.

การศึกษาวิธีใหม่ของการสังเคราะห์โลหะไดไอโซเอมิลไดไทโอฟอสเฟต(MDDP) โดยวิธี การสังเคราะห์มี 3 ขั้นตอน คือ (I) การเตรียมกรดไดไอโซเอมิลไดไทโอฟอสฟอริก(DPDA) จากการทำ ปฏิกิริยาของไอโซเอมิลแอลกอฮอล์ กับฟอสฟอรัสเพนตะซัลไฟด์ (II) การทำปฏิกิริยาของ DPDA กับสาร ละลายโพแทสเซียมไฮดรอกไซด์ เพื่อเปลี่ยนให้เป็นเกลือโพแทสเซียมไดไอโซเอมิลไดไทโอฟอสเฟต (KDPS) และ (III) การทำปฏิกิริยาของเกลือโพแทสเซียมไดไอโซเอมิลไดไทโอฟอสเฟต และเกลือโลหะ จะได้สาร MDDP เกลือโลหะที่เหมาะสมสำหรับสังเคราะห์ MDDP คือ $ZnCl_2$ และ $CuCl_2$ เพื่อให้ได้ ZDDP(95%) และ CuDDP(98%) นี้มีสูตรโมเลกุล $Zn[PS_2(OR)_2]_2$ และ $Cu_2[PS_2(OR)_2]_3OH$ ตามลำดับ โดย ZDDP และ CuDDP ที่ได้รับแสดงถึงสมรรถนะที่ดีต่อการใช้เป็นสารต้านออกซิเดชันในน้ำมันหล่อลื่น

ภาควิชา _____-_____   ลายมือชื่อนิสิต ___สริยาภรณ์ มาพบสุข___
สาขาวิชา __ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์__   ลายมือชื่ออาจารย์ที่ปรึกษา _____
ปีการศึกษา ____2542____   ลายมือชื่ออาจารย์ที่ปรึกษาร่วม _____-_____

The new synthesis method of metal diisoamyldithiophosphate, MDDP, has been studied. Its synthetic pathway has three steps including (I) the preparation of DPDA by reaction of isoamyl alcohol with P_2S_5, (II) the reaction of DPDA with potassium hydroxide to form potassium diisoamyldithiophosphate salt, KDPS and (III) the reaction of KDPS and metal salts to obtain MDDP. The suitable metal salts for MDDP synthesis were found to be $ZnCl_2$ and $CuCl_2$, which resulted in ZDDP(95%) and CuDDP(98%) with the molecular formula of $Zn[PS_2(OR)_2]_2$ and $Cu_2[PS_2(OR)_2]_3OH$, respectively. The obtained ZDDP and CuDDP showed good performance as antioxidants used in lubricant oil.

ภาควิชา _____-_____   ลายมือชื่อนิสิต _____

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่ออาจารย์ที่ปรึกษา _____

ปีการศึกษา _____2542_____   ลายมือชื่ออาจารย์ที่ปรึกษาร่วม _____-_____

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

DPDA	=	Dialkyl dithiophosphoric acid
KDPS	=	Potassium dithiophosphate salt
MDDP	=	Metal dialkyldithiophosphate
ZDDP	=	Zinc dialkyldithiophosphate
CuDDP	=	Copper dialkyldithiophosphate
BaDDP	=	Barium dialkyldithiophosphate
MgDDP	=	Magnesium dialkyldithiophosphate
SnDDP	=	Stannous dialkyldithiophosphate
TAN	=	Total Acid Number
TBN	=	Total Base Number
FT-IR	=	Fourier Transform Infrared Spectrophotometer
NMR	=	Nuclear Magnetic Resonance Spectrometer
EA	=	Elemental Analyzer
XRF	=	X-Ray Fluorescence
ICPS	=	Inductively Coupled Plasma Spectroscopy
TGA	=	Thermogravimetric Analyzer
ASTM	=	American National Standard Test Method
%Wt	=	Percent Weight
ppm	=	Part per million
°C	=	Degree Celcious
g	=	Gram
ml	=	Millilite
Vol	=	Volume

CHAPTER I

INTRODUCTION

The most important form of chemical breakdown of oils and additives is oxidation. Most chemical substances react more or less slowly with oxygen, and because lubricating oils usually operate in contact with air, the various chemicals present react slowly – but continuously – with the oxygen in the air. The effects of oxidation are to produce aldehydes and acidic compounds, which cause corrosion, together with an increase in viscosity, and eventually lacquering, tarry deposits, and insoluble oxidation products. All these effects are undesirable, thus, lubricating oils with good oxidation resistance are required. In order to solve these problems antioxidants are used to improve an oxidation resistance of lubricating oils.

Antioxidants are additives, which reduce the harmful effects of oxidation. The oxidation of most lube base components and additives proceeds via a sort of chain reaction, involving organic peroxides. Most antioxidants act as the chain blocking by reacting with organic peroxide. Due to this very specific blocking action of antioxidants, they continue to prevent oxidation as long as they are present, even in very small concentration. Ultimately, however, they become completely used up and there is nothing left to inhibit oxidation.

The one commoner antioxidant widely used many years ago is metal dialkyl dithiophosphates (MDDP). The dominating position of MDDP as additives for lubricating oils is due to their multifunctional performance. Not only do they act as antioxidant, but also improve the wear inhibition of the lubricant and protect metals against corrosion.

The commercial MDDP was prepared by reaction of a dialkyldithiophosphoric acid (DPDA) with a basic metal compound such as zinc oxide. The variation of MDDP by this method has been studied previously by Supawadee, 1997. The author has pointed that dialkyldithiophosphoric acid selectively reacts with some basic metal compounds.

In the present study, the new method of MDDP synthesis was developed by reacting DPDA with a strong basic solution to form dialkyldithiophosphate salts and later add metal salt to yield MDDP. Furthermore, DPDA in this study was prepared from isoamyl alcohol, which is the by-product of ethyl alcohol fermentation process. Thus, it promotes a higher value of isoamyl alcohol and increases more environmental concern. Finally, the oxidation stability of metal dialkyldithiophosphates prepared by isoamyl alcohol was tested.

The objective of the research

The main objective of this study is to prepare and characterize metal diisoamyl dithiophosphates by the new method and test oxidation stability of these compounds.

Scope of the research

The necessary procedures for this research are shown as follows:

1. Synthesize metal diisoamyldithiophosphate by the new method using metal salts

2. Study all variables involving synthesis steps

3. Characterize metal diisoamyldithiophosphate by FT-IR, NMR, XRF, ICP and EA.

4. Test oxidation stability of synthesized metal diisoamyldithiophosphate by thermo gravimetric method (TGA).

CHAPTER II

THEORY

2.1 Oxidation of based lubricant [1-3]

The based stocks used for lubricants are a mixture of C_{20}-C_{45} hydrocarbons, which can be subdivided into three main groups: paraffins, naphthenes and aromatics. When hydrocarbons are heated in the presence of oxygen, oxidation occurs and hydrocarbons are degraded.

2.1.1 Low-temperature oxidation (30-120°C)

The self-accelerating oxidation of hydrocarbons at low temperature is called auto-oxidation. Its initial stage is characterized by slow reaction with oxygen followed by a phase of increased conversion until the process comes to a standstill. The degradation is driven by an autocatalytic reaction, which can be described by the well-established free radical mechanism [1].

The hydrocarbon oxidation process takes place in four stages:

- Initiation of the radical chain reaction
- Propagation of the radical chain reaction
- Chain branching
- Termination of the radical chain reaction

In the initiation stage, a hydrocarbon molecule loses an atom of hydrogen to give a hydrocarbon free radical. In the propagation stage, a hydrocarbon free radical reacts with a

molecule of oxygen to form a peroxy radical. The peroxy radical then reacts with a fresh hydrocarbon molecule to form a hydroperoxide molecule and new hydrocarbon free radical. In the chain branching stage, hydroperoxides may be cleaved homolytically or may react via bimolecular mechanism to yield an alkoxy and a hydroxy radical. Finally, in the termination stage, two free radicals interact to produce one or more stable molecules.

The four stages are presented as follows

Initiation $RH \longrightarrow R\bullet + H\bullet$ (1)

     Hydrocarbon   Hydrocarbon   Hydrogen

     Free radical   atom

Propagation $R\bullet + O_2 \longrightarrow ROO\bullet$ (2)

     Free radical   Oxygen   Peroxy radical

     $ROO\bullet + RH \longrightarrow ROOH + R\bullet$ (3)

     Peroxy radical   Hydrocarbon   Hydroperoxide

Chain branching $ROOH \longrightarrow RO\bullet + HO\bullet$ (4)

     Hydroperoxide

Termination $2ROO\bullet \longrightarrow$ Various stable molecules   (5)
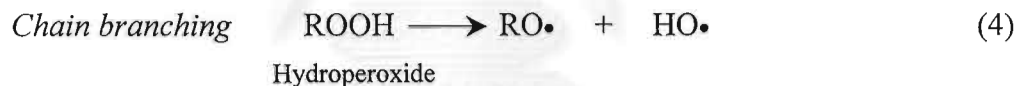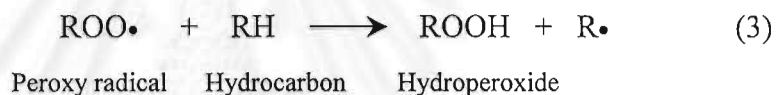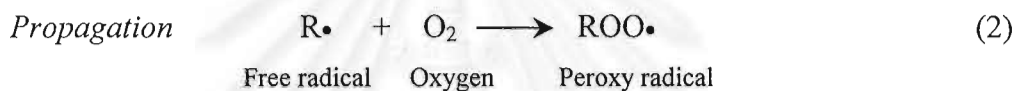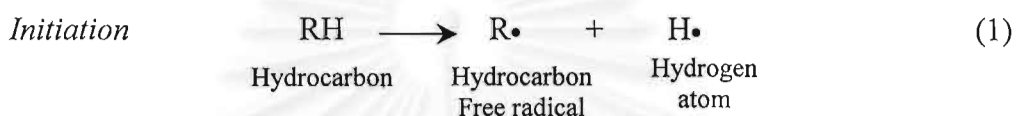
Each of the stages will now be considered in more detail.

2.1.1.1 Initiation of the radical chain reaction

The oxygen can react directly with a hydrocarbon. The mechanism is based on the fact that the oxygen molecule itself behaves like a diradical, because it has two unpaired electrons. As a result, it will attack a hydrocarbon and remove hydrogen.

     $RH + \bullet O\text{---}O\bullet \longrightarrow R\bullet + HOO\bullet$ (6)

     Hydroperoxy radical
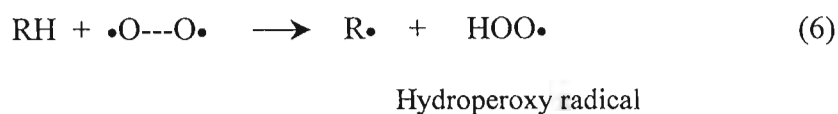
The site of the oxygen attack is determined by the strength of the C—H bond, and the reactivity for hydrocarbon abstraction increases in the following order:

$$RCH_2\text{-}H < R_2CH\text{-}H < R_3C\text{-}H < RCH=CH(R)HC\text{-}H < C_6H_5(R)HC\text{-}H \qquad (7)$$
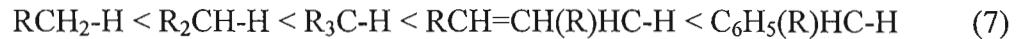
The alkyl radical can then react with oxygen to form an alkylperoxy radical.

$$R\bullet + \bullet O\text{---}O\bullet \longrightarrow R\text{--}O\text{--}O\bullet \qquad (8)$$

The hydroperoxy radical can also attack a hydrocarbon molecule to produce an alkyl hydroperoxide.

$$RH + HOO\bullet \longrightarrow ROOH + H\bullet \qquad (9)$$
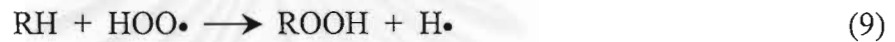
The initiation stage of low-temperature oxidation is encouraged by higher temperature.

2.1.1.2 *Propagation of the radical chain reaction.*

The simplest propagation mechanism is shown in equation (2) and (3). Reaction (2) is extremely fast and has very low activation energy. The rate of reaction of carbon centered radicals with oxygen depends on the type of substituents attached to the C-atom and increases in the following order:

$$H_3C\bullet < C_6H_5(R)CH\bullet < RCH=CH(R)CH\bullet < R_2CH\bullet < R_3C\bullet \qquad (10)$$
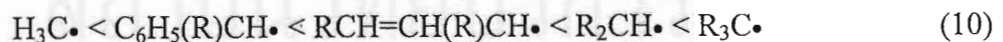
The next step in equation (3) produces an alkyl hydroperoxide ROOH and an alkyl radical R• which can again react with oxygen according to reaction (2). The rate of reaction of step (3) is slow.

2.1.1.3 Chain branching

During the early stage of autoxidation various types of hydroperoxides are generated. At low concentrations, they may be cleaved homolytically to yield an alkoxy and a hydroxy radical:

$$ROOH \longrightarrow RO\bullet + HO\bullet \qquad (11)$$

$$\text{Alkoxy radical} \quad \text{Hydroxy radical}$$
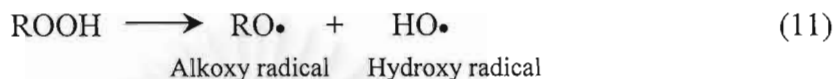
However, this process rarely occurs because of high activation energy. Hence reaction (11) only plays a significant role at higher temperatures or under catalysed conditions. Once formed, hydroxy and especially primary alkoxy radicals are so active that they abstract hydrogen atoms in non-selective reactions:

$$HO\bullet + CH_3\text{-}R \longrightarrow H_2O + RCH_2\bullet \qquad (12)$$

$$HO\bullet + R\text{-}CH_2\text{-}R^1 \longrightarrow H_2O + R(R^1)HC\bullet \qquad (13)$$

$$RCH_2O\bullet + CH_3\text{-}R \longrightarrow RCH_2OH + RH_2C\bullet \qquad (14)$$
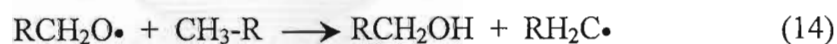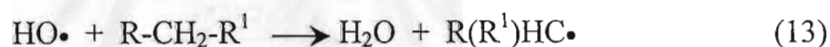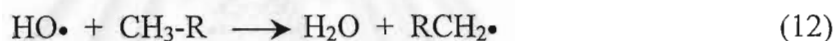
Secondary and tertiary alkoxy radicals prefer to form aldehydes and ketone:

$$R-\underset{\displaystyle R^1}{\overset{\displaystyle H}{C}}-O\bullet \longrightarrow RCHO + R^1\bullet \qquad (15)$$

$$R^2-\underset{\displaystyle R^3}{\overset{\displaystyle R^1}{C}}-O\bullet \longrightarrow R^1COR^2 + R^3\bullet \qquad (16)$$
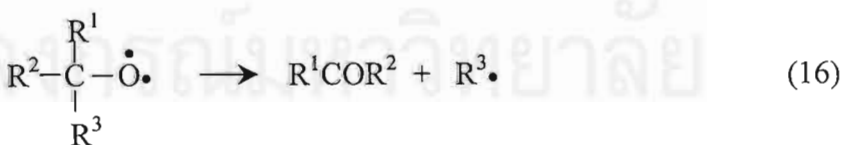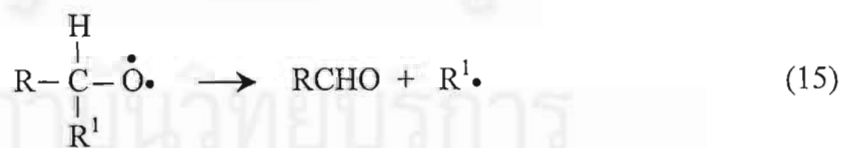
At high concentrations, i.e. at an advanced state of oxidation, hydroperoxides may react via a bimolecular mechanism:

$$R-O-O-H$$

$$ROOH + ROOH \longleftrightarrow \quad H-O-OR \longleftrightarrow ROO\bullet + RO\bullet + H \qquad (17)$$
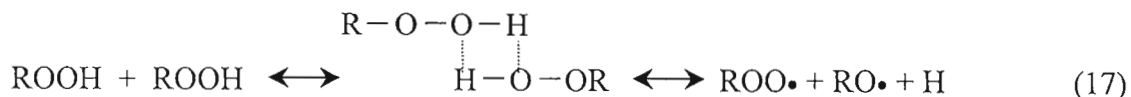
As a consequence of hydroperoxide accumulation and subsequent cleavage, the concentration of reactive free radicals initiating new chains increase. The time from the beginning of the oxidation to the autocatalytic phase of the autoxidation is called the 'induction period'.

2.1.1.4 Termination of the radical chain reaction

The basic termination stage is shown in equation (5), the combination of radical species (such as peroxy radicals) to yield unreactive species (such as ketones and alcohols):

$$2RR^1CHOO\bullet \longleftrightarrow [R(R^1)CHOOOOCH(R^1)R]$$
$$\longrightarrow R(R^1)C=O + O_2 + HO{-}CH(R^1)R \qquad (18)$$
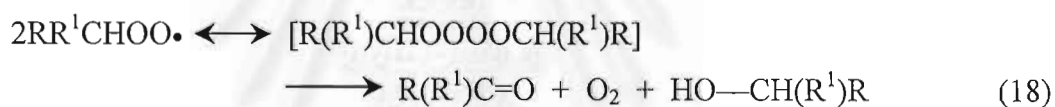
In this example, primary and secondary peroxy radicals form intermediates, which disproportionate to non-radical degradation products. In contrast, tertiary peroxy radicals may either combine to give di-tertiary alkyl peroxides or undergo a cleavage reaction leading to ketones and alkyl radicals. Furthermore, many alternative terminations are possible in which any pair of free radicals combine together to form a larger stable molecule. Examples are

$$R\bullet + R\bullet \longrightarrow R{-}R \qquad (19)$$
$$\text{Hydrocarbon (dimer)}$$

$$R\bullet + RO\bullet \longrightarrow ROR \qquad (20)$$
$$\text{Ether}$$

$$R\bullet + ROO\bullet \longrightarrow ROOR \qquad (21)$$
$$\text{Alkyl peroxide}$$
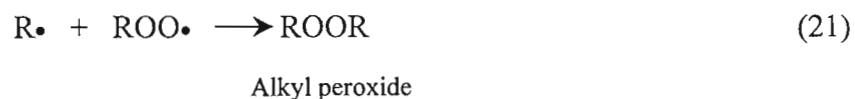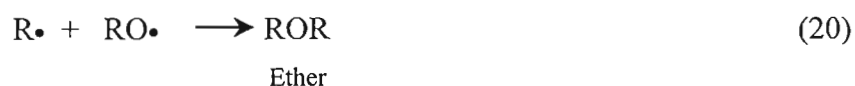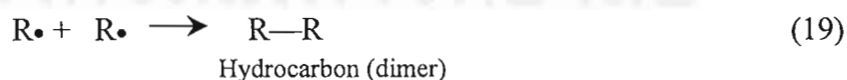
Chain termination can also take place by reaction of a free radical with an unsaturated molecule (olefin) or aromatic molecule to produce a large free radical.

$$R\bullet + PhH \longrightarrow PhR\bullet + H\bullet \qquad (22)$$

Certain non-hydrocarbons, such as hindered phenols or amines, are readily attacked by free alkyl radicals to form stable compounds.

2.1.2   High-temperature oxidation (> 120°C)

The effect of heat on all chemical reactions is to increase reaction rates. In the case of mineral oil oxidation, the degradation process can be divided into a primary and a secondary oxidation phase.

2.1.2.1   Primary oxidation phase

Initiation and propagation of the radical chain reaction are the same as discussed under low-temperature conditions, but the selectivity is reduced and the reaction rate is increased. At high temperature the cleavage of hydroperoxides plays the most important role.

Reaction (11) leads to a proliferation of hydroxy radicals, which non-selectivity abstracts hydrogen atoms (see reactions (12) and (13)). Acids are formed by the following two reactions, which start from a hydroperoxy-peroxy radical and an aldehyde:

$$
\begin{array}{ccc}
\overset{\bullet OO}{\underset{OOH}{R-CH-CH_2-\overset{|}{\underset{|}{C}}-R^1}} & \longleftrightarrow & \overset{\bullet}{\underset{OOH}{RC-CH_2-\overset{OOH}{\underset{|}{C}}-R^1}} \xrightarrow[-HO\bullet]{} \\
R^2 & & R^2
\end{array}
$$

$$
\underset{R^2}{R-CO-CH_2-\overset{OOH}{\underset{|}{C}}-R^1} \longleftrightarrow R-COOH + R^2-CH_2-\overset{O}{\overset{||}{C}}-R^1 \quad (23)
$$

$$R-CHO \xrightarrow[-ROOH]{ROO\bullet} R-\overset{\displaystyle O}{\overset{\|}{C}} \xrightarrow{O_2} R-\overset{\displaystyle O}{\overset{\|}{C}}OO\bullet \xrightarrow[-R\bullet]{RH}$$

$$R-\overset{\displaystyle O}{\overset{\|}{C}}OOH \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}OH + 1/2O_2 \qquad (24)$$
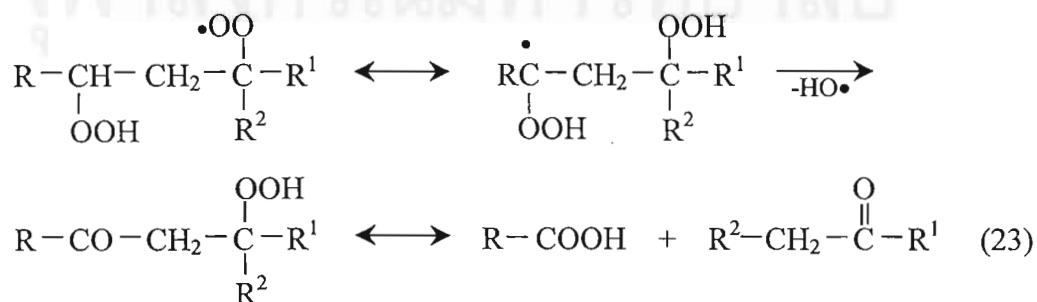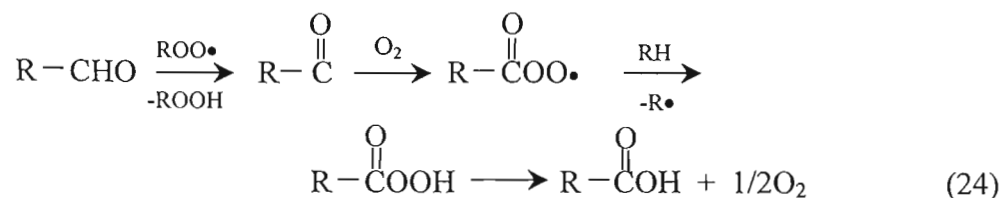
In addition, when the rate of oxidation becomes limited by diffusion, ethers are formed.

$$R-\overset{\overset{\displaystyle OO\bullet}{\mid}}{CH}-CH_2-CH_2-\overset{\bullet}{R} \longrightarrow R\overset{\overset{\displaystyle OOH}{\mid}}{CH}-CH_2-\overset{\bullet}{CH}-\overset{\bullet}{R} \xrightarrow{-HO\bullet}$$

$$\overset{\overset{\displaystyle \lceil -O-\rceil}{}}{R-CH-CH_2-CH-R'} \qquad (25)$$
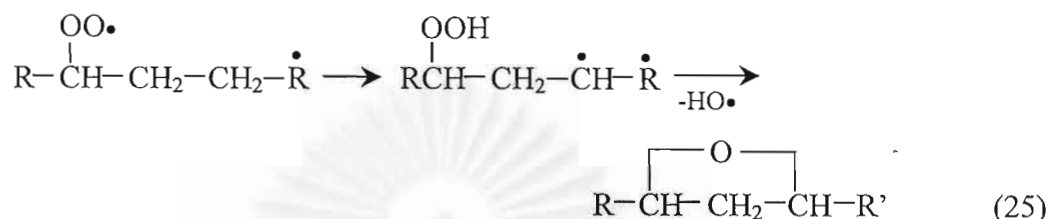
The termination reaction proceeds through primary and secondary peroxy radicals according to reaction (18). But at temperatures above 120°C, these peroxy radicals also interact in a non-terminating way to give primary and secondary alkoxy radicals:

$$2ROO\bullet \longrightarrow [ROOOOR] \longrightarrow 2RO\bullet + O_2 \qquad (26)$$
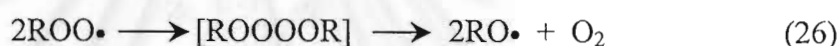
These radicals again contribute to the formation of cleavage products via reaction (14) and (15).

2.1.2.2 Secondary oxidation phase

With a higher temperature, the viscosity of the bulk medium increases as a result of the polycondensation of the difunctional oxygenated products formed in the primary oxidation phase. Further polycondensation and polymerization reactions of these high molecular weight intermediates result in products, which are no longer soluble in the hydrocarbon. The resulting precipitate is called sludge. Under thin-film oxidation conditions, as in the case of a lubricant film on a metal surface, varnish-like deposits are formed. The polycondensation reactions, which lead to high molecular weight intermediates (sludge precursors), can be described as follows. In a first step, aldehydes or

ketones formed in the primary oxidation phase combine via an acid- or base-catalysed aldol condensation to form alpha, beta-unsaturated aldehydes or ketones. Further aldol condensations with these products lead to oil-soluble polycondensation products (molecular weight about 2000).

When the reaction becomes diffusion controlled, as a result of the increased viscosity of the oil, alkoxy radicals can initiate polymerization of polycondensation products. This leads to sludge and deposit formation as well as to additional oil-soluble high molecular weight products, which contribute to the viscosity increase.

Under high-temperature conditions there is always the possibility of thermal cleavage of a hydrocarbon chain, especially when the availability of oxygen is limited by diffusion:

$$R(CH_2)_6R \longrightarrow 2[RCH_2CH_2-CH_2\bullet] \longrightarrow 2RCH_2CH=CH_2 + H_2 \qquad (27)$$

Reaction (27) leads to unsaturated molecules with lower molecular weight and higher volatility. The model for high temperature oxidation can be described in Figure 2.1 [3]
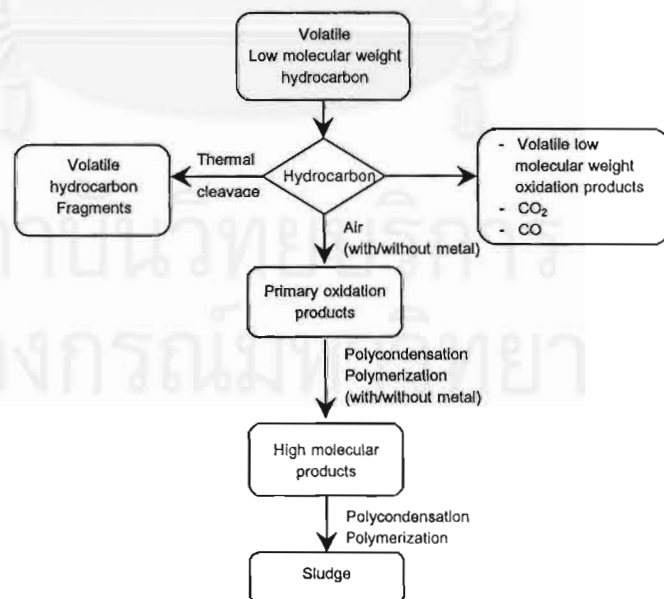
Figure 2.1 Model of lubricant degradation under high temperature conditions.

2.1.3 Effects of catalysts [3]

The decomposition of an alkyl hydroperoxide molecule occurs at temperatures of about 150°C. Transition metal ions having two ionic valence states, such as $Fe^{2+/3+}$, $Pb^{2+/4+}$ and $Cu^{1+/2+}$, reduce the activation energy of this decomposition process. The homolytic hydroperoxide decomposition is accelerated at ambient temperatures by small concentrations (0.1-50 ppm) of this metal:

$$ROOH + M^{n+} \longrightarrow RO\bullet + M^{(n+1)+} + OH^-$$
(28)

$$ROOH + M^{(n+1)+} \longrightarrow ROO\bullet + M^{n+} + H^+$$
(29)
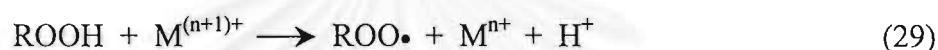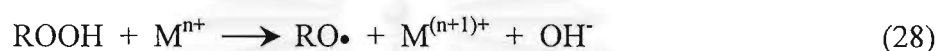
Reaction (28) and (29) can be summarized as (30).

$$2ROOH \xrightarrow{\quad M^{n+1}/M^{(n+1)+} \quad} ROO\bullet + RO\bullet + H_2O$$
(30)
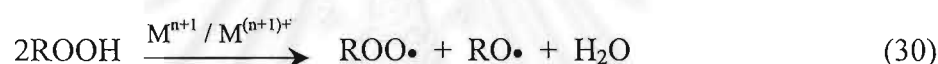
Chain branching under the influence of a catalyst at a given temperature proceeds faster when compared with the uncatalysed reaction. The consequence is a high rate of hydroperoxide formation (and hence oxidation) as illustrated in Figure 2.2.
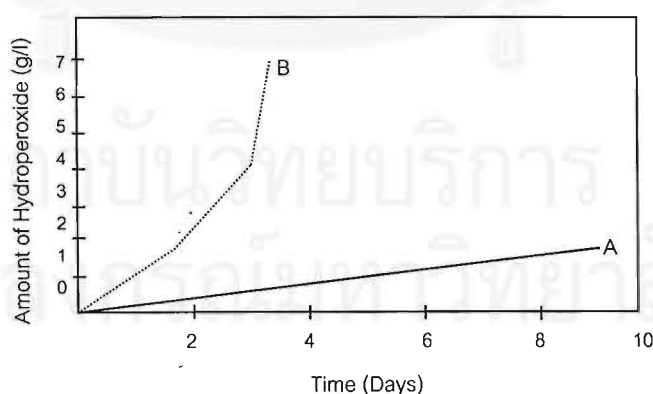
Figure 2.2 Increase of hydroperoxide concentration under the influence of $Fe(OOCC_7H_{15})_3$ catalysis: (A) pure model hydrocarbon; (b) pure model hydrocarbon plus 500 ppm $Fe(OOOC_7H_{15})_3$. Conditions: 95°C bath temperature; 300 ml oil volume; 3 L/hour oxygen flow.

The precursor steps of soap formation, shown below with Fe as the metallic surface, arise from the attack of the metal surface by alkylperoxy radicals and alkylhydroperoxide. This process may be called 'corrosive wear':

$$ROO• + Fe \longrightarrow FeO + RO• \qquad (31)$$

$$ROOH + Fe \longrightarrow FeO + ROH \qquad (32)$$
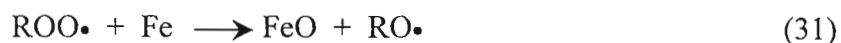
The FeO reacts further with organic acids and forms the iron soaps:

$$2RCOOH + FeO \longrightarrow Fe(OCOR)_2 + H_2O \qquad (33)$$

The catalytic activity of cooper and iron is summarized as follows:

- In the presence of iron, copper soaps in general retard oxidation and polycondensation/polymerization reactions. In iron ion-free systems organocopper salts behave as pro-oxidation.

- Iron soaps accelerate oxidation and polycondensation/polymerization reactions with increasing concentration.

In conclusion, the oxidation of model hydrocarbons proceeds via a radical chain mechanism and is strongly influenced by temperature and by certain transition metal ions. This results in the formation of insoluble sludge as well as a continuous increase in viscosity. So the lubricant is necessary to develop stabilizers against oxidation, which will extend its useful life. The types of antioxidants used and how they perform, as well as their synthesis, will be dealt with in the next section.

2.2 Antioxidants

The use of additives to control lubricant degradation requires a focus on alkyl radical, alkylperoxy radicals and hydroperoxides. Primary alkoxy radicals and hydroxy radicals rapidly abstract hydrogen from the substrate. It is therefore very unlikely that they can be deactivated by natural or synthetic antioxidants. In practice, three additive types have proven to be successful in controlling the degradation of lubricating oils:

- Radical scavengers
- Hydroperoxide decomposers
- Synergistic mixtures of these

Radical scavengers

The most widely used types of radical scavengers are phenolic and aminic antioxidants. Recently, organo-copper salts have been introduced to control the oxidative degradation of engine oils.

Hydroperoxide decomposers

These compounds convert hydroperoxides into non-radical products, thus preventing the chain propagation reaction. Traditionally, organosulphur and organophosphorus additives have been used for this purpose. They can be separated by structure as follows:

- Organosulphur compounds
- Zinc dialkyldithiocarbamates
- Organophosphorus compounds

Multifunctional additives

- Zinc dialkyldithiophosphates (ZDDP)

The dominating position of ZDDPs as additives for lubricating oils is due to their multifunction performance. Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricant, and protect metals against corrosion. ZDDPs are mainly used to formulate antiwear hydraulic fluids and engine oils.

- Organomolybdenum compounds

These compounds are of general interest in the engine oil area. They are antioxidants and in addition improve the frictional and antiwear characteristics of the lubricants.

- Overbased phenates and salicylate

Both phenates and salicylates of magnesium or calcium behave as antioxidants at high temperature.

- Sulphur/nitrogen and sulphur/phosphorus compounds

Other multifunctional sulphur/nitrogen, sulphur/phosphorus based additive have antioxidant and antiwear properties. These additives interact with peroxy radicals and hydroperxides thus stabilizing industrial lubricants and engine oils.

2.3 Zinc dialkyldithiophosphates or metal dialkyldithiophosphates

Zinc dialkyldithiophosphates have been used for many years as antioxidants and antiwear additives in lubricating oils. Furthermore, ZDDPs are frequently used in the

presence of other additives such as polar hydroxy compounds-hydroxyesters (glyceryl mono oleate) imidazolines, alkylphenol/ethylene oxide condensates and the hydroxyester formed by esterification of dimer acid of linoleic acid and diethylene glycol, which act as friction modifiers, fuel economy additives or rust inhibitors.

2.3.1 Reaction mechanism

The performance of ZDDPs is strongly influenced by the type of alcohol used for their synthesis. Table 2.1 gives an overview of the variance of performance with type of alcohol.

Table 2.1 Structure activity dependency of ZDDP

Structure	Function		Property	
	Oxidation inhibition	Wear protection	Thermal stability	Hydrolytic stability
Primary ZDDP $Zn\left[S-P(OCH_2R)_2\right]_2$	satisfactory	satisfactory	good	satisfactory
Secondary ZDDP $Zn\left[S-P(OCHR_1R_2)_2\right]_2$	good	good	moderate	good
Aryl ZDDP $Zn\left[S-P(O-\bigcirc-R)_2\right]_2$	moderate	bad	very good	good

The way ZDDPs performs as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxy radicals. The performance matrix is additionally influenced by other additives, which are present in industrial or engine oil formulations.

There are two inter-related mechanisms for the formation of the acid catalyst. In the first, a rapid, initial reaction of ZDDPs and hydroperoxide forms a basic ZDDP and a disulfide (VII).

$$4[(RO)_2PS_2]_2Zn + R_1OOH \xrightarrow[\text{heat}]{-R_1OH} [(RO)_2PS_2]_6Zn_4O + [(RO)_2PS_2]_2 \quad (34)$$
$$\text{VII}$$
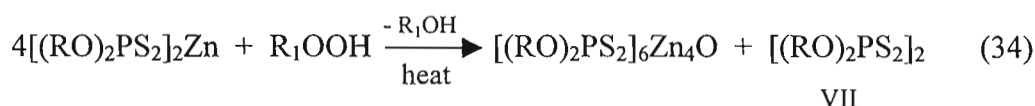
An induction period follows where the rate of decomposition of the hydroperoxide is slow. In this reaction phase the basic ZDDP dissociates to form ZDDP and ZnO.

$$[(RO)_2PS_2]_6Zn_4O \rightleftharpoons 3 [(RO)_2PS_2]_2Zn + ZnO \quad (35)$$
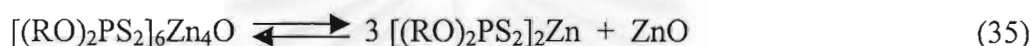
The ZDDP then reacts with hydroperoxide to form additional disulfide (VII) via the dithiophosphate radical (VIII):

$$[(RO)_2PS_2]_2Zn + R_1OOH \xrightarrow[-R_1O\bullet]{} [(RO)_2PS_2]ZnOH + (RO)_2PS_2 \bullet$$
$$\text{VIII}$$
$$(RO)_2PS_2 \bullet \longrightarrow [(RO)_2PS_2]_2 \quad (36)$$
$$\text{VIII} \qquad\qquad\qquad \text{VII}$$
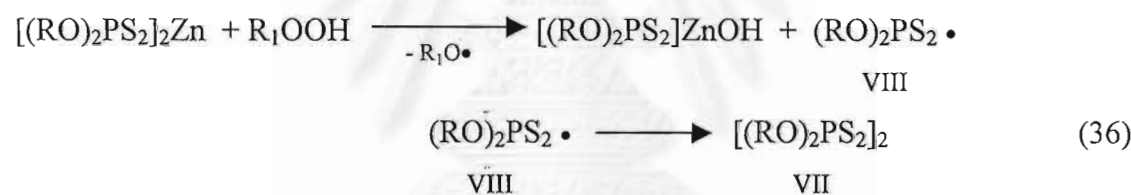
The kinetics of reaction result in a final rapid decomposition of the hydroperoxide provided the concentration of the basic ZDDP is low. Under these conditions the sulphur radical is unable to dimerize. Instead it reacts with hydroperoxide leading to the catalytically active acid:

$$(RO)_2PS_2 \bullet + ROOH \xrightarrow[-ROO\bullet]{} (RO)_2PS_2H \quad (37)$$
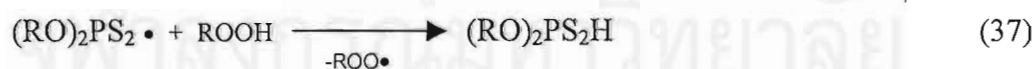
The second source of this acid arises when the ZDDP concentration falls below a critical level. The traces of water interact with the ZDDP forming the acid catalyst:

$$[(RO)_2PS_2]_2Zn + H_2O \longrightarrow [(RO)_2PS_2]ZnOH + (RO)_2PS_2H \quad (38)$$
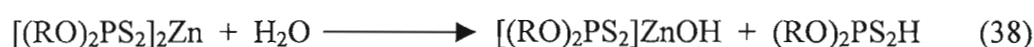
It was demonstrated that at temperatures above 125°C, the disulfide (VII) could be an additional source of the acid catalyst via reaction (18) followed by reaction (37):

$$[(RO)_2PS_2]_2 \longrightarrow (RO)_2PS_2\bullet \qquad (39)$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$

$$(RO)_2PS_2\bullet + ROOH \xrightarrow{-ROO\bullet} (RO)_2PS_2H \qquad (37)$$
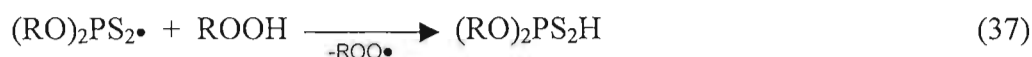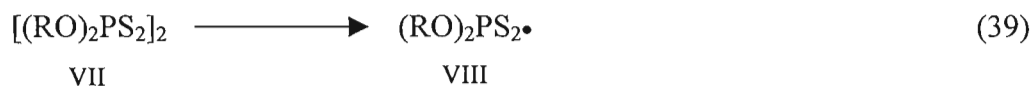
A general scheme for the decomposition of hydroperoxides may be:

$$ROOH \xrightarrow{H^+} [ROOH \overset{+}{\rightleftharpoons} \underset{H}{\overset{+}{RO}-OH}] \longrightarrow \text{reaction products} \qquad (40)$$
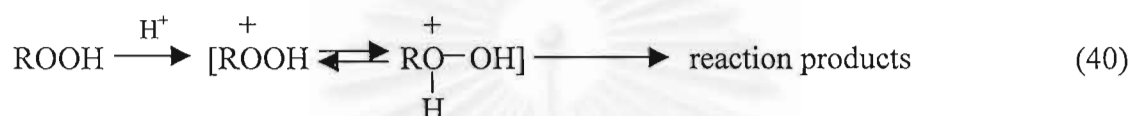
ZDDP may also interact with peroxy radicals according to the following mechanism:

$$[(RO)_2PS_2]_2Zn \xrightarrow{ROO\bullet} RO_2^- + (RO)_2PS_2Zn^+\bullet + (RO)_2PS_2\bullet \qquad (41)$$
$$\text{VIII}$$
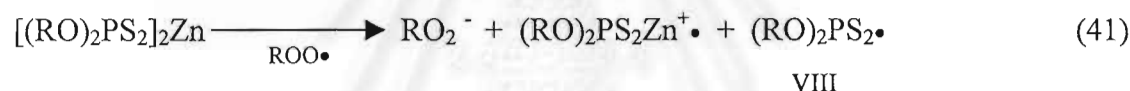
The radical (VIII) may react again with hydroperoxide according to reaction(37) thereby regenerating the DPDA, $(RO)_2PS_2H$, which is a better inhibitor than the ZDDP.

2.3.2 Synthesis of metal dialkyldithiophosphate

2.3.2.1 The conventional method [4-13]

Nowadays, about 150,000-160,000 tones of ZDDP are produced per year in the western world using the following synthetic route:

Step 1 $\qquad P_2S_5 + 4ROH \longrightarrow 2(RO)_2PS_2H + H_2S \qquad (42)$

Step 2 $\qquad 2(RO)_2PS_2H + ZnO \longrightarrow Zn[(RO)_2PS_2]_2 + 2H_2O \qquad (43)$
$\qquad\qquad$ Dialkyldithiophosphoric acid $\qquad\qquad$ ZDDP
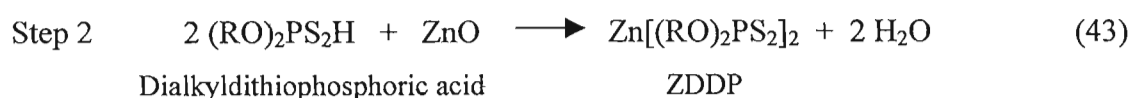
Dialkyldithiophosphoric acids from the first step (reaction (42)) are formed by the reaction of P_2S_5 and alcohol or phenol. Then, the acid is reacted with zinc base or with ZnO in the second step (reaction (43)). The structures of ZDDP are shown in Figure 2.3

Normal structure molecule of MDDP

Oligomer (dimer)
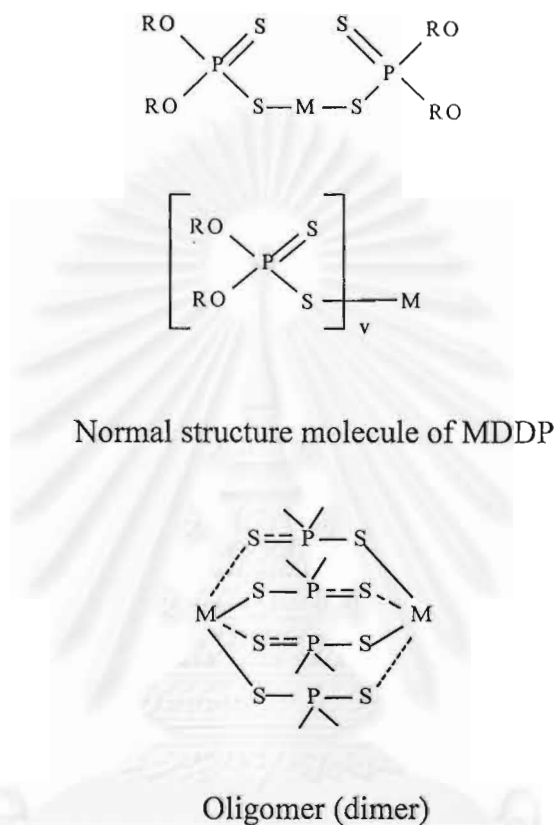
Figure 2.3 The structure of ZDDP or MDDP

The group R is an aliphatic hydrogen and carbon-containing group having at least 4 carbon atoms, e.g. 4 to 10 carbon atoms. This may, for example, be an alkenyl group, but preferably, it is C_4 to C_{10} alkyl and may, for example, be a n-butyl, i-butyl, sec-butyl, amyl, sec-hexyl, n-heptyl, n-octyl, i-octyl or n-decyl. Preferably, R is an 2-ethyl hexyl. Alternatively, R can be an alkaryl group and this is preferably an alkyl phenyl group, especially a C_7 to C_{12} alkyl phenyl group, e.g. branched nonyl phenyl or branched dodecyl phenyl. R may be a mixture, i.e. derived from a mixture of alcohols ROH.

The basic metals used in reacting with dialkyldithiophosphoric acid can be metal groups IIB, IIIB, IVB, VIII of the periodic system of element, i.e. ZnO, CuO, CaO, MgO, MoO_3, SnO_2, preferably zinc oxide. v is valency of the metal M.

2.3.2.2   The new method

The new method for synthesis of metal dialkyldithiophosphate in this research is a 3-steps method. First, dialkyldithiophosphoric acid is prepared by reacting phosphorus pentasulphide with alcohol. Next, DPDA from the first step is titrated with a solution of potassium hydroxide to form potassium dialkyldithiophosphate salt. The last step is the addition of metal salts into the solution of potassium dialkyldithiophosphate salt to form MDDP. All steps are shown as follows:
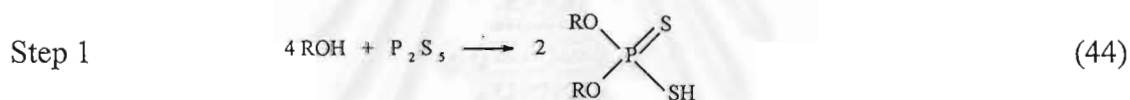
Step 1

$$4\,ROH + P_2S_5 \longrightarrow 2 \quad \begin{array}{c} RO \\ RO \end{array}\!\!P\!\!\begin{array}{c} S \\ SH \end{array} \tag{44}$$

Dialkyldithiophosphoric acid

Step 2

$$\begin{array}{c} RO \\ RO \end{array}\!\!P\!\!\begin{array}{c} S \\ SH \end{array} + KOH \longrightarrow \begin{array}{c} RO \\ RO \end{array}\!\!P\!\!\begin{array}{c} S \\ SK \end{array} + H_2O \tag{45}$$

Potassium dialkyldithiophosphate salt

Step 3

$$2 \begin{array}{c} RO \\ RO \end{array}\!\!P\!\!\begin{array}{c} S \\ SK \end{array} + \text{Metal Salts} \longrightarrow \begin{array}{c} RO \\ RO \end{array}\!\!P\!\!\begin{array}{c} S \\ S-M-S \end{array}\!\!P\!\!\begin{array}{c} RO \\ RO \end{array} + 2KCl \tag{46}$$
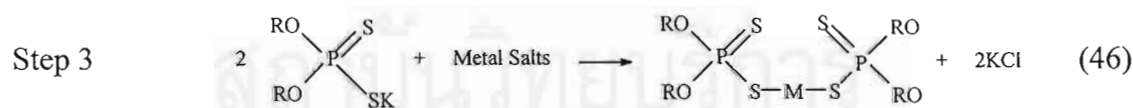
Metal dialkyldithiophosphate

Alcohol used in this research is isoamyl alcohol, a by-product of the ethyl alcohol fermentation industry (the fermentation of crude potato starch of ethyl alcohol) [14]. Metal salts used in this method are groups of metal chloride and metal sulfate such as $ZnCl_2$, $CuCl_2$ and $MgSO_4$.

2.3.3 Performance evaluation of metal dialkyldithiophosphates in lubricating oils

2.3.3.1   Composition of lubricating oil [6]

Compositions, when containing the conventional additive, are typically blended into the base oil in amounts, which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated in Table 2.2.

Table 2.2 The effective amounts of additives blended into the base oil

Additives	Vol %	Wt % a.i.
Viscosity modifier	0.01-4	0.01-4
Corrosion inhibitor	0.01-1	0.01-1.5
Oxidation inhibitor	0.01-1	0.01-1.5
Dispersant	0.1-7	0.1-8
Pour point depressant	0.01-1	0.01-1.5
Anti-foaming agents	0.001-1	0.001-0.15
Antiwear agents	0.001-1	0.01-1.5
Friction modifiers	0.01-1	0.01-1.5
Detergents/Rust inhibitor	0.01-2.5	0.01-3
Mineral oil base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solution or dispersions of the dispersant, together with one or more of other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby

several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the dispersant additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant.

Additives for lubricating oils are generally supplied as concentrates in solvent for incorporation into bulk lubricant. Due to polar nature, metal dialkyldithiophosphates may have poor oil solubility, which can limit the treat levels at which they are used. Also, when MDDPs have been tried in certain packages or blends, compatibility problems have been experienced involving sediment formation during storage and this precludes the use of these additives in specific packages. According to this research, a concentration of MDDP package comprises 10 %Wt. of toluene and 90 %Wt. of the metal dialkyldithiophosphate. Then, MDDP package may be diluted with lubricant basestock to form a lubricating oil composition.

2.3.3.2 *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) is the method for determination of oxidation stability of lubricating oil. Although, oxidation stability of lubricating oil (lube base, turbine oil, gear oil transformer oil, etc.) can be measured by many methods, but they usually need a long test duration time and require a large sample size as can be seen in Table 2.3.

usually need a long test duration time and require a large sample size as can be seen in Table 2.3.

Table 2.3 Standard test method for oxidation stability

TEST METHOD	SAMPLE	CATALYST	OXIDIZING AGENT	TEMP °C	TEST PARAMETERS	TEST DURATON TIME	SAMPLE SIZE
IP 48/67	Base oils	No catalyst	Air at flow rate 15 L/h	200	Kinematic viscosity at 100°F rambottom carbon residue	Two periods each of 6 them h	40 ml
IP 56/64	Transformer oils	Copper sheet	Air at flow rate 2 L/h	150	- Acidity - Sludge value	45 h	100 g
IP 114/67T	Turbine oils	Copper sheet	Air at flow rate 2 L/h	110	Increase in acidity	90 h	100 g
IP 157/64	Steam turbine oils	Copper and iron coils	Oxigen at flow rate 3 L/h	59	Increase in acidity	1000 h or until TAN varying from 0.25 to 2.0 mg.KOH sample	300 ml
IP 229/68T	Steam turbine oils	Copper coil	Oxygen pressure at 90 psi	150	Induction periods	Until pressure is 25 lb Less than established between pressure	50 g
IP 269/67T	Automatic transmission fluids	Steel plate	Air at flow rate 100 ml/min	149 or 163	Rating of formed sludge	312 h	4.55 L
IP 280/73	Turbine oils	Copper napthenate&iron napthenate solutions	Oxygen at floe rate 1 L/h	120	- Volatile acids - Soluble acids - Sludge	164 h	30 g
IP 306/79	Stright mineral oils	No catalyst or copper wire	Oxygen at floe rate 1 L/h	120	- Volatile acidity - Soluble acidity - Total Sludge - Total oxidation products (TOP)	48 h	25 g
IP 307/80	Insulating oil	Copper wire	Oxygen at floe rate 1 L/h	100	- Sludge content - Soluble acidity	164 h	25 g
IP 335/80	Inhibited mineral	Copper wire	Oxygen 1 L/h	120	Induction	236 h	25 g

Apart from the difficulties above, these methods also have the temperature limit of 200°C and sample size of 4.55 liters. Furthermore, they need to perform other property tests simultaneously in order to see the change in the properties of lubricating oils.

TGA technique has been developed extensively and used to determine the oxidation stability of lubricating oils at a given temperature as high as 600°C with oxygen flow. This method requires less test duration time, lower amount of sample as well as increase in accuracy.

The general principle of TGA

TGA is the method that the weight loss of sample is continuously recorded during heating until above 300°C. The weight loss increases rapidly and continuously in the oxygen environment. This is because the weight change does not result from its thermal decomposition alone but also its oxidation reaction until approximately 350°C (or above). This weight change is stable at oxidation point where the compound is oxidized by oxygen molecule. The difference in this point of lubricating oils depends on properties of their lube base and additives.

At a temperature above the oxidation point, the weight loss takes place rapidly and continuously again until the thermal decomposition of oils and its oxidation reaction are completed. Although there is an increase in temperature, the weight change of the rest of the oil and oxidation product is stable. Consider the curve as presented in Figure 2.4.

This curve shows the weight change of lubricating oils with temperature in the oxygen flow. At the beginning (ab) is consistent when heating, until it reaches the temperature at b(tb) of the curve. The weight loss decreases continuously until b'. After this point (b'c), the weight loss increases rapidly with oxidizing and later falls quickly until c. After this point up to D (cd), the weight change is very small or almost stable. This loss (bb') results from thermal decomposition and evaporation of oil; but, the loss (b'c) comes from the oxidizing of oil. The temperature at b'(tb') is called the oxidation point.
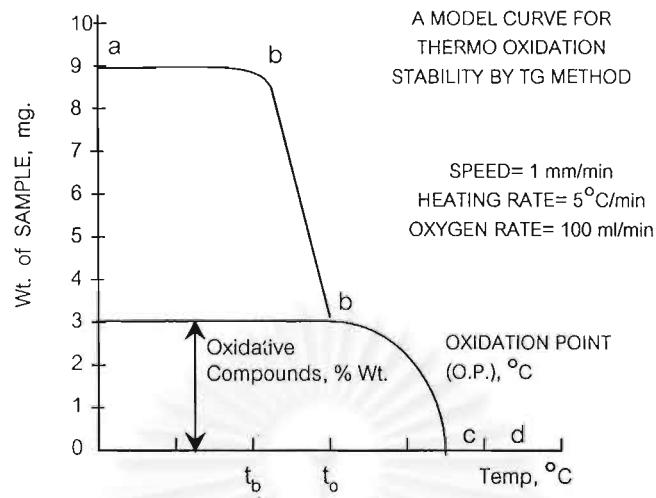
Figure 2.4 The model curve for thermo oxidation stability by TGA method

The following are explanations of words generally found in the determination of oxidation stability in lubricating oils by TGA techniques.

Oxidation point :   the temperature at which the rate of weight loss decreases due to the formation of compound in oxidation reaction.

Oxidation product :   the weight of compounds from oxidation reaction remains when the temperature reaches the oxidation point. Above this temperature these compounds will be decomposed to carbon and evaporated as carbon dioxide.

The graph shows that the sample evaporates slowly and then fast in the end. This means that the decomposition takes place continuously from 300°C to 400°C. The weight loss is as high as 90°C of the initial total weight of the sample. When the temperature is above 400°C, the remaining sample and compound produced changes into carbon and is consistent until 600°C.
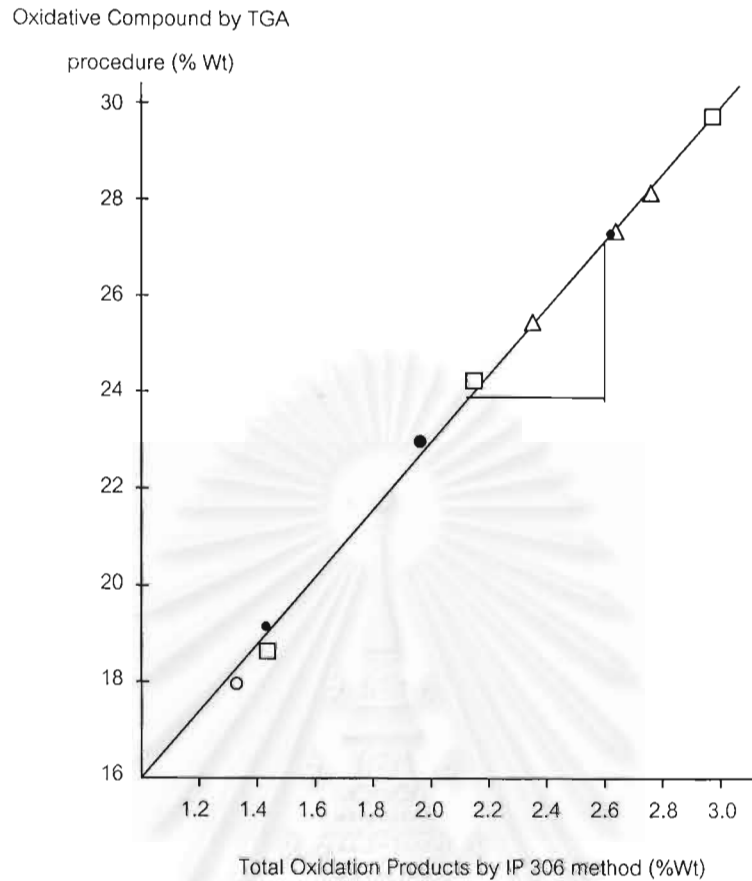
Figure 2.5 The relationship between oxidation product by TGA and by IP306

The percentage of oxidation product at the oxidation point can be used as a measuring value of stability of lubricating oil to oxidation reaction.

The determination of stability of lubricating oil by TGA techniques is compared with standard method of IP306 as in Figure 2.5. It is found that the temperature at oxidation point has a linear relationship between oxidative compound (by TGA technique) and total oxidation products (by IP306).

The linear equation is Y = 7.8X + 8

Where Y = oxidation products by TGA technique

X = total oxidation products by IP306 method
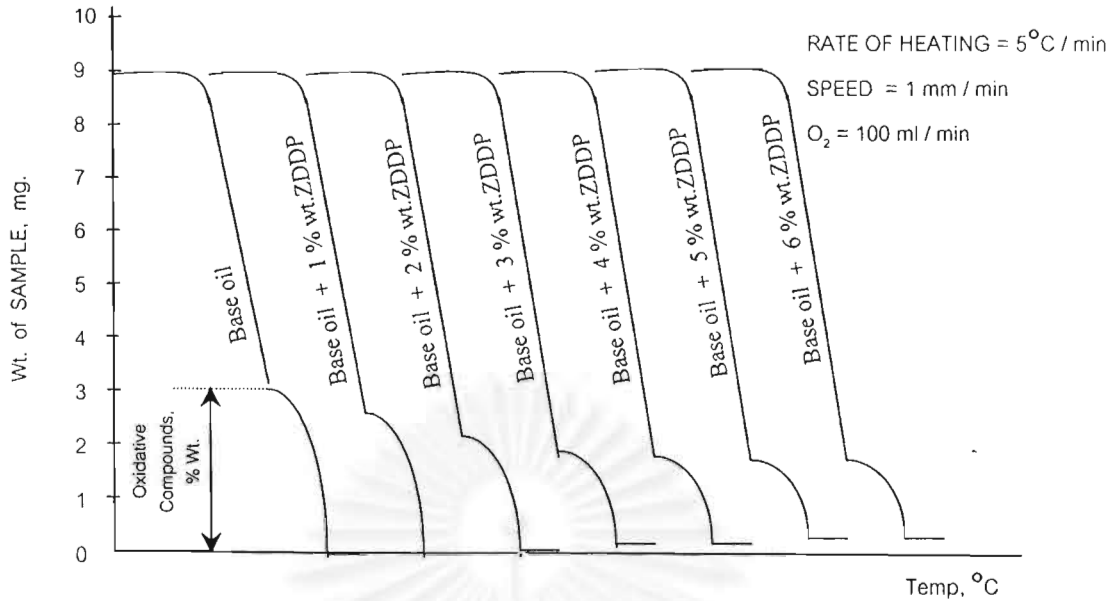
Figure 2.6 The relationship between ZDDP concentration and oxidation product by TGA

When a portion of the additive, zinc dialkyldithiophosphate (ZDDP), at various concentration ranges from 1 to 6%, is added to the same lube base and the tested with TGA, the amount of oxidation product decreases when the concentration of ZDDP increases to 4% as shown in Figure 2.6. At higher concentrations, the amount of oxidative compounds remains constant. This means that there is no need to add any additive higher than this level. This level is the most suitable for an additive in lubricating oil. This is probably due to the mass balance between alkyl groups of additive and molecular chain of hydrocarbon of lube base or the balance of ZDDP molecular structure between the structure of internalchelate, monomer and oligomers.

For the case of concentration of ZDDP higher than 4%, the ZDDP molecule may be changed completely from normal structure to internalchelate monomers or oligomers.

Generally, TGA techniques may be used in determination of stability of lubricating oils after mixing with additive or of proper concentration of its additive.

2.4 Literature review

Metal dialkyldithiophosphates, especially zinc dialkyldithiophosphates (ZDDP), have long been used as antioxidants and antiwear additives in hydraulic oils, motor oils, automatic transmission fluids.

In the manufacture of MDDP, *Caspari (1978)*, [4] suggested that MDDP could be prepared by neutralizing dialkyldithiophosphoric acid with zinc, barium, cadmium, magnesium or nickel base in the presence of an acidic promoter followed by reacting a substantial portion of excess acidic promoter with a weak base. Acidic promoter are generally acids which form water or oil soluble metal salts or metal hydroxy salts.

During the 1960s-1970s, the structure of MDDP used as extreme-pressure and antiwear additives was generally prepared from "neo" monoalcohol. However, this method was cost intensive. *Rivier (1981)*, [5] suggested that monoester alcohol could be reacted with P_2S_5 to form dialkyldithiophosphoric acid and then neutralized with Metal oxide from group IIB, IIIB, IVB, VIII. These MDDP can be used industrially, in particular, in order to improve the extreme-pressure and antiwear properties of lubricating oils.

The nature of MDDP made from the alcohols containing a polar group is often oil-insoluble. *Colclough (1989)*, [6] reported that dithiophosphate was derived from the reaction of P_2S_5 with the mixture of alcohols ROH and $R^1(OH)_m$, where m is 1 or 2. The group R is an aliphatic hydrogen and carbon-containing group having at least 4 carbon atoms or is an alkaryl group, R' is a hydrogen and carbon-containing group containing at least 12 carbon atoms. Usually there are four equivalents plus a slight excess of ROH and $R^1(OH)_m$ reacted with P_2S_5. Usually there is more of ROH is present than $R^1(OH)_m$ on a molar basis so as to ensure that mobile liquid oil-soluble product is formed.

This report also provides the use of the defined metal dithiophosphates in lubricating oil as an antioxidant.

Born (1989), [7] reported the manufacture and use of metal dihydrocarbyl dithiophosphyl-dithiophosphate compound. These compounds provided particular protection against wear similar to that achieved with additives of the prior art, but at substantially lower concentrations, or giving better protection at equal concentration. This author selected metal from zinc, cadmium, lead and antimony or an oxygen-and/or sulphur-containing molybdenum complex.

Maeda (1990), [8] reported that lubricating oil composition containing molybdenum dithiophosphate having secondary alkyl group from 5-8 carbon atoms and zinc dialkyldithiophosphate having primary alkyl group from 3-8 carbon atoms was excellent in the prevention of abrasion in the internal combustion engines.

Sarin (1993), [9] has shown that O,O-dialkylphosphorodithioic disulfides have good antiwear, extreme pressure and antioxidant performance. These additives were studied in a 150 N mineral base oil for testing antiwear and extreme-pressure properties by used a four-ball machine and tested anti-oxidation performance by using differential scanning calorimetry. It was concluded that these additives showed good antiwear, antioxidant and EP properties.

Kadkhodayan (1995), [10] suggested a process for the production of overbased metal salt of hydrocarbyl dialkyldithiophosphoric acid having a base metal to phosphorus ratio within the range of about 1.15:1 to about 1.3:1. Zinc oxides were preferred with high surface area (greater than about 3 m^2 per gram), preferably from about 5 to about 10 m^2 per

gram. Then, hydrocarbyl dialkyldithiophosphoric acid was treated with an amount of phosphorus sulfide at temperature 50-200°C.

Wallfahrer (1997), [11] reported that a significant reduction of the ZDDP level is possible in the presence of polymer esters (a special class of synthetic esters) without negatively affecting the antiwear performance of the engine oil. Due to the environmental awareness and legislation, ever-greater demands have been made on the emission of motor vehicles. The use of exhaust port catalysts is almost inevitable. However, there are concerns that lubricant derived phosphorus compounds over the long term could be detrimental to those catalysts which could it make necessary to reduce the ZDDP content in the lubricating oil.

Delfort (1998), [12] showed colloidal calcium carbonate conventionally used as a detergent in lubricants, i.e., overbased calcium sulfonate, functionalized by the product of the reaction of calcium hydroxide and tetraphosphorus decasulfide with isopropanol to yield an organic calcium dialkyldithiophosphate. These species are respectively comicelized with the initial calcium carbonate colloidal core. The colloidal nature of these products was confirmed and it was evaluated in a four-ball test and compared to the original nonfunctionalized colloidal additive. The modified product exhibited improvement in extreme-pressure performances, while its antiwear property compared to those of the original overbased substrate remains at least at the same level.

Rakchitt (1997), [13] reported that metal dithiophosphate was prepared by a two step reaction. First, dialkyl phosphorodithioic acid (DPDA) was prepared by reacting P_2S_5 with alcohol; n-butanol,2-ethyl hexanol, n-octanol and isoamyl alcohol. Next, DPDA reacted with metal oxides; ZnO, CuO, CaO, MgO, MoO_3 and SnO_2 to form metal

dithiophosphates. Products were then characterized by FT-IR, ^{13}C-NMR, EA, and XRF. Finally, the lubricant antioxidant property of the products was studied by TGA. The optimum condition for synthesize DPDA was found to be 80°C for 3 hours and the molar ratio between P_2S_5 and alcohol was 1.2:4. The appropriate metal oxide for the synthesis of metal dithiophosphate, in this study, was ZnO and CuO.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 *Isoamyl alcohol ($C_5H_{11}OH$)*

Isoamyl alcohol was obtained from distilled alcoholic refinery by product

3.1.2 *Phosphorus pentasulfide (P_2S_5)*

Analytical grade; Merck

3.1.3 *Zinc chloride ($ZnCl_2$)*

Analytical grade; Carlo Erba

3.1.4 *Copper chloride dihydrate ($CuCl_2.2H_2O$)*

Analytical grade; Carlo Erba

3.1.5 *Stannous chloride dihydrate ($SnCl_2.2H_2O$)*

Analytical grade; Merck

3.1.6 *Barium chloride dihydrate ($BaCl_2.2H_2O$)*

Analytical grade; Riedel-de haen

3.1.7 *Magnesium sulfate heptahydrate ($MgSO_4.7H_2O$)*

Analytical grade; Fluka

3.1.8 *Potassium hydroxide (KOH)*

Reagent grade; Merck

3.1.9 *Toluene*

Reagent grade; Carlo Erba

3.1.10 *Potassium hydrogen phthalate*

Analytical grade; AJAX CHEMICALS

3.1.11 *Sodium sulfate anhydrous*

Reagent grade; Scharlak Chemie S.A.

3.1.12 *Phenolphthalein*

3.2   Instruments and apparatus

3.2.1   Apparatus for synthesis DPDA

A three-necked round-bottomed flask, gas inlet, gas scrubber, condenser and dropping funnel were used to synthesize DPDA. A Buchner funnel and a suction flask were used for separation of unreact initiator from DPDA.

3.2.2   Apparatus for synthesis potassium diisoamylkdithiophosphate salt

A round-bottomed flask and a 50-ml burette were used for titration of DPDA with solution of potassium hydroxide.

The 500-ml conical separatory funnels were used for separation and extraction of potassium diisoamyldithiophosphate salt from solvent mixture in the second step.

3.2.3   Apparatus for synthesis MDDP

A two-necked round-bottomed flask, dropping funnel and condenser were used to synthesize MDDP. And the 500-ml conical separatory funnels were used for extraction of MDDP from solvent mixture.

3.2.4   Fourier Transform Infrared Spectrometer (FT-IR Spectrometer)

The FT-IR model 1760x from Perkin Elmer was used.

3.2.5   Nuclear Magnetic Resonance Spectrometer (NMR Spectrometer)

The NMR model AC-F200 from Bruker at 50 MHz for ^{13}C spectra and ^{1}H spectra was used.

3.2.6   Inductively Coupled Plasma Spectroscopy (ICPS)

The ICPS model Optima-3000 from Perkin Elmer was used.

3.2.7   X-ray Fluorescence

The x-ray fluorescence model ED-2000 from Oxford was used.
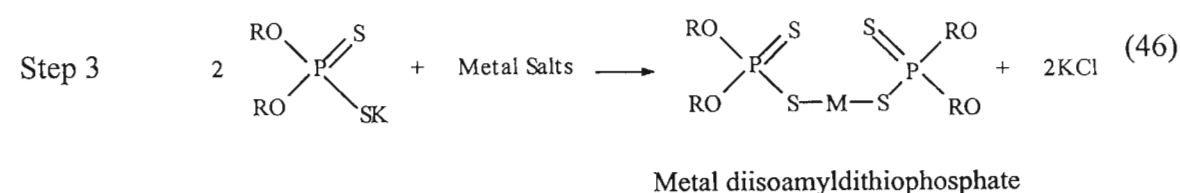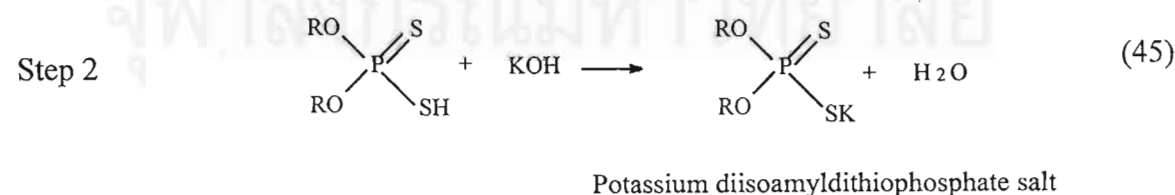
3.2.8   CHNS/O analyzer

The elemental analyzer model PE 2400 Series II from Perkin Elmer was used.

3.2.9   Thermogravimetric analyzer (TGA)

The TGA model TGA7 from Perkin Elmer was used.

3.3 Procedure

The synthesis of MDDP was prepared by a 3-steps method. First, isoamyl alcohol was reacted with phosphorus pentasulphide to form DPDA. Next, DPDA from the first step was titrated with a solution of potassium hydroxide to form potassium diisoamyldithiophosphate salt. The last step was the addition of metal salt into the solution of potassium diisoamyldithiophosphate salt to form MDDP. All steps are shown in chemical equations (44-46).

Step 1

$$4\ ROH\ +\ P_2S_5\ \longrightarrow\ 2\ \begin{array}{c} RO \\ \diagdown \\ RO \end{array} P \begin{array}{c} \diagup S \\ \diagdown SH \end{array} +\ H_2S \qquad (44)$$

Diisoamyldithiophosphoric acid

Step 2

$$\begin{array}{c} RO \\ \diagdown \\ RO \end{array} P \begin{array}{c} \diagup S \\ \diagdown SH \end{array} +\ KOH\ \longrightarrow\ \begin{array}{c} RO \\ \diagdown \\ RO \end{array} P \begin{array}{c} \diagup S \\ \diagdown SK \end{array} +\ H_2O \qquad (45)$$

Potassium diisoamyldithiophosphate salt

Step 3

$$2\ \begin{array}{c} RO \\ \diagdown \\ RO \end{array} P \begin{array}{c} \diagup S \\ \diagdown SK \end{array} +\ Metal\ Salts\ \longrightarrow\ \begin{array}{c} RO \\ \diagdown \\ RO \end{array} P \begin{array}{c} \diagup S \\ \diagdown S-M-S \end{array} P \begin{array}{c} S \diagdown \\ \diagup \\ RO \end{array} +\ 2KCl \qquad (46)$$

Metal diisoamyldithiophosphate

3.3.1 The synthesis of DPDA

In a 250-ml 3-necked round-bottomed flask, fitted with a condenser, a dropping funnel and a nitrogen gas inlet, phosphorus pentasulfide (0.03 mole, 6.67 g) and 100 ml of toluene, a magnetic bar were placed. The flask was then placed in a silicone bath. Nitrogen gas was flushed through the flask while the mixture was magnetically stirred and continually heated. A solution of isoamyl alcohol (0.1 mole, 10.86 ml in 50 ml of toluene) was added from a dropping funnel. The rate of dropping was 30 droplets per minute. Therefore, the total addition of isoamyl alcohol was completed in 1 hour. The temperature of the reaction mixture rose to 110°C following the boiling point of toluene and it was maintained for 3 hours. The evolution of hydrogen sulfide was trapped by a caustic scrubber, which was set on the top of a condenser. The reaction was then allowed to cool to ambient temperature under a nitrogen blanket and the solution was filtered to eliminate the unreacted P_2S_5. Furthermore, the solution of diisoamyldithiophosphoric acid in toluene was titrated with a solution of potassium hydroxide according to the procedure in step 2.

3.3.2 The synthesis of potassium diisoamyldithiophosphate salt

4 Molar of potassium hydroxide solution (0.2 mole, 11.22 g. in 50 ml of deionized water) was prepared in a 50-ml burette for titration. Its definite concentration was obtained by titration with a primary standard solution of 0.1 M KHP (5.11 g, 0.025 mole) in 250 ml of water. Phenolphthalein was used as an indicator.

10 ml of DPDA from step 1 was pipetted into a 25 ml-Erlenmeyer flask. 0.5 ml of the indicator solution was then added. The mixture was cooled in the ice bath and titrated immediately with KOH solution. The definite end point was considered when the color changed. The quantity of KOH solution required to reach the end point was

recorded. At the end point, potassium diisoamyldithiophosphate salt occurred in the aqueous phase. The yield of DPDA and potassium diisoamyldithiophosphate salt can be calculated as described in Appendix B1.

The volume of KOH solution was calculated by adding the solution to the remaining DPDA. KOH solution was gradually added to the cooled DPDA drop by drop. The mixture was vigorously stirred until the red color of phenolphthalein persisted in the product as long as 30 seconds.

The obtained product was transferred into a separatory funnel. After shaking the organic and aqueous phases were allowed to separate. The lower layer was drained off and kept; whereas the upper layer was washed with 20 ml cooled deionized water and was separated again in the same separatory funnel.

The solution of potassium diisoamyldithiophosphate salt in aqueous phase was further reacted with metal salts according to the procedure in step 3.

3.3.3 The synthesis of metal diisoamyldithiophosphate (MDDP)

A solution of potassium diisoamyldithiophosphate salt and a magnetic bar were placed in a two-necked round-bottomed flask, fitted with a condenser, and dropping funnel in a silicone bath. A solution of metal salts (0.033 mole) in 20 ml of deionized water was added dropwise over 30 minutes and the solution of potassium diisoamyldithiophosphate salt was stirred at room temperature. 50 ml of Toluene was added into the mixture and the mixture was heated under reflux with stirring for various reaction times.

The solution of MDDP was transferred to a separatory funnel. After shaking, the organic and aqueous phases were allowed to separate. The aqueous layer was drained off and extracted with 50 ml organic solvent. Whereas, the organic layer was washed 2 times with 30 ml saturated NaCl. The solution of MDDP in organic solvent

was then transferred into a round bottom flask and stripped off solvent using a Buchi rotavap at approximately 70°C under vacuum to yield a sediment.

In this step, the metal salts (0.033 mole) were zinc chloride (4.50 g), copper chloride dihydrate (5.63 g), barium chloride dihydrate (8.06 g), magnesium sulfate heptahydrate (8.14 g) and stannous chloride dihydrate (7.44 g).

All types of synthesized MDDPs were varied during the reaction time in order to obtain the highest yield of product by ICPS technique. The yields were compared to %Wt of metal in the composition. The product which was used the suitable reaction time was later characterized for determination of the functional group, structure, composition, total acid/base number and oxidation stability.

3.4 Characterization

The products were characterized by various techniques as shown below.

3.4.1 Determination of the functional group

The functional group of the MDDP was determined by FT-IR Spectrometer. The sample was prepared by casting on KBr cell.

3.4.2 Determination of structure

^{13}C-NMR and ^{1}H-NMR analyzed the structure of MDDP. The sample was dissolved by deuterochloroform (CDCl$_3$)

3.4.3 Composition of product

The compositions of product were characterized by ICPS, EA and XRF.

3.4.3.1 The ICPS was used to measure the amount of metal and phosphorus in the sample by comparing the sample with the standard solution. The

solution of product (100 ml) in toluene was pipetted as 0.05-0.1 ml (24-70 PPM) into 25 ml-volumetric flask and diluted with white spirit.

3.4.3.2 X-ray fluorescence was used to measure the amount of sulphur in the sample. The sample was prepared by pipetting 0.1 ml of the product solution (100 ml) in toluene and diluted with white spirit in 10 ml-volumetric flask.

3.4.3.3 The elemental analyzer was used to obtain the ratio of C/H/S in the sample. A small quantity of accurate weight of the sample was used for this investigation.

3.4.4 Total acid number (TAN) and total base number (TBN) of product

3.4.4.1 Total acid number (TAN) by ASTM D974

In a 250 ml-Erlenmeyer flask, nearly 0.1 g of the weight quantity of the sample was introduced. 100ml of the titration solvent and 0.5 ml of an indicator solution were added. Without stoppering, the mixture was swirled until the sample was entirely dissolved in the solvent. The mixture was titrated immediately at temperature below 30°C. 0.1 M KOH solution was added and the end point was considered to be definite when the color changed. A blank titration on 100 ml of titration solvent and 0.5 ml of the indicator solution, along with 0.1 M KOH solution was carried out and the quantity of KOH solution required to reach the end point was recorded. The calculation is described in Appendix B2.

3.4.4.2 Total Base number (TBN) by ASTM D2896

Approximately 0.3 g. of sample was measured and transferred into the titration beaker. 60 ml of titration solvent (10.2 ml of 60% $HClO_4$ solution with 500 ml

of gracial and 35 ml of acetic anhydride, then dilute to 1 L with glacial acetic acid.) was added to the sample.

The sample was placed on the titration stand and stirred until the sample dissolved. The electrodes were then immersed as deep as possible in the solution. The burette was filled with 0.1 N $HClO_4$ solution and was placed in position in the titration assembly. The initial burette and meter (cell potential) readings were recorded. Automatic Recording Titration-Adjustment for the instrument was made in accordance with the manufacture's instructions and the titration speed was set at 1.0 ml/min maximum.

In completion of the titration, the beaker was removed and the electrodes and burette tip were rinsed with titration solvent, then with water, then again with the titration solvent. The electrodes were stored in water when not in use. For each set of samples a blank was made by using 60 ml of titration solvent.

The interpretation of the end point from the graph was obtained from automatic titration. The end point was the midpoint of the inflection, a point at which the curve changed from concave to convex. A useful, but not mandatory, guide was that the end point was preceded and followed by a deflection of a least 50 mV/0.1 ml of titrant. The calculation of TBN is described in Appendix B3.

3.4.5 Determination of oxidation stability of metal diisoamyl dithiophosphates

The oxidation stability was measured by using the thermogravimatric analyzer of Perkin Elmer TGA 7. Data were recorded at heating rate of 20°C/min. The temperature ranged from 50°C to 800°C with an oxygen flow rate of 100 ml/min. The sample was prepared, weighed 1.0% by weight of MDDP, and mixed with 150 SN mineral base oil.
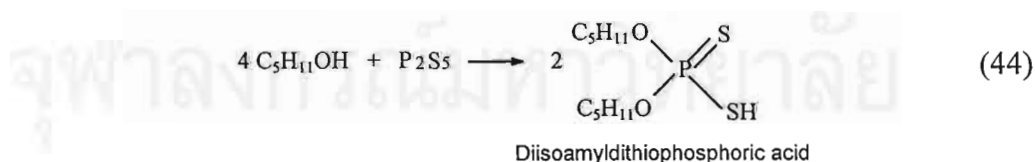
CHAPTER IV

RESULTS AND DISCUSSION

In this study, metal diisoamyldithiophosphates (MDDPs) were investigated by varying the groups of metals and later blending the MDDPs with lubricating base oil for testing their oxidation properties.

The results from each synthesized step were characterized by FT-IR and NMR; likewise, the synthesized MDDPs were characterized by EA, XRF and ICPS. The interpretation of results from these techniques can identify the functional group, structure and composition of MDDPs.

Furthermore, these synthesized products were mixed with lubricating based oil for the oxidation property testing by TGA technique. With good oxidation stability, various MDDPs can be used in commercial lubricating oil.

4.1 Synthesis of diisoamyldithiophosphoric acid

Diisoamyldithiophosphoric acid (DPDA) was obtained by reacting isoamyl alcohol with P_2S_5 at the optimum condition following previous works [9], [13]. The molar ratio of isoamyl alcohol and P_2S_5 was 4: 1.2. The temperature ranged from 60 – 110 °C and the reaction time was set at 4 hours. The reaction is illustrated as follows:

$$4\ C_5H_{11}OH\ +\ P_2S_5\ \longrightarrow\ 2\ \begin{matrix} C_5H_{11}O \\ \\ C_5H_{11}O \end{matrix} \!\! P \!\! \begin{matrix} S \\ \\ SH \end{matrix} \qquad (44)$$

Diisoamyldithiophosphoric acid

The synthesized DPDA appeared as a clear light yellow solution in toluene. Its average yield was approximately 90% obtained by titration with potassium hydroxide solution as described in Appendix B1.

Product characterization

The synthesized DPDA was characterized by FT-IR and NMR as presented in Table 4.1 and Appendices A1, A8, A15.

The FT-IR spectrum shows the essential functional group of S-H stretching at 2460 cm^{-1}. Likewise, the important functional group of C-O-P stretching and P-S stretching are shown at 982 cm^{-1} and 665 cm^{-1}, respectively. Also, the FT-IR spectrum represents the functional group of C-H stretching and C-H bending at 2958 cm^{-1} and 1466, 1387 cm^{-1}, respectively. The spectrum is shown in Appendix A1.
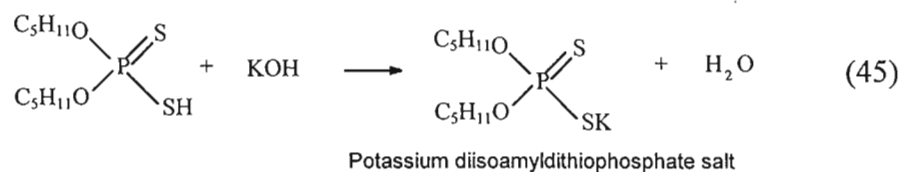
The ^{13}C-NMR indicates important chemical shifts of the CH$_2$-O-P group at 66.48 ppm that is in a higher position than the CH$_2$-OH group from Sadtler standard [16]. This result also showed good agreement with FT-IR spectrum above; that is no initial isoamyl alcohol remained and it was completely changed to DPDA. Furthermore, the chemical shifts of base group from isoamyl alcohol in DPDA were found at lower positions such as H$_3$C-C (C primary) at 22.17 ppm, CH-C (C tertiary) at 24.33 ppm and -CH$_2$-C (C secondary) at 38.43 ppm. These ^{13}C-NMR spectra are presented in Appendix A8.

The ^{1}H-NMR shows chemical shifts of 6H (2xCH$_3$) at 0.92 ppm, 3H (CH$_2$, CH) at 1.22-1.77 ppm and 2H (CH$_2$) at 3.96-4.22 ppm are shown in Appendix A15. It should be noted that there was no appearance of SH spectrum. This was probably due to the fact that the proton of SH group shows special characteristics and it may be removed by deuteriation or affected by solvent, temperature and concentration.

4.2   Synthesis of potassium diisoamyldithiophosphate salt

Potassium diisoamyldithiophosphate salt (KDPS) was obtained by reaction of DPDA with potassium hydroxide solution (KOH). Total volume of KOH used in the

reaction as used to calculate the yield of KDPS as described in Appendix B1.The reaction is shown in equation (45)

$$\underset{C_5H_{11}O}{\overset{C_5H_{11}O}{>}}P\underset{SH}{\overset{S}{<}} + KOH \longrightarrow \underset{C_5H_{11}O}{\overset{C_5H_{11}O}{>}}P\underset{SK}{\overset{S}{<}} + H_2O \qquad (45)$$

Potassium diisoamyldithiophosphate salt

The appearance of synthesized KDPS in the aqueous solution was a white cloudy solution. After evaporation for characteristic test, the product was a white solid, but it was not stable at room temperature. This is due to its property is similar to salt; that is it is easy to absorb moisture. As a result, vacuum storage is suitable for the product. However, since water was used as a solvent in the next step, this synthetic pathway was not necessary for evaporation.

Product characterization

The synthesized KDPS were characterized by FT-IR, NMR as presented in Table 4.1 and Appendices A2, A9, A16.

Table 4.1: Characterization of DPDA and KDPS

|	IR (neat) (cm^{-1})	^{13}C-NMR (δ PPM)	^{1}H-NMR (δ PPM)
DPDA	2958(a),2460(b), 1466, 1387(c), 982(d), 665(e)	22.17 (H$_3$C-C) 24.33 (-CH-C) 38.43 (-CH$_2$-C) 66.48 (CH$_2$-O-P)	0.92 (d,6H,2xCH$_3$) 1.22-1.77(m, 3H, CH$_2$,CH) 3.96-4.22 (m, 2H, CH$_2$)
KDPS	2958(a), 1466, 1387(c), 982(d), 675(e)	22.17 (H$_3$C-C) 24.33 (-CH-C) 38.43 (-CH$_2$-C) 66.48 (CH$_2$-O-P)	0.89 (d,6H,2xCH$_3$) 1.24-1.78(m, 3H, CH$_2$,CH) 3.74-4.05 (m, 2H, CH$_2$)

(a) C-H St.; (b) S-H St.; (c) C-H bend.; (d) C-O-P St.; (e) P-S St.

In comparison with the IR spectrum of DPDA, the spectrum of S-H stretching at 2460 cm^{-1} disappeared. This indicated that the reaction in the second step was completed because of no remaining diisoamyldithiophophoric acid. Furthermore, the absorption band of P-S stretching shifted to a higher position of 675 cm^{-1} probably resulting from the influence of potassium bonded with P-S. Besides this, the unchanged positions of C-H stretching and C-H bending at 2960 cm^{-1} and 1468, 1393 cm^{-1} appeared, respectively. It was also C-O-P stretching at 985 cm^{-1}. The FT-IR spectrum of KDPS is shown in Appendix A2.

The ^{13}C-NMR showed the same chemical shifts of carbon group in KDPS spectrum compared with ^{13}C chemical shifts of DPDA spectrum. Likewise, the ^{1}H-NMR showed chemical shifts of each proton group that were hardly different from ^{1}H chemical shift of DPDA. The ^{13}C-NMR, ^{1}H-NMR spectra are described in Appendices A9 and A16, respectively.

4.3 Synthesis of MDDP with various metal salts

In this study, MDDP was synthesized by reaction between KDPS and metal salts. The metal salts were ZnCl$_2$, CuCl$_2$, BaCl$_2$, MgSO$_4$ and SnCl$_2$. The reaction is shown as follows:

Metal diisoamyldithiophosphate
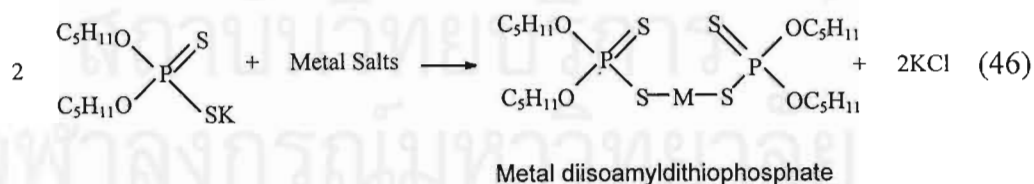
The various MDDPs appeared as sediments, which had different colors because they were influenced by the natural colors of the various metals as shown in Table 4.2.

Table 4.2: The appearance of various MDDPs

MDDP	Color of Products
ZDDP	Clear light yellow
CuDDP	Muddy pale blue porcelain
SnDDP	Muddy dark red
BaDDP	Clear light yellow
MgDDP	Clear light yellow

Product characterization

MDDPs were characterized by IR, NMR, ICPS, EA and XRF. The interpretation of results from these techniques can identify the functional group, structure and composition of products.

4.3.1 Interpretation of FT-IR spectra of MDDPs

The FT-IR spectra of various MDDPs are illustrated in the Table 4.3 and Appendices A3-A7.

Table 4.3 : The IR spectra of various MDDPs

Product	IR Data (cm^{-1})
ZDDP	2954(a), 1466, 1387(b), 980(c), 663(d)
CuDDP	2954(a), 1466, 1387(b), 987(c), 648(d)
BaDDP	2954(a), 1466, 1387(b), 980(c), 663(d)
MgDDP	2954(a), 1466, 1387(b), 987 (c), 663(d)
SnDDP	2954(a), 1466, 1387(b), 987(c), 648(d)

(a) C-H St.; (b) C-H bend.; (c) C-O-P St.; (d) P-S St.

C-H Vibrations

The observation of carbon-hydrogen stretching and bending vibration of all various MDDPs spectra appeared at the same positions. These are the same frequencies appeared in the IR spectrum of KDPS.

C-O-P Vibrations

Small change in the C-O-P vibration frequencies takes place in all MDDPs spectra when compared with DPDA and KDPS spectra. The lower frequencies of ZDDP and BaDDP spectra appeared at 980 cm^{-1}. Whereas, CuDDP, MgDDP and SnDDP spectra showed little change of higher C-O-P frequencies at 987 cm^{-1}.

P-S Vibrations

Not only the P-S stretching frequencies of ZDDP, BaDDP and MgDDP spectra were found at the same position of 663 cm^{-1}, but there were also the same P-S stretching frequencies of CuDDP and SnDDP at 648 cm^{-1}.

4.3.2 Interpretation of NMR spectra of MDDPs

^{13}C-NMR and ^{1}H-NMR spectra of various MDDPs are presented in the Table 4.4, Table 4.5 and Appendices A10-A14, A17-A21.

Table 4.4: The ^{13}C chemical shifts of various MDDPs spectra

The group of carbon	The ^{13}C chemical shifts of various MDDPs (δ ppm)				
	ZDDP	CuDDP	BaDDP	MgDDP	SnDDP
(H$_3$C-C)	22.11	22.15	22.15	22.15	22.15
(-CH-C)	24.27	24.18	24.20	24.29	24.29
(-CH$_2$-C)	38.36	38.39	38.37	38.49	38.51
(CH$_2$-O-P)	65.77	66.77	65.68	65.57	65.68

Table 4.5: The proton chemical shifts in various MDDPs spectra

The group of proton	The proton chemical shifts of various MDDPs (δ ppm)				
	ZDDP	CuDDP	BaDDP	MgDDP	SnDDP
($2 \times CH_3$, 6H, d)	0.92	0.91	0.93	0.92	0.92
(CH_2,CH, 3H,m)	1.54-1.78	1.55-1.78	1.54-1.79	1.54-1.78	1.54-1.78
(CH_2, 2H, m)	4.04-4.20	4.04-4.20	4.05-4.24	4.04-4.20	4.05-4.24

The results of ^{13}C-NMR, ^{1}H-NMR spectra of various MDDPs showed the signals at the same positions, so the characterization of MDDPs by NMR technique was unable to differentiate each MDDP.

4.3.3 Composition of products

Since the MDDP synthesized in this study was sediment that may contain small amounts of solvent, the exact weight was unobtainable for calculating the yield. In this report, the yield was calculated by comparing the obtained % weight of metal with the theoretical % weight of metal. The technique being employed to obtain the % weight was ICPS. This technique, furthermore, can be used to obtain the % weight of phosphorus in synthesized MDDPs. The other equipment for evaluating the composition of product was XRF, which can provide the % weight of sulphur. The % weight of each element obtained from these analytical techniques was finally concluded and led to the confirmation of the chemical formula of the synthesized MDDP.

In this study, MDDP, from various metals, was synthesized with a variation of reaction time in order to obtain the shortest reaction time for MDDP. The ratio of metal / P / S of synthesized product obtained from the analysis above was compared to the theoretical metal / P / S ratio. The reaction time of each product providing the same molar ratio as the theory was the proper reaction time for that metal as shown in Table 4.6 and Figures 4.1-4.5.

Table 4.6 Comparison of molar ratio of metal/P/S in various MDDPs molecule

with various reaction time

	Molar ratio of metal/P/S in molecule with various reaction times				
	2 hours	4 hours	6 hours	8 hours	24 hours
ZDDP	1 / 2 / 2	1 / 2 / 4	1 / 2 / 4	1 / 2 / 4	1 / 2 / 4
CuDDP	2 / 2 / 4	2 / 3 / 6	2 / 3 / 6	2 / 3 / 6	2 / 3 / 6
BaDDP	1 / 8 / 17	1 / 8 / 17	1 / 7 / 17	1 / 4 / 7	1 / 4 / 8
MgDDP	1 / 4 / 4	1 / 4 / 6	1 / 3 / 8	1 / 4 / 7	1 / 4 / 8
SnDDP*	0 / 2 / 2	0 / 2 / 2	0 / 2 / 3	0 / 2 / 3	0 / 2 / 3

* Sn in SnDDP was not characterized
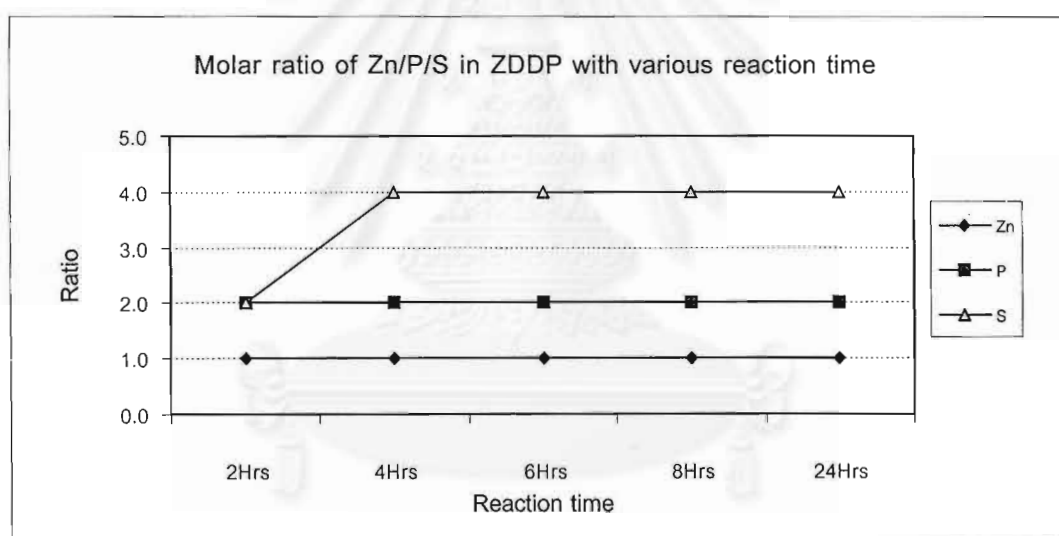
Figure 4.1 The relationship between molar ratio of Zn/P/S in ZDDP and reaction time

In Figure 4.1, the molar ratio of Zn / P / S in ZDDP was stable at 1 / 2 / 4 from 4 hours onwards. This shows a good agreement with the theoretical ratio. Thus, the proper reaction time for the synthesis of ZDDP in step 3 is 4 hours onwards. The elemental analysis of synthesized ZDDP from this reaction time was carried out. The result shows %C and %H as described in Appendix A22. The data from the

characterization of ZDDP were finally analyzed and concluded the chemical structure as follows:
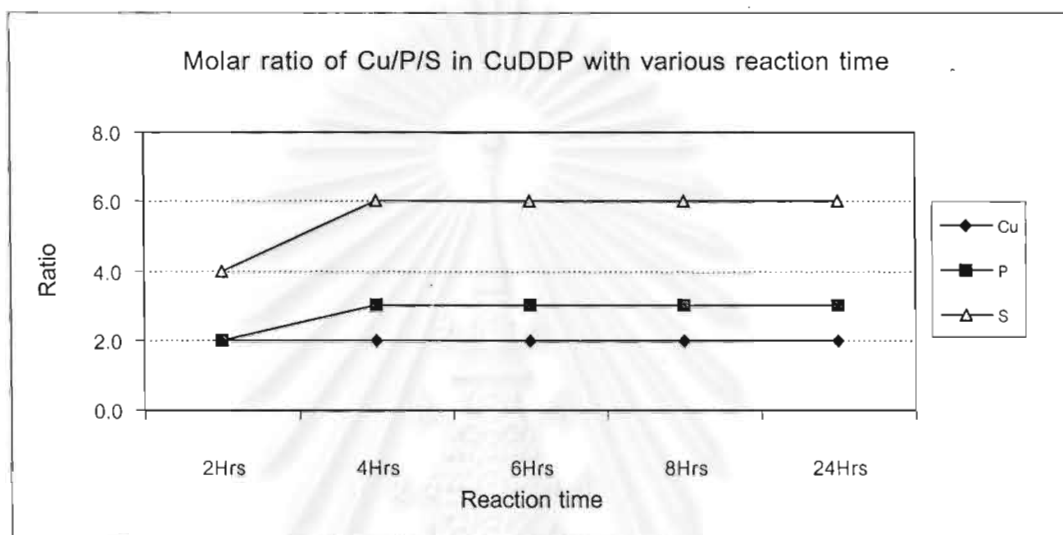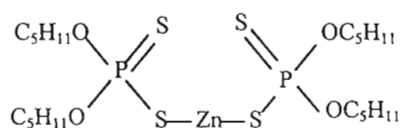
Figure 4.2 The relationship between molar ratio of Cu/P/S in CuDDP and reaction time

Figure 4.2 shows that CuDDP showed the stability of ratio of 2 / 3 / 6 from 4 hours onwards. This ratio was different from the theoretical ratio of 1 / 2 / 4. The elemental analysis showed %C and %H as described in Appendix A22. The characterization of CuDDP was finalized and resulted in the expected chemical formula as $Cu_2[(C_5H_{11}O)_2PS_2]_3OH$

This was probably due to the fact that, in this case, the synthesis of CuDDP via this new method gave the product with the above structure rather than that of the theoretical structure.
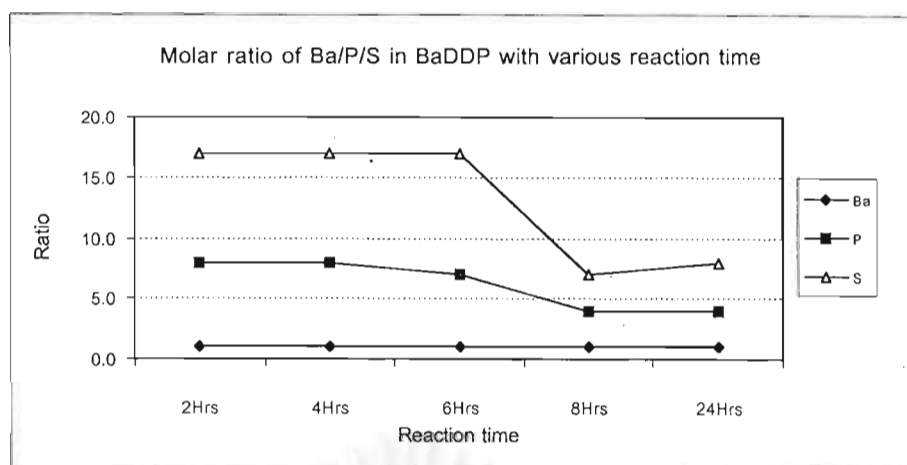
Figure 4.3 The relationship between molar ratio of Ba/P/S in BaDDP and reaction time
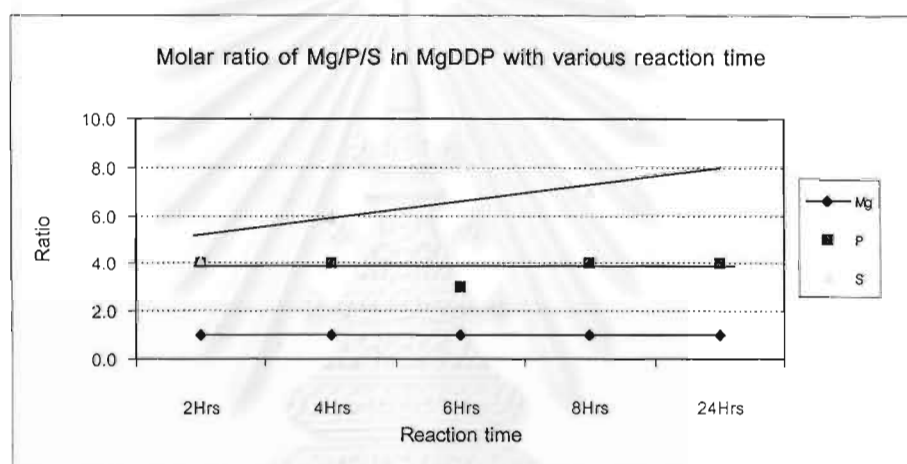
Figure 4.4 The relationship between molar ratio of Mg/P/S in MgDDP and reaction time
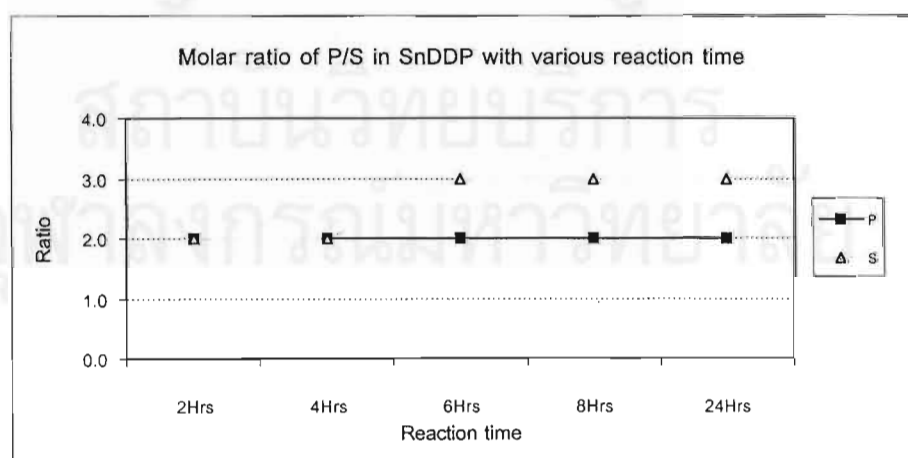
Figure 4.5 The relationship between molar ratio of P/S in SnDDP and reaction time

For BaDDP, MgDDP and SnDDP, the molar ratio, Metal / P / S, showed a fluctuation as seen in Figures 4.3-4.5. Although, the variation of reaction time was performed up to 24 hours, it was observed that the molar ratio was likely to decline. This may be described in two categories. Firstly, the expected molar ratio of these metals may be obtained at a longer reaction time that is unsuitable for this study. Secondly, the molecular size between metals may be too big or too small to form ionic bonds with potassium diisoamyldithiophosphate salt. This probably leads to the decomposition of the chemical structure all of the time in the aqueous solution.

4.4 Total acid number (TAN) and total base number (TBN)

The results are shown in Table 4.7 and Appendices B2, B3

Table 4.7: TAN and TBN in mg. KOH / g. of products

PRODUCTS	TAN (ASTM D974)	TBN (ASTM D2896)
DPDA	205.8	-
KDPS	6.51	-
ZDDP	3.4	8.29
CuDDP	2.6	15.64

The total acid number was used to indicate the completion of reaction in the second step. The decrease in TAN of KDPS showed that DPDA from the first step reacted completely with KOH. TAN of the synthesized MDDP in this study was close to the theoretical TAN, which is 0 mg of KOH/g of MDDP. The comparison between TBN of ZDDP and CuDDP showed that the TBN of ZDDP was less than that of

CuDDP. Thus, the formula of ZDDP was a neutral compound, whereas those of CuDDP was likely to form a basic compound.

4.5 Performance evaluation of products

The synthesized MDDP were evaluated for antioxidant property as described in previous works [9],[13]. Due to the polar nature of MDDP and its sediment formation having poor oil solubility, a limited amount of MDDP was used in lubricating base oil. This study selected the effective amount of MDDP at 1% to be blended with 150 SN mineral base oil. Antioxidant performance of the blends was determined by thermogravimetric analyser (TGA). The results are shown in Table 4.8, Figure 4.6 and Appendices A23-A25.

Table 4.8: Effect of 1 % ZDDP and CuDDP on oxidation point and oxidation product

Sample	Oxidation Point ($^\circ$C)	Oxidation Product (% Weight)
Pure Base Lube	357.12	1.897
Add 1 % ZDDP	387.24	0.628
Add 1 % CuDDP	386.65	0.461

The temperature at the onset of oxidation was taken as a criterion for the assessment of antioxidant performance. The antioxidant action of MDDP was primarily attributed to their ability to decompose hydroperoxides[9]. MDDP showed good antioxidant performance, as shown by an increase in the onset of oxidation point. Thus, at 1% concentration, an improvement in the onset of oxidation point for ZDDP was 30°C over the base oil, while CuDDP increased in the onset of oxidation point by 29.5°C. It may be concluded from the results that either ZDDP or CuDDP from the

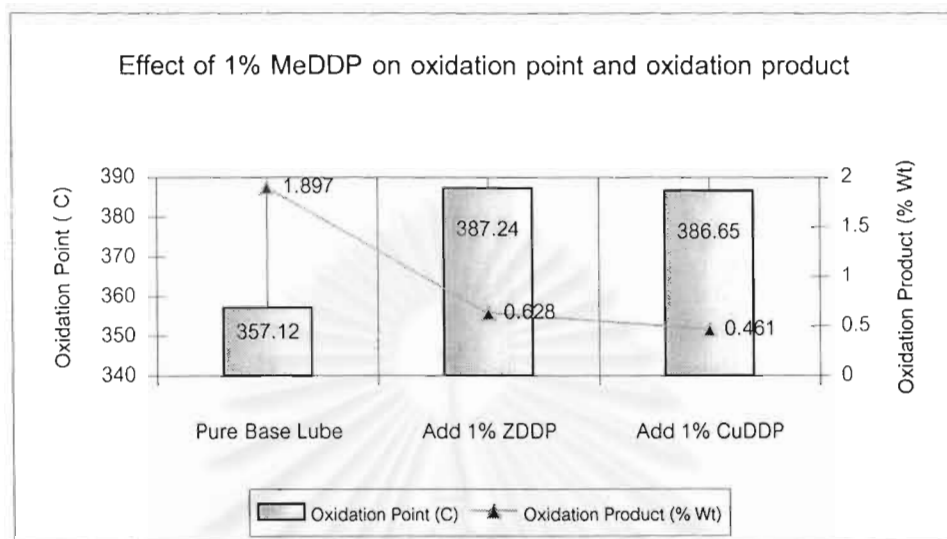new synthesized method significantly increases the antioxidant performance in lubricating oil.

Figure 4.6 Effect of 1% ZDDP and CuDDP on oxidation point and oxidation product

CHAPTER V

CONCLUSION

The new method for synthesis of metal diisoamyldithiophosphate (MDDP) was a three-step reaction. First, diisoamyldithiophosphoric acid (DPDA) was prepared by reacting P_2S_5 with isoamyl alcohol in a molar ratio of 1.2:4 at 110 °C for 4 hours. The yield of DPDA was about 90%. Next, DPDA reacted with KOH by titration to form potassium diisoamyldithiophosphate salts (KDPS). The resulting KDPS then reacted with metal salts in a molar ratio of 2:1.3 to form metal diisoamyldithiophosphate at varying reaction times. The metal salts used in this research were $ZnCl_2$, $CuCl_2$, $BaCl_2$, $MgSO_4$ and $SnCl_2$. MDDP was then characterized by FT-IR, ^{13}C-NMR, ^{1}H-NMR, XRF, ICP and EA. The composition of ZDDP was $Zn[PS_2(OR)_2]_2$: Zn,10.28, P,10.23, S,21.18, C,40.16, H,7.47, O,10.68 whereas, CuDDP was $Cu_2[PS_2(OR)_2]_3OH$: Cu,13.27, P,9.70, S,20.76, C,38.49, H,6.71, O,11.07. The suitable reaction time for the synthesis of, ZDDP and CuDDP was 4 hours, yielding 95% and 98%, respectively.

For the study of antioxidant performance, ZDDP and CuDDP obtained from the new method showed good antioxidant property. At 1% concentration of MDDP in lubricating base oil, the increase in oxidation temperature for ZDDP was 30°C and for CuDDP was 29.5°C, which are considerably higher than for those in lube base oil.

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APPENDIX
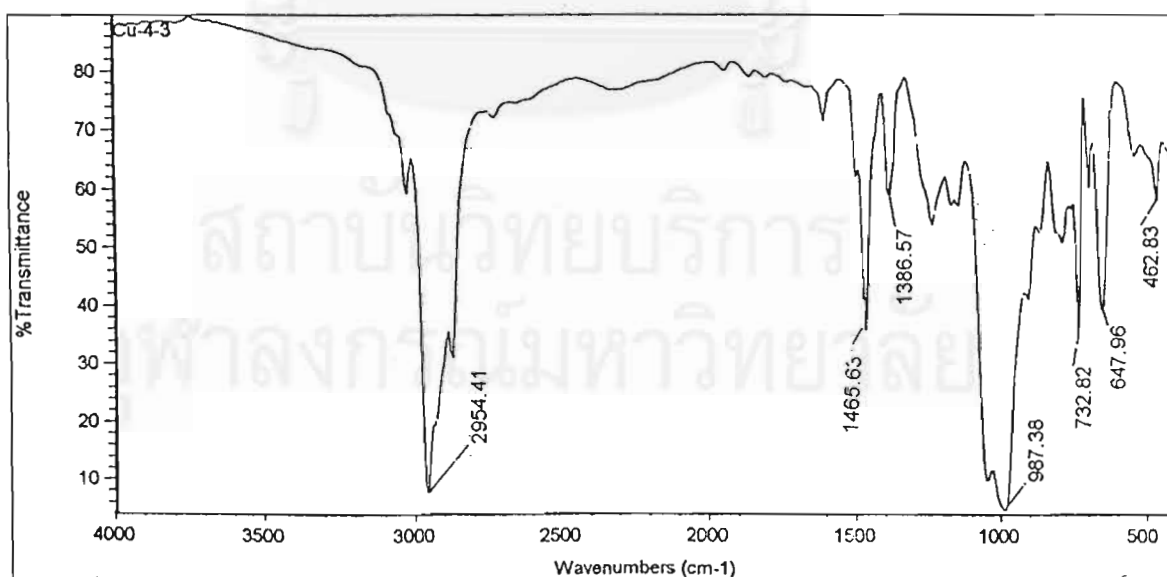
APPENDIX A1 FT-IR Spectrum of DPDA
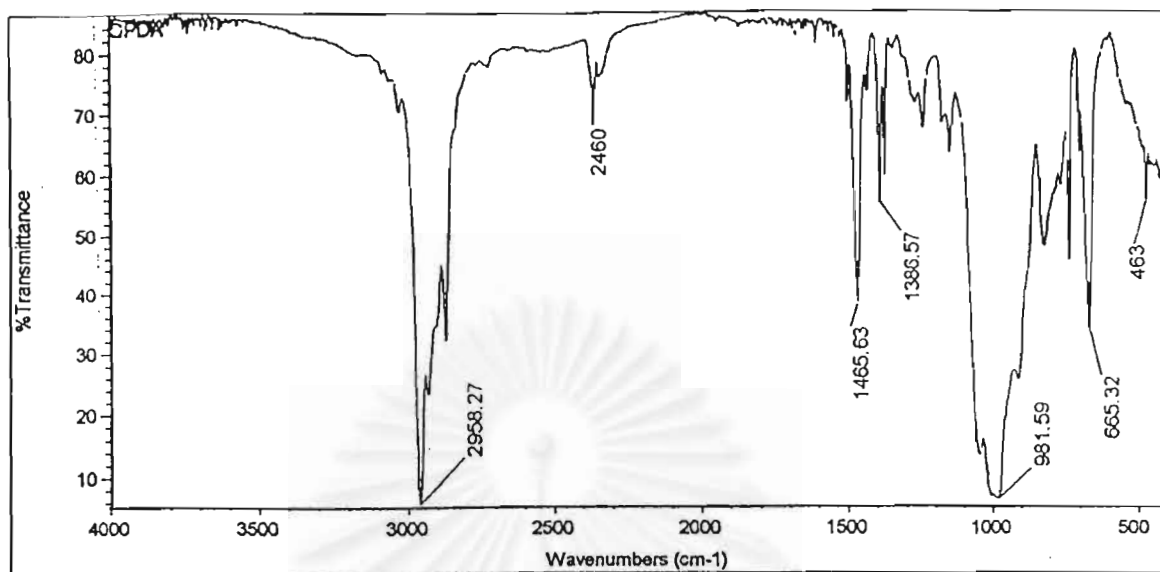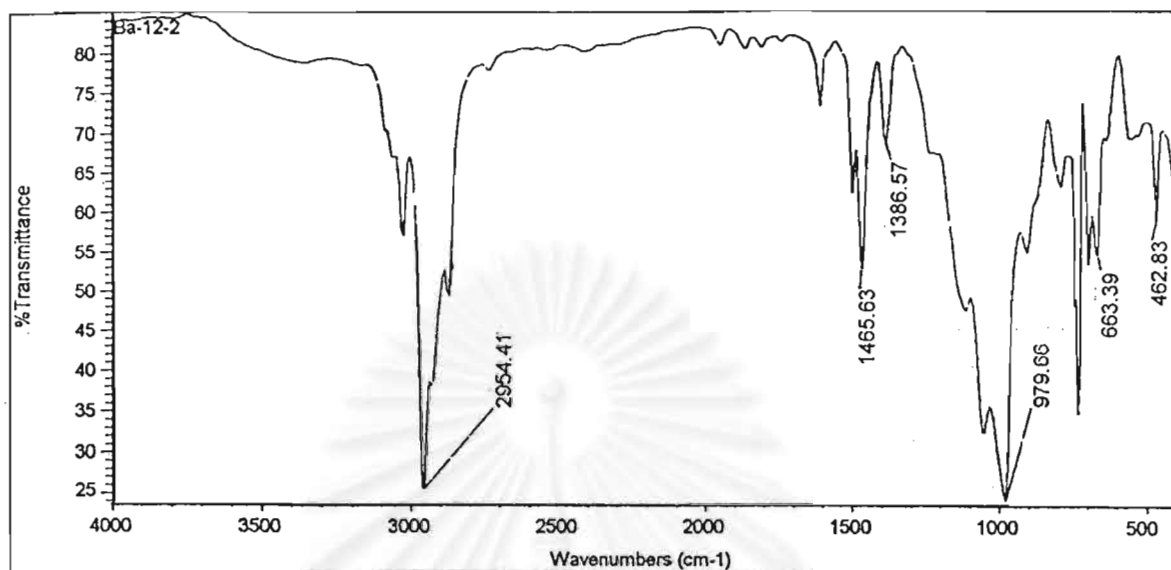

APPENDIX A2 FT-IR Spectrum of KDPS
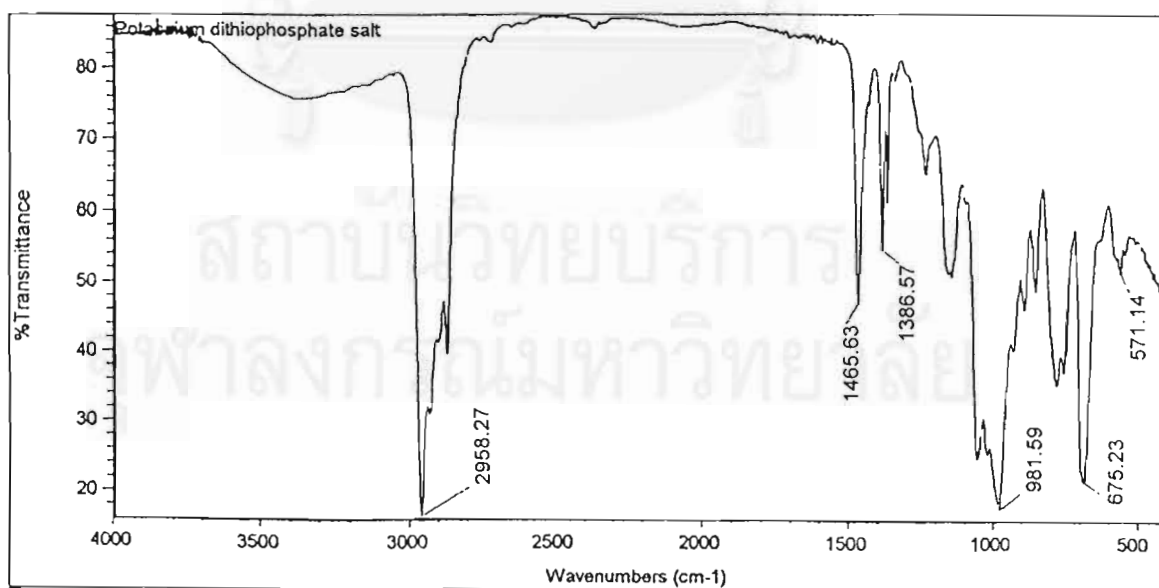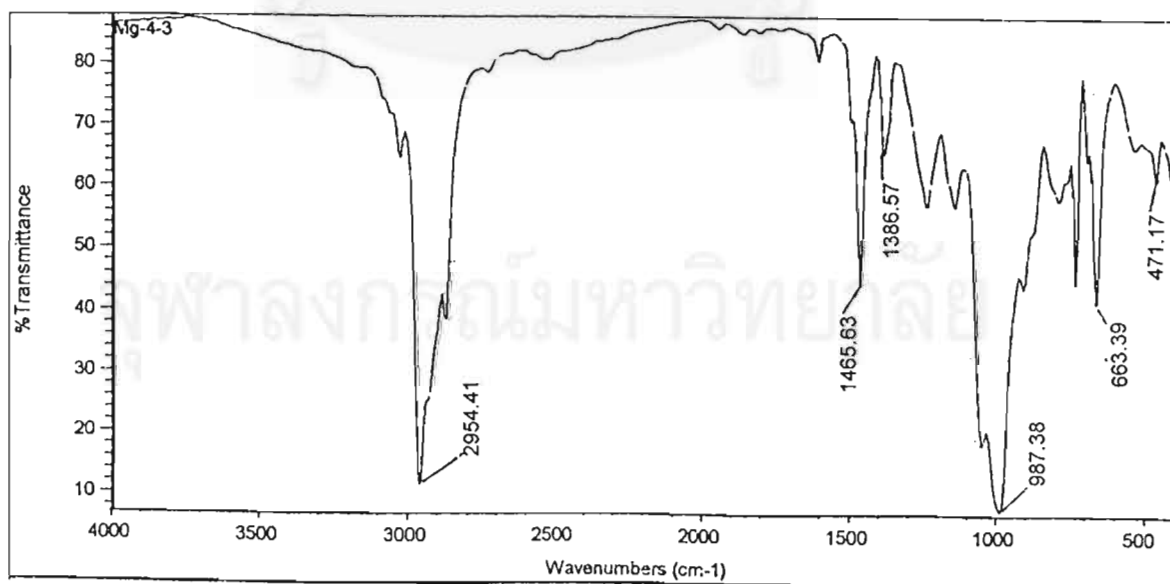
APPENDIX A3 FT-IR Spectrum of ZDDP
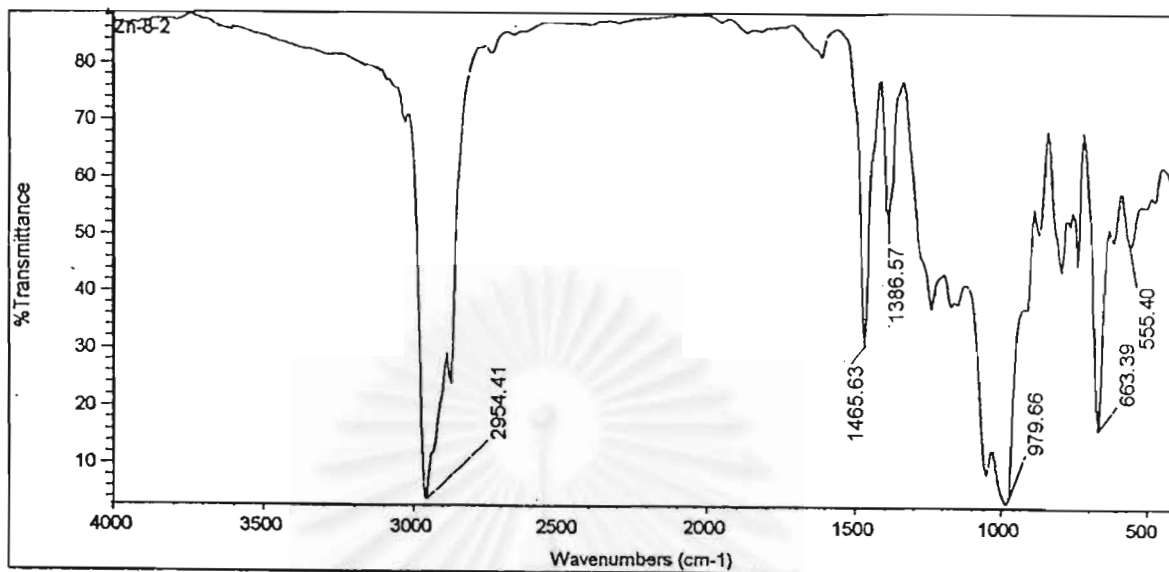
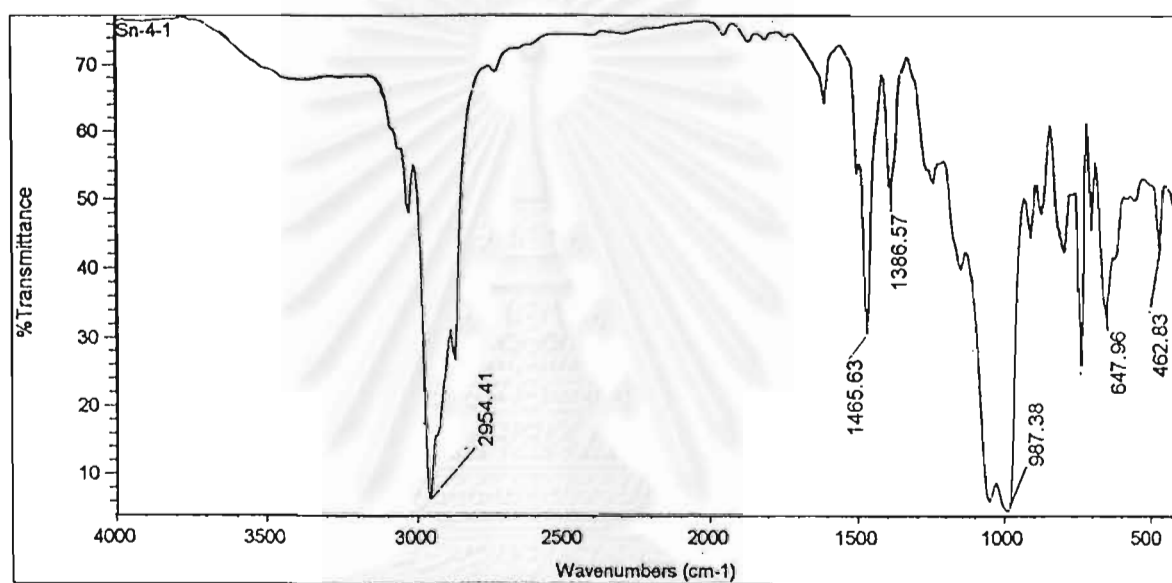**APPENDIX A4** FT-IR Spectrum of CuDDP
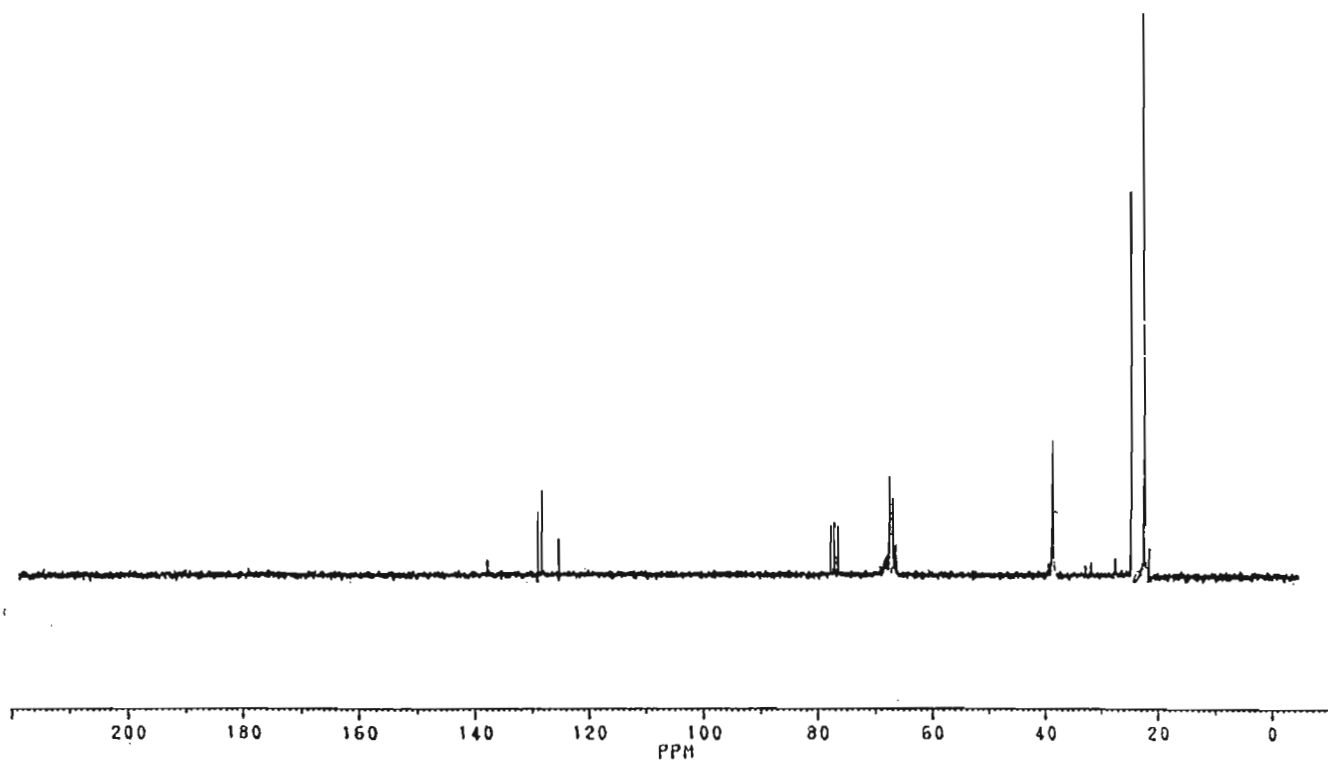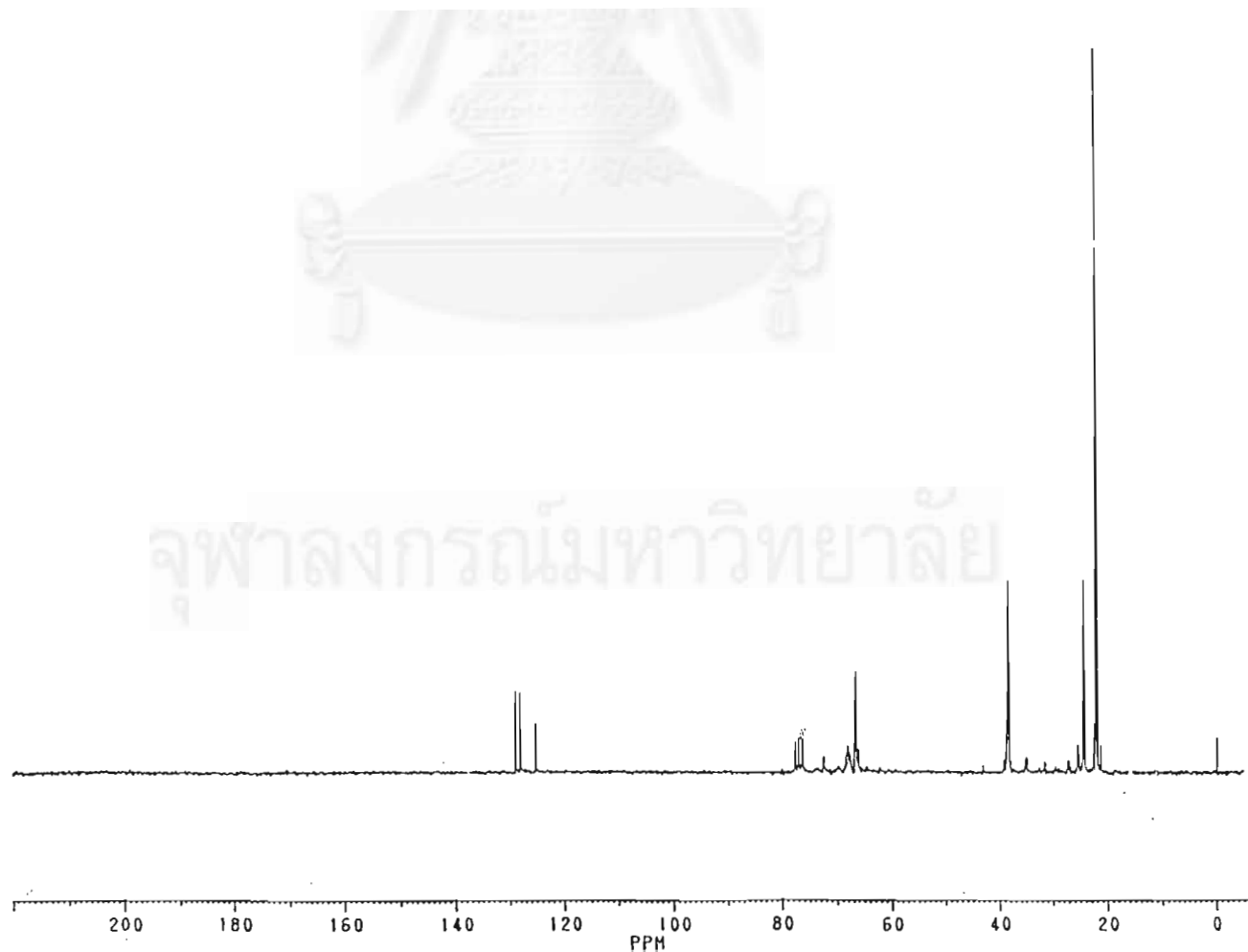
APPENDIX A5 FT-IR Spectrum of BaDDP

APPENDIX A6 FT-IR Spectrum of MgDDP

APPENDIX A7   FT-IR Spectrum of SnDDP

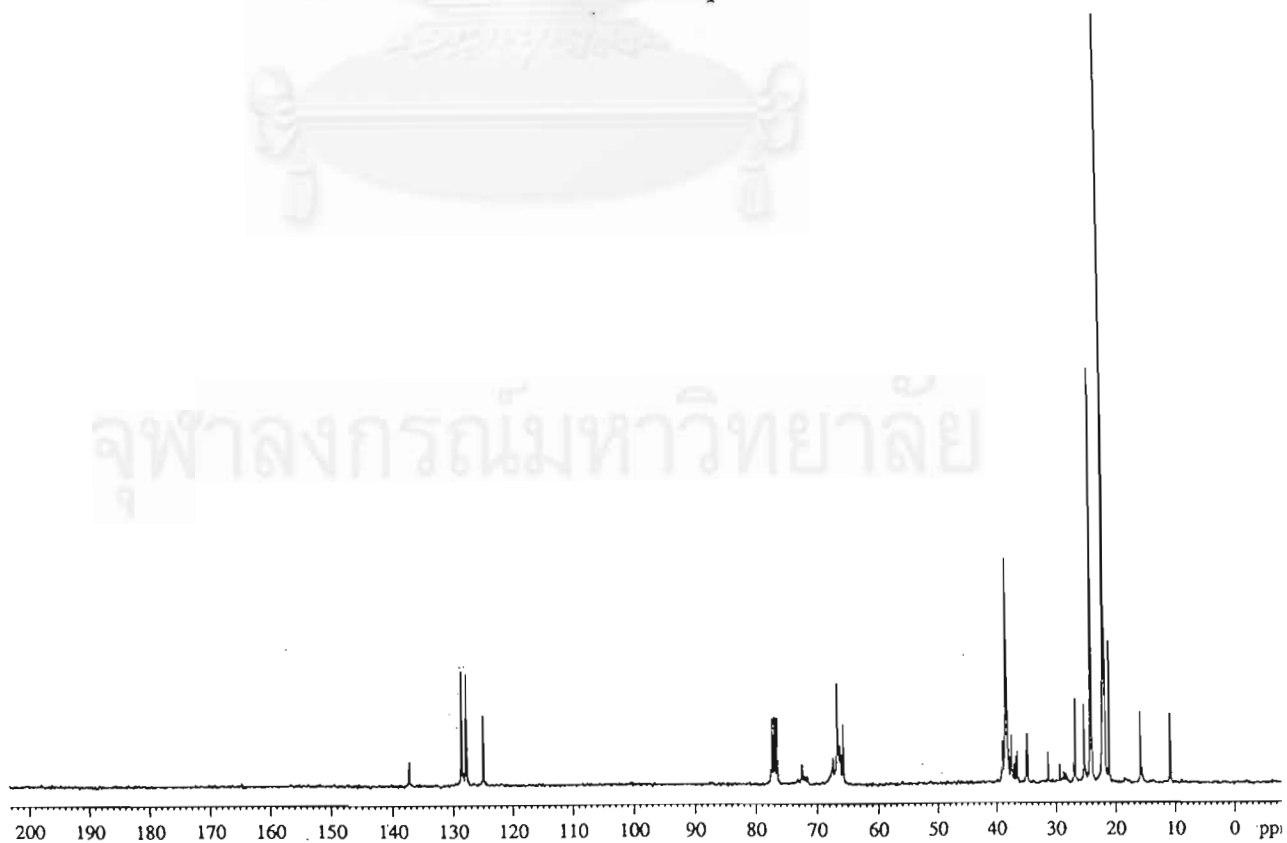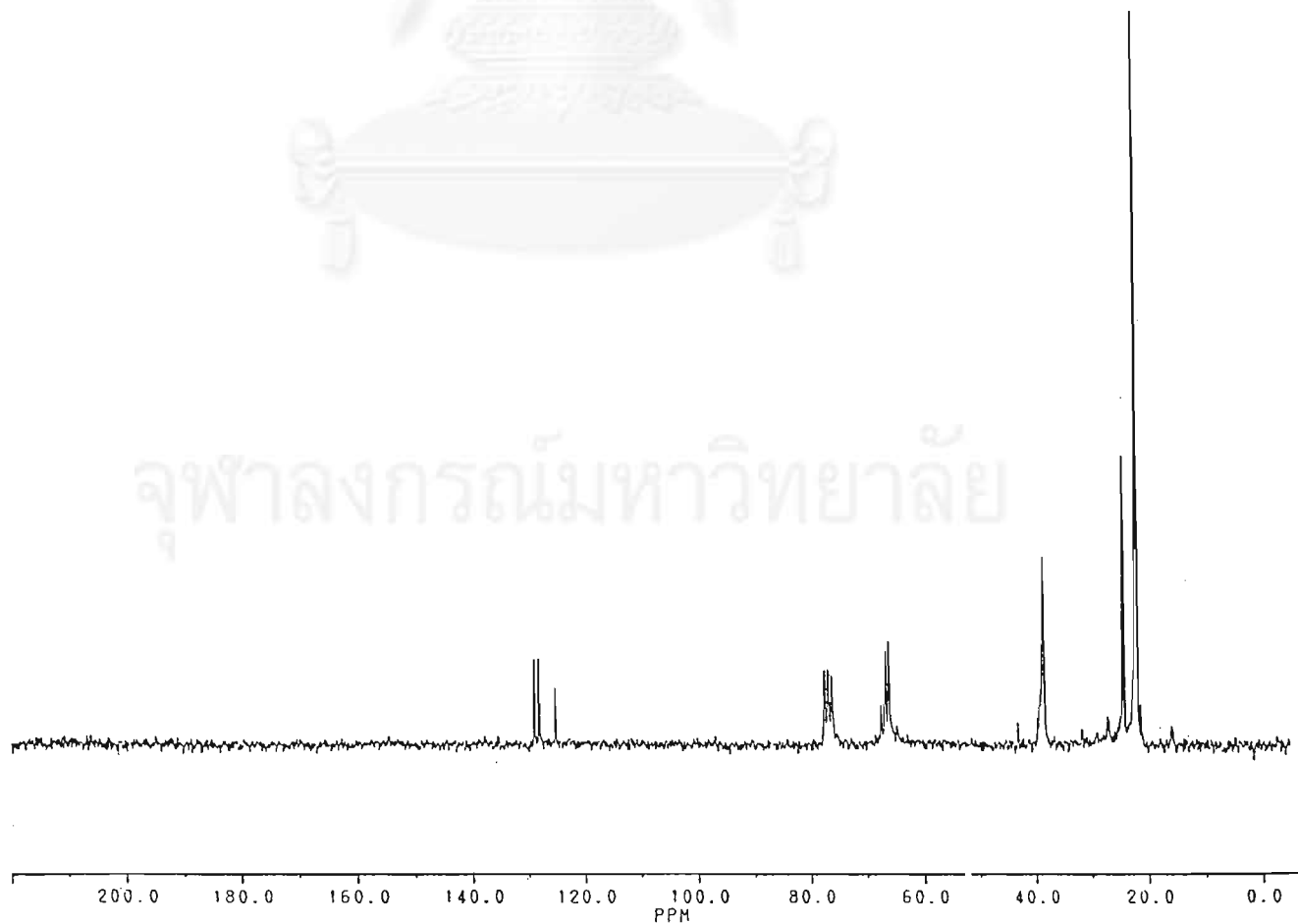**APPENDIX A8** ^{13}C-NMR Spectrum of DPDA

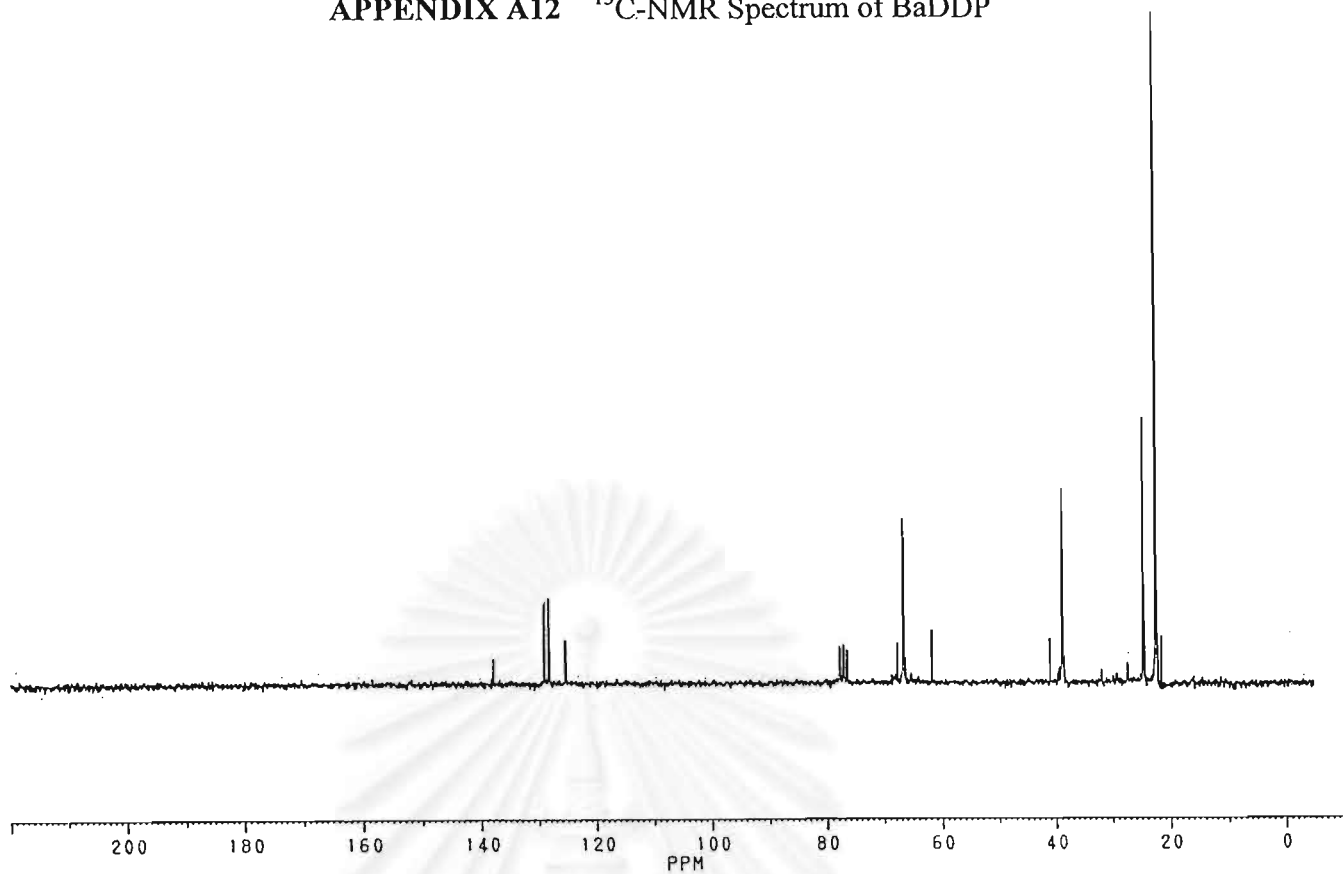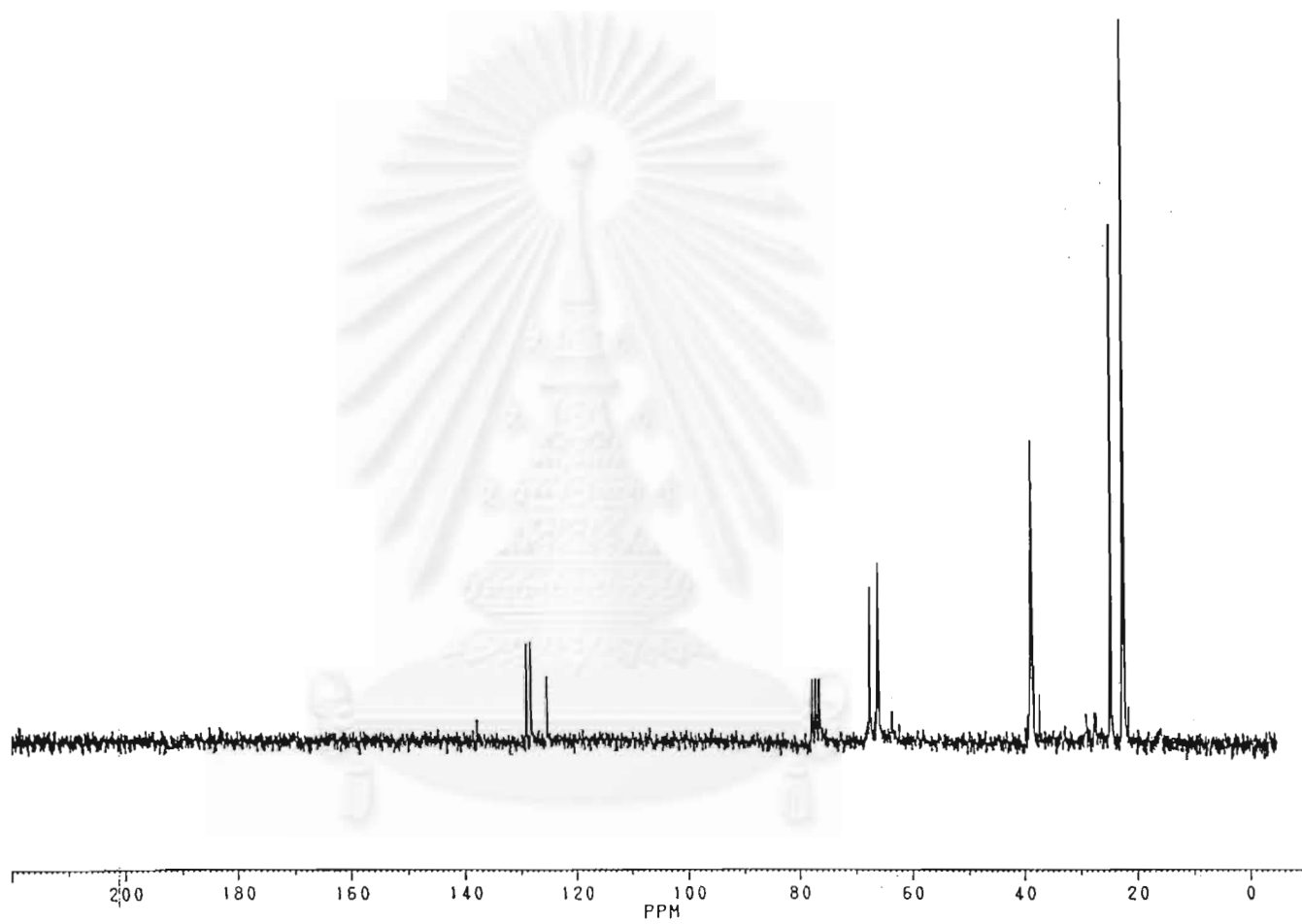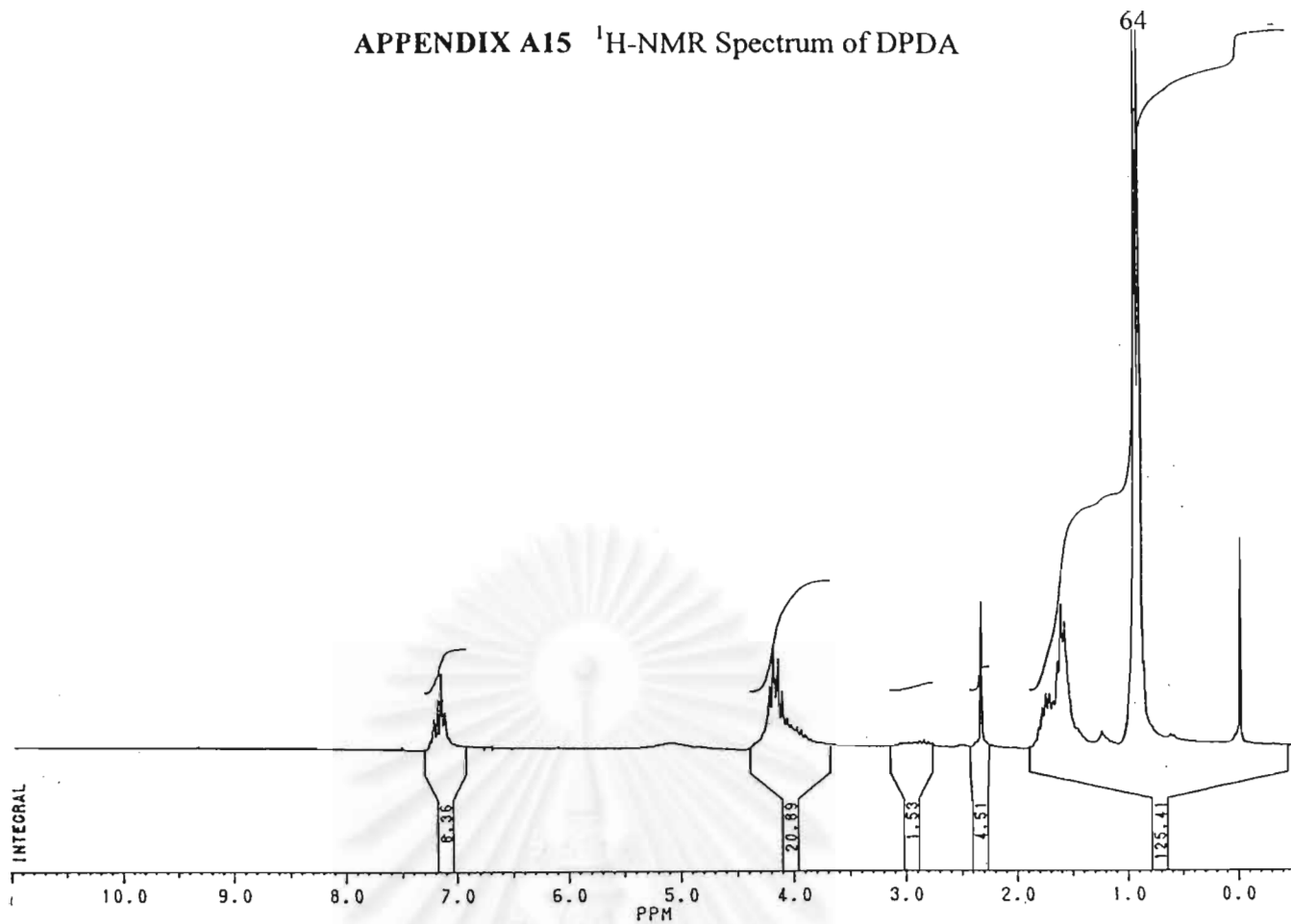**APPENDIX A9** ^{13}C-NMR Spectrum of KDPS

APPENDIX A10 ^{13}C-NMR Spectrum of ZDDP
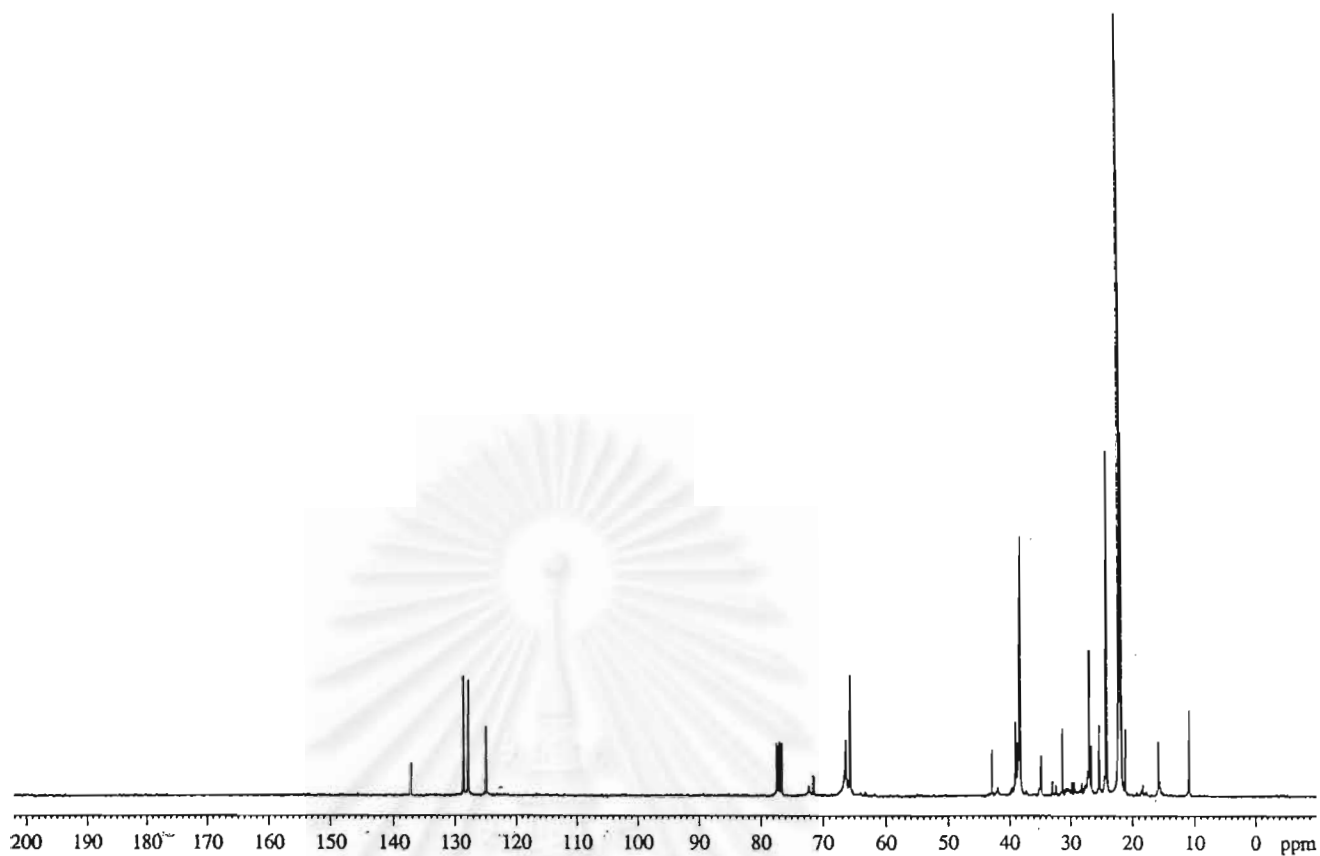
APPENDIX A11 ^{13}C-NMR Spectrum of CuDDP

APPENDIX A12 ^{13}C-NMR Spectrum of BaDDP

APPENDIX A13 ^{13}C-NMR Spectrum of MgDDP

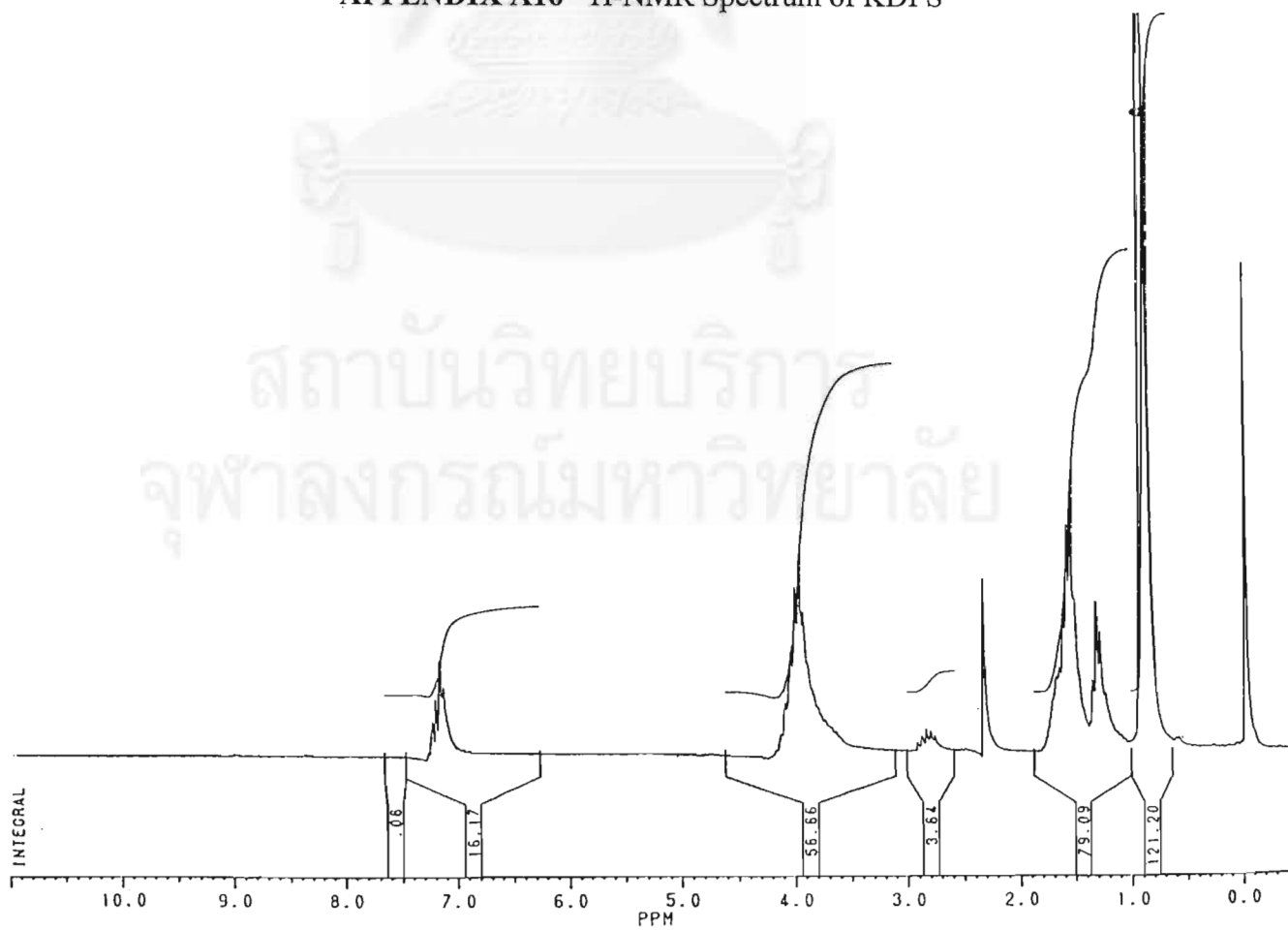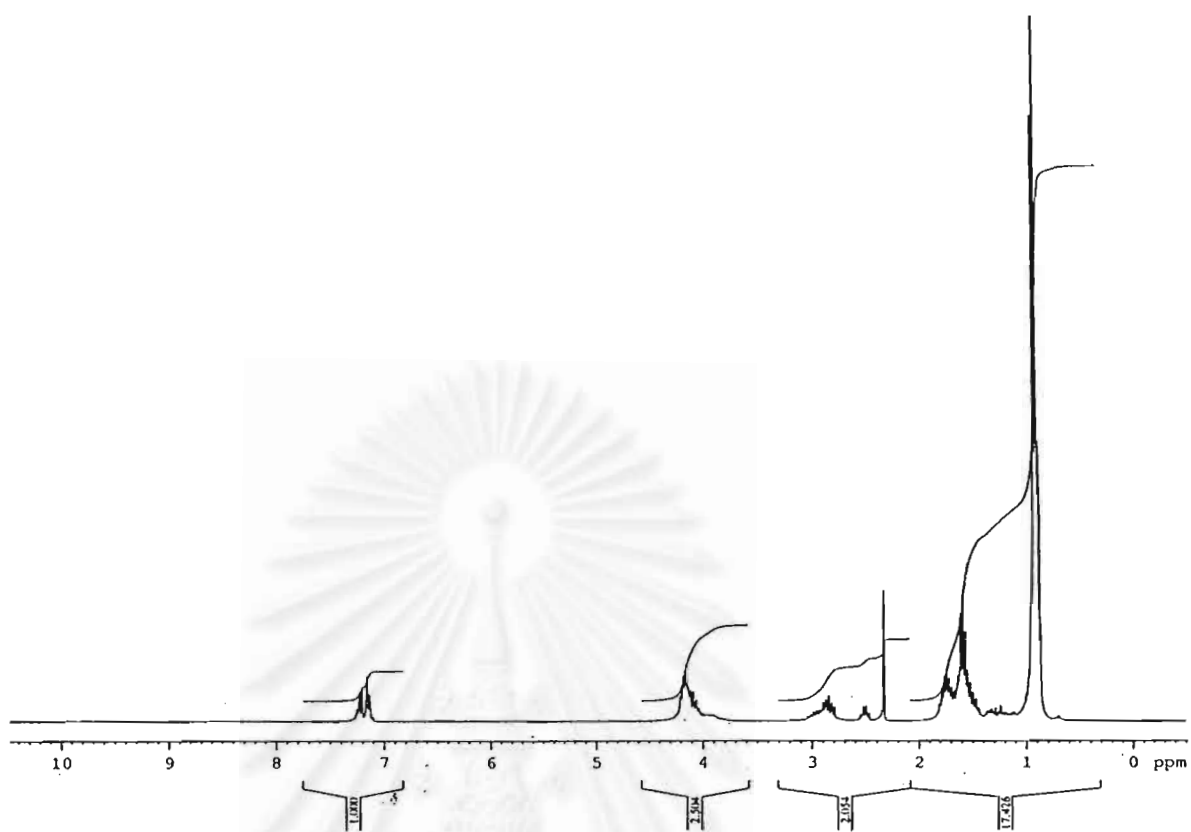**APPENDIX A14** ^{13}C-NMR Spectrum of SnDDP

APPENDIX A15 ¹H-NMR Spectrum of DPDA

APPENDIX A16 ¹H-NMR Spectrum of KDPS

APPENDIX A17 ^{1}H-NMR Spectrum of ZDDP

APPENDIX A18 ^{1}H-NMR Spectrum of CuDDP

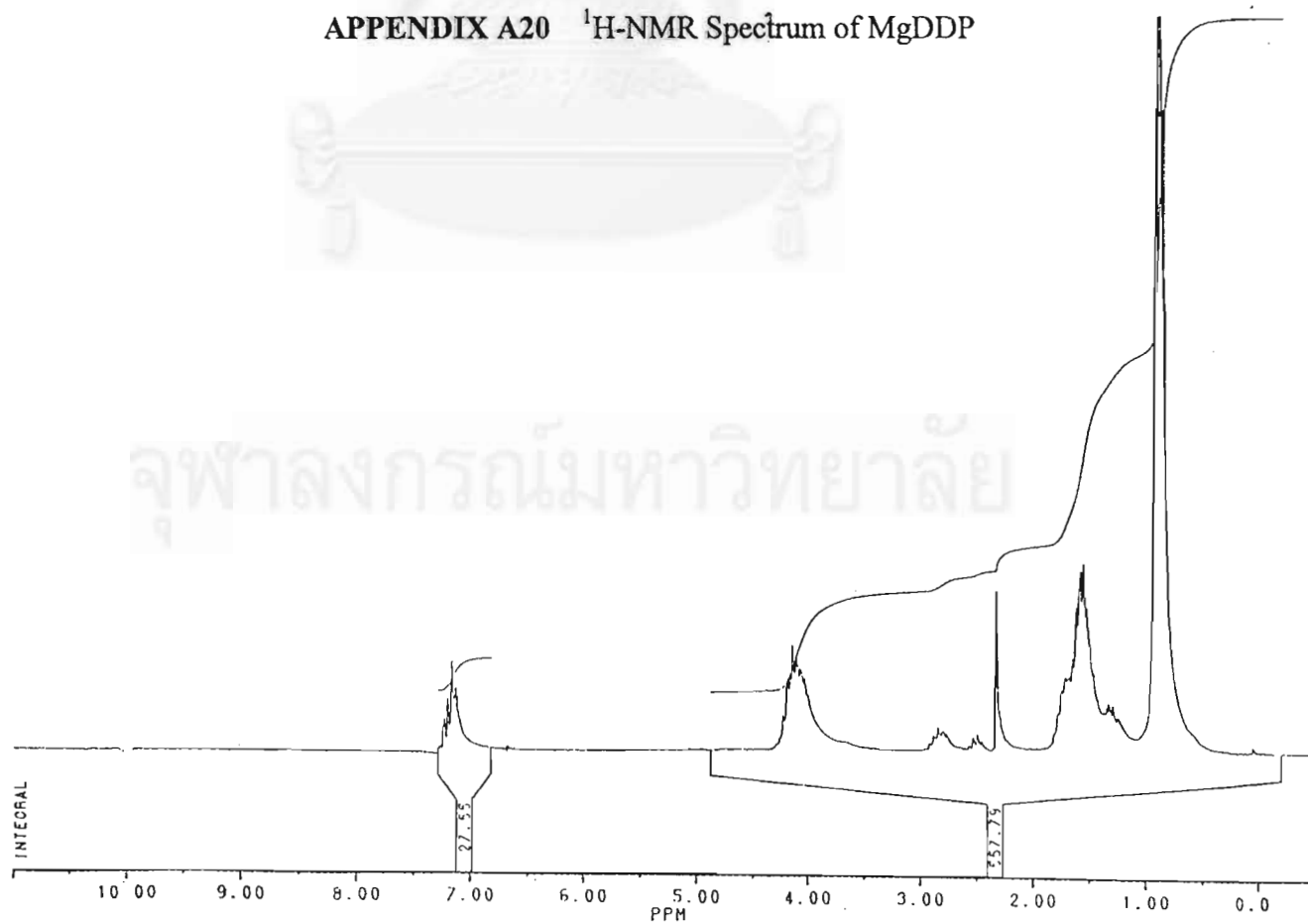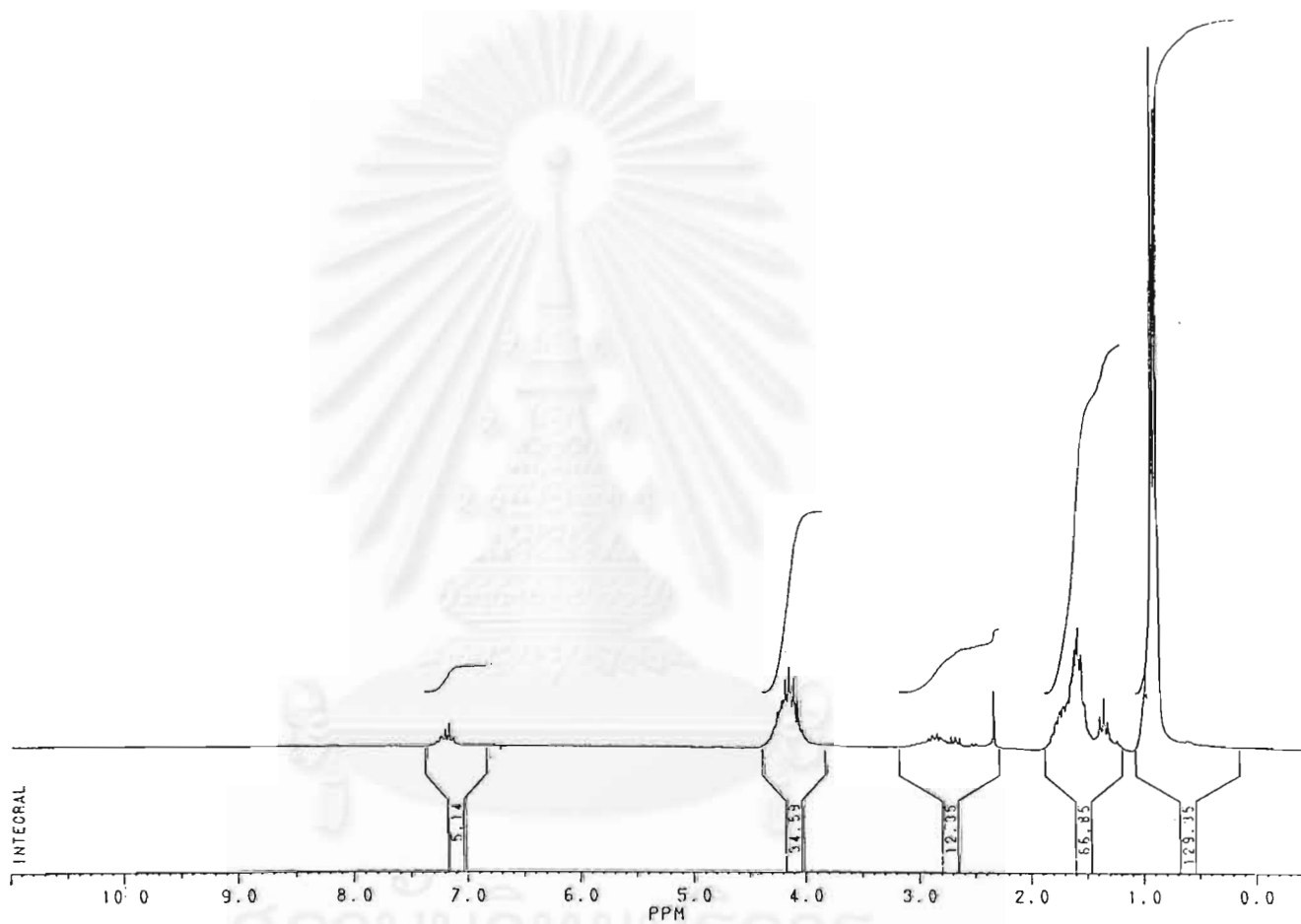**APPENDIX A19** ^{1}H-NMR Spectrum of BaDDP
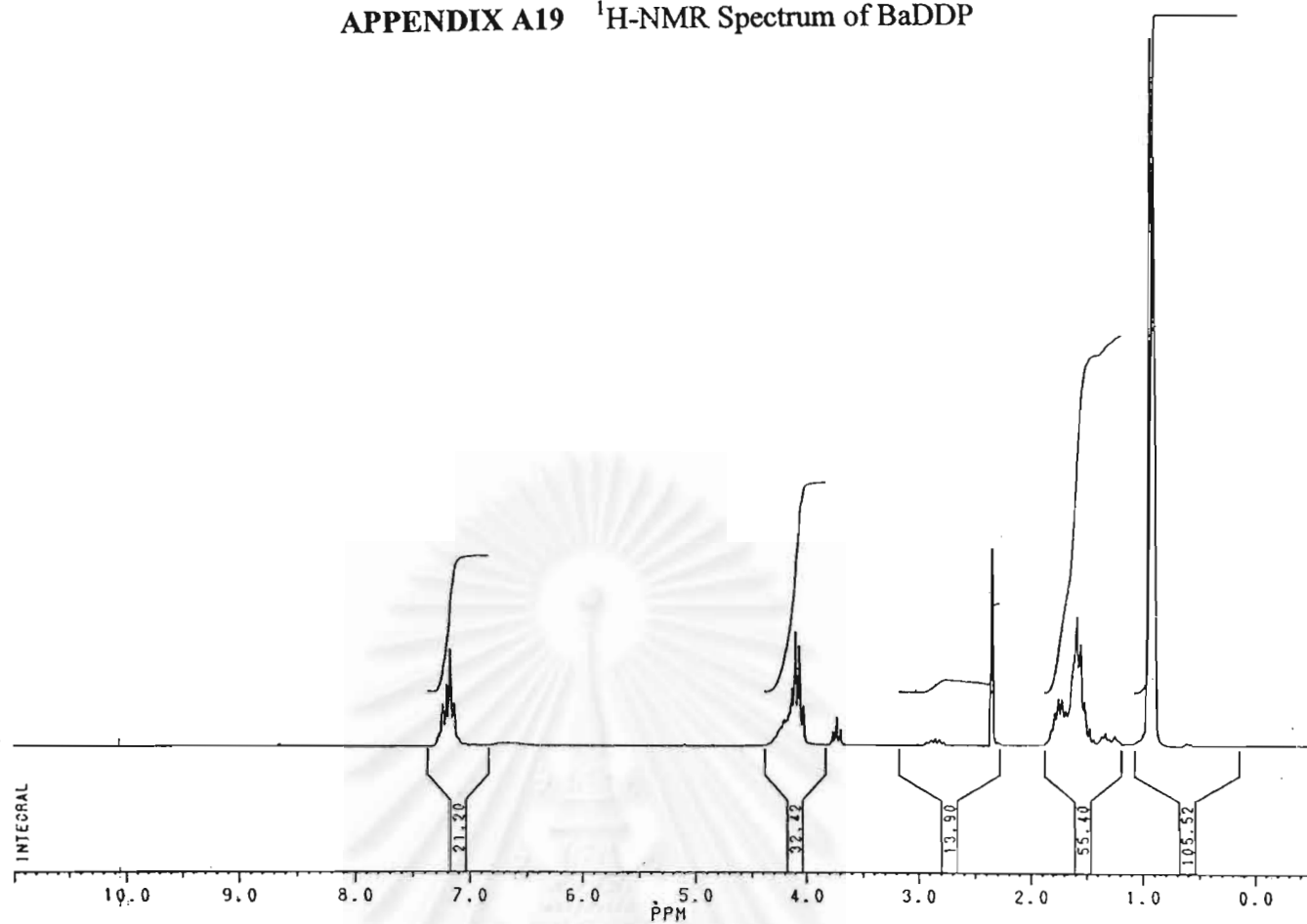
APPENDIX A20 ^{1}H-NMR Spectrum of MgDDP

APPENDIX A21 ^{1}H-NMR Spectrum of SnDDP

APPENDIX A22   Composition of MDDPs with various reaction time

Table 1: Composition of ZnDDP with various reaction time.

	% Zn	% P	% S	% C	% H	%O	Zn/ P/ S	% Yield
Calculated	10.82	10.25	21.23	39.72	7.28	10.60	1 / 2 / 4	
Found :								
2 hours	9.68	9.63	11.40	-	-	-	1 / 2 / 2	89.46
4 hours	10.28	10.23	21.18	40.16	7.47	10.68	1 / 2 / 4	95.00
6 hours	10.65	10.09	20.90	-	-	-	1 / 2 / 4	98.43
8 hours	10.79	10.22	21.17	-	-	-	1 / 2 / 4	99.72
24 hours	10.81	10.24	21.21	-	-	-	1 / 2 / 4	99.90

Table 2: Composition of CuDDP with various reaction time.

	% Cu	% P	% S	% C	% H	% O	Cu/ P/ S	% Yield
Calculated	13.49	9.86	20.42	38.2	7.00	11.03	2 / 3 / 6	
Found :								
2 hours	9.68	4.25	9.28	-	-	-	2 / 2 / 4	71.75
4 hours	13.27	9.70	20.76	38.49	6.71	11.07	2 / 3 / 6	98.36
6 hours	13.39	9.13	20.94	-	-	-	2 / 3 / 6	99.25
8 hours	13.50	9.87	19.07	-	-	-	2 / 3 / 6	100
24 hours	13.48	9.85	20.40	-	-	-	2 / 3 / 6	99.93

Table 3: Composition of BaDDP with various reaction time.

Calculated	% Ba	% P	% S	Ba/ P/ S
	20.31	9.16	18.97	1 / 2 / 4
Found :				
2 hours	2.00	3.61	7.85	1 / 8 / 17
4 hours	1.80	3.21	7.15	1 / 8 / 17
6 hours	5.53	9.23	21.95	1 / 7 / 17
8 hours	8.78	7.33	14.76	1 / 4 / 7
24 hours	8.94	7.06	15.66	1 / 4 / 8

Table 4: Composition of MgDDP with various reaction time.

Calculated	% Mg	% P	% S	Mg/ P/ S
	4.29	10.93	22.64	1 / 2 / 4
Found :				
2 hours	3.20	14.68	16.90	1 / 4 / 4
4 hours	1.43	6.87	11.67	1 / 4 / 6
6 hours	1.37	5.73	15.66	1 / 3 / 8
8 hours	1.06	5.82	9.05	1 / 4 / 7
24 hours	0.89	4.70	8.78	1 / 4 / 8

Table 5: Composition of SnDDP with various reaction time.

Calculated	% P	% S	P/ S
	9.43	19.53	2 / 4
Found :			
2 hours	5.05	6.28	2 / 2
4 hours	6.93	6.45	2 / 2
6 hours	6.99	11.58	2 / 3
8 hours	7.05	10.94	2 / 3
24 hours	7.03	10.20	2 / 3

APPENDIX A23 Thermogram of lubricating base oil

Onset X = 280.145 _C
Onset Y = 97.995%

1st Derivative curve

Y1 = 11.616 %
X1 = 351.530 _C

Onset X = 357.123 _C
Onset Y = 1.897%
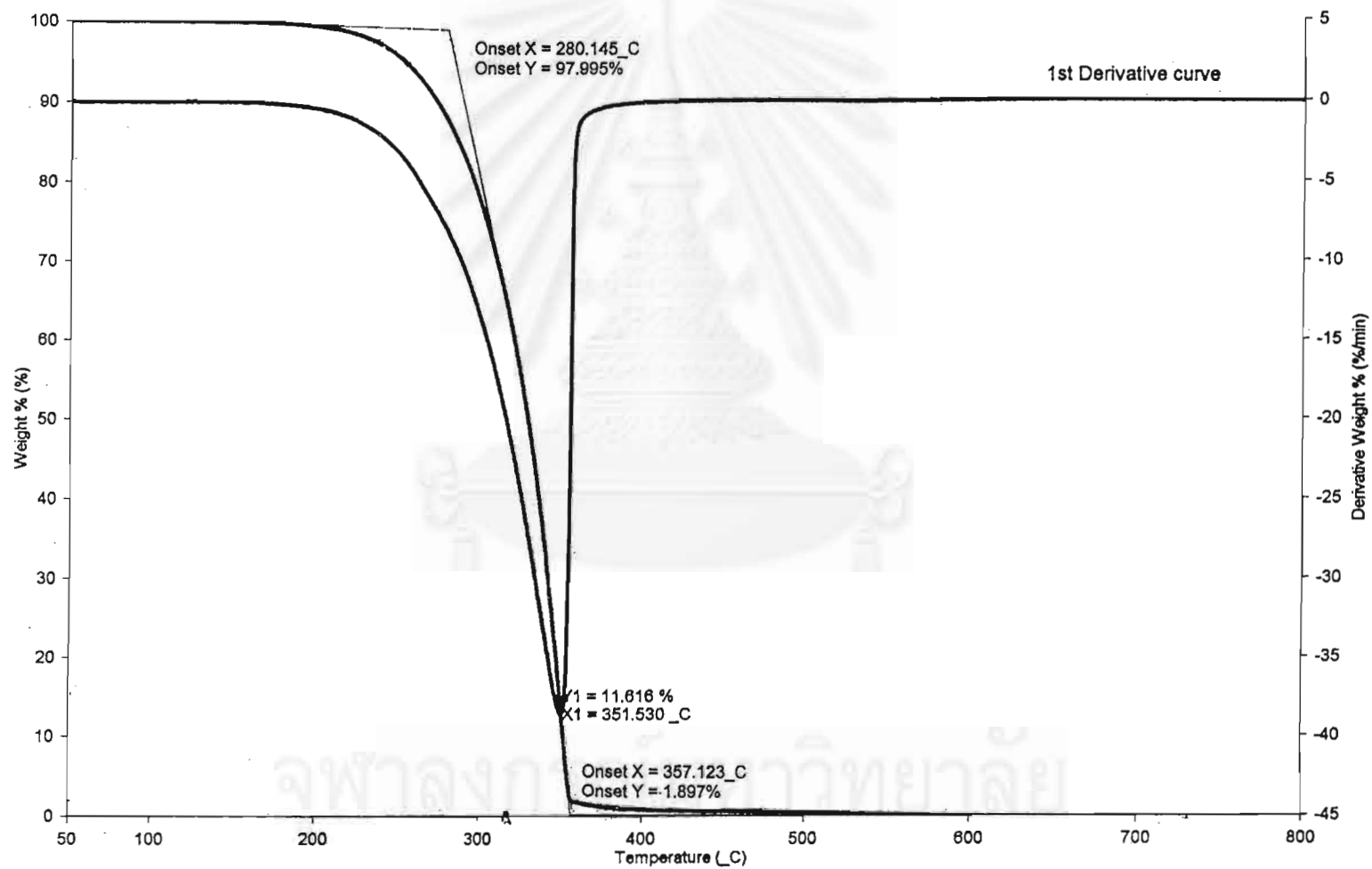
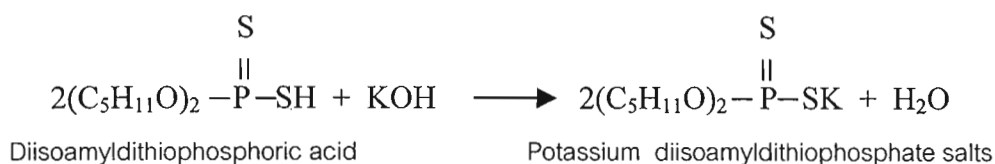**APPENDIX A24** Thermogram of lubricating base oil with 1% concentration ZDDP
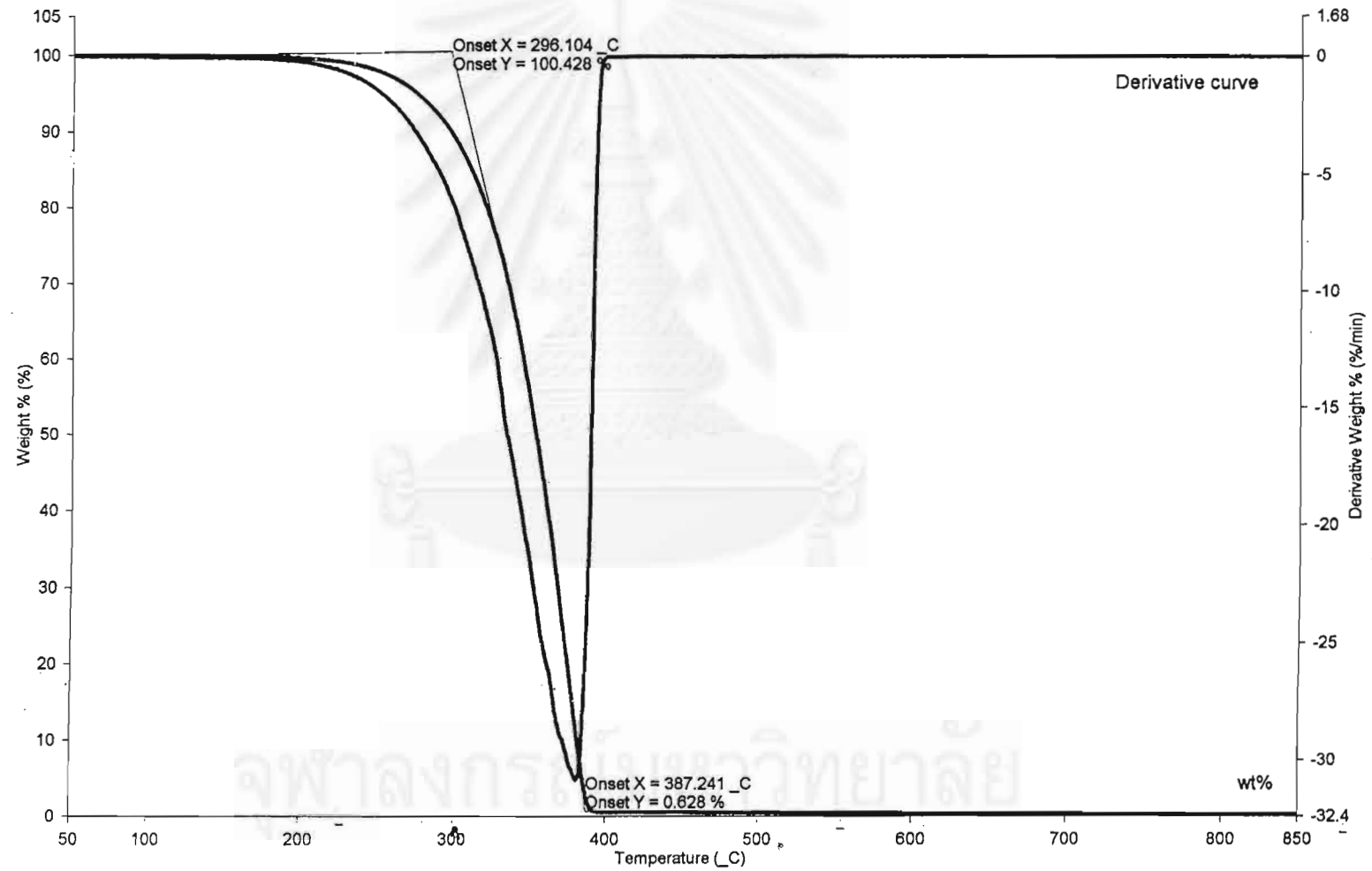
APPENDIX A25 Thermogram of lubricating base oil with 1% concentration CuDDP
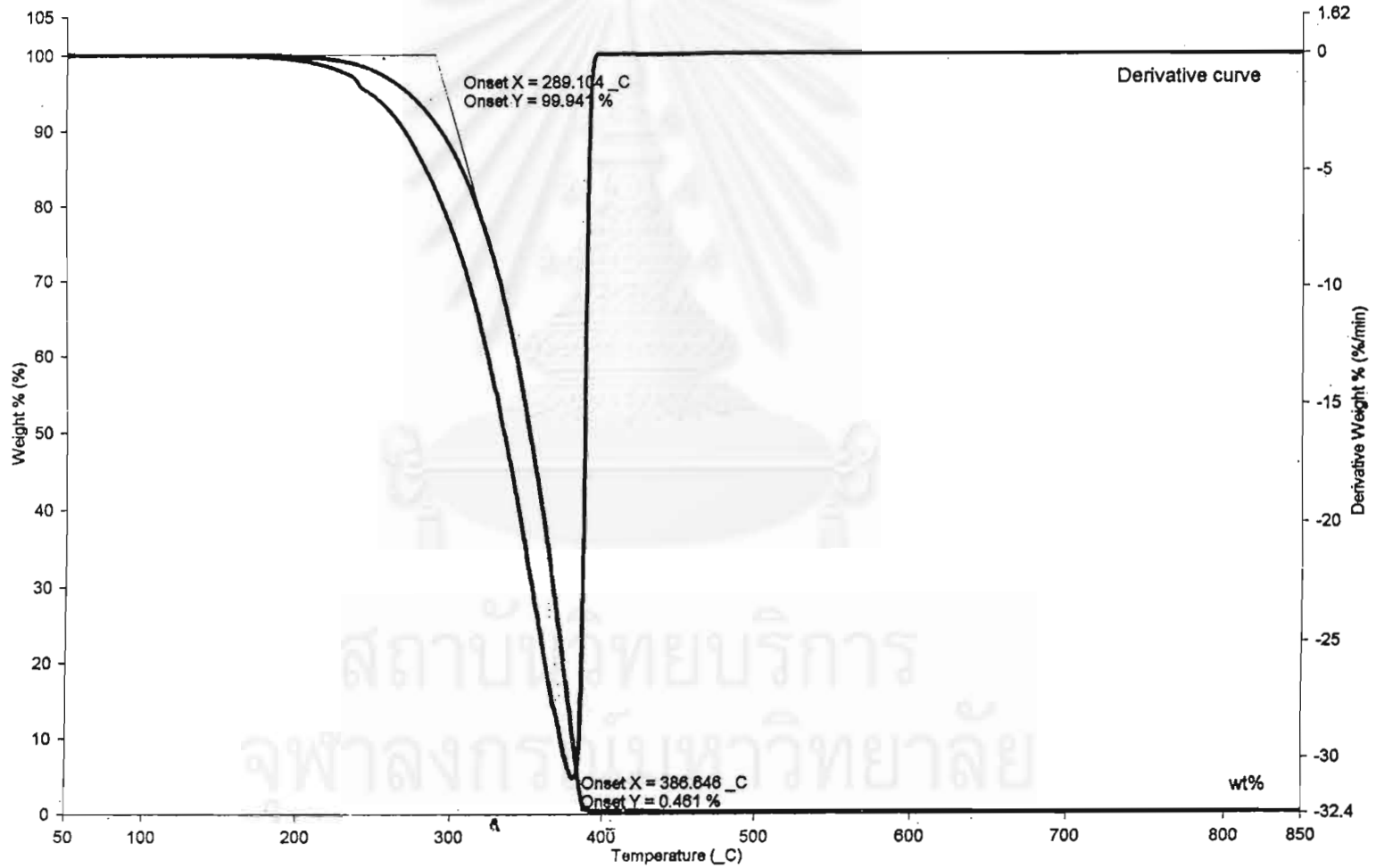
APPENDIX B1 Calculation of %yield DPDA

From the reaction

$$2(C_5H_{11}O)_2-\overset{\overset{\displaystyle S}{\|}}{P}-SH \ + \ KOH \ \longrightarrow \ 2(C_5H_{11}O)_2-\overset{\overset{\displaystyle S}{\|}}{P}-SK \ + \ H_2O$$

Diisoamyldithiophosphoric acid   Potassium diisoamyldithiophosphate salts

At equivalent point,

mole of DPDA   =   mole of KOH solution requires for titration

This work expected theoretical mole of DPDA was 0.05 mole

So,

$$\textbf{\% Yield of DPDA} \ = \ \frac{(\textbf{M} \times \textbf{V}) \times 100}{0.05}$$

Where:

M   =   morality of KOH solution, mole/lite,

V   =   KOH solution used to titrate the DPDA to the end point, ml,

APPENDIX B2 Calculation of TAN from ASTM D974 (Standard test method for acid number by color-indicator titration.)

Calculate the acid number as follows :

$$\textbf{Acid number, mg of KOH/g} \ = \ [(A\text{-}B)M \times 56.1]/W$$

Where :

A =   KOH solution requires for titration of the sample, ml,

B =   KOH solution requires for titration of the blank, ml,

M =   molarity of the KOH solution, and

W =   sample used, g.

APPENDIX B3 Calculation of TBN from ASTM D 2896 (Standard Test Method for Base Number by Potentiometric Perchloric Acid Titration.)

Interpret the end point from the graph obtained from automatic titration. The end point is the midpoint of the inflection, that point at which the curve changes from concave to convex. A useful but not mandatory guide is that the end point is preceded and followed by a deflection of a least 50 mV/0.1 ml of titrant.

Calculate the base number, *BN*, as follows:

$$BN, \text{mg KOH/g} = [(E\text{-}F) \times N_A \times 56.1]/S$$

Where:

E = HClO$_4$ solution used to titrate the sample to the inflection point on the titration curve, ml,

F = volume corresponding to E for blank titration at same potential as sample, ml,

N_A = normality of HClO$_4$ solution, and

S = sample, g.

APPENDIX B4 Calculation %wt/wt of metal and phosphorus in MDDP by ICP

The sample was pipetted only 0.1 ml from 100 ml MDDP stock solution and was diluted into 25 ml volumetric flask. The results were reported by ppm of metal or phosphorus.

So, **mg of metal or phosphorus in sample = (A/(B×1000)) ×(C/D)**

Where:

A = detected ppm of metal or phosphorus

B = volume of sample that was pipetted; 0.1 ml

C = volume of volumetric flask that was used to dilute sample; 25 ml

D = volume of MDDP stock solution; 100 ml

And **%wt/wt Metal or P =** $\dfrac{\text{total weight of metal or P in stock solution} \times 100}{\text{theoretical weight of sample}}$

APPENDIX B5 Calculation % wt/wt of sulphur in MDDP by X-ray fluorescence

0.1 ml of the sample was pipetted from 100 ml MDDP stock solution and was diluted to 10 ml in volumetric flask. The results show % wt/wt of sulphur in diluted sample 10 ml

$$\textbf{Weight of S in stock solution, g} = \textbf{((E} \times \textbf{F)/100)} \times \textbf{(V}_1\textbf{/V}_2\textbf{)}$$

Where:

E   =   detected sulphur in 10 ml diluted sample ,% wt/wt

F   =   weight of 10 ml diluted sample, g

V_1 =   volume of MDDP stock solution;100 ml

V_2 =   volume of sample that was pipetted; 0.1 ml

So;

$$\%\text{wt/wt S} = \frac{\textbf{weight of S in stock solution} \times \textbf{100}}{\textbf{theoretical weight of sample}}$$

VITA

The author was born on October 17,1974 in Bangkok, Thailand. She received the Bachelor Degree of Science in Chemistry at Chulalongkorn University in 1996. Since 1997 she has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed her M.Sc. degree in 1999.