การเตรียมสารทำให้ข้นเหนียวสำหรับจาระบีจากน้ำมันปาล์มอิพอกซิไดซ์

นางสาว สุวิตานันท์ บุญศรี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2544

ISBN 974-03-1310-8

PREPARATION OF THICKENING AGENTS FOR GREASE FROM EPOXIDIZED PALM OIL

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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

Chulalongkorn University

Academic Year 2001

ISBN 974-03-1310-8

Thesis Title	PREPARATION OF THICKENING AGENTS FOR GREASE FROM EPOXIDIZED PALM OIL
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Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Sophon Roengsumran, Ph.D.

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

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สุวิตานันท์ บุญศรี : การเตรียมสารทำให้ข้นเหนียวสำหรับจาระบีจากน้ำมันปาล์มอิพอกซิไดซ์ (PREPARATION OF THICKENING AGENTS FOR GREASE FROM EPOXIDIZED PALM OIL)
อ.ที่ปรึกษา : รศ.ดร.โสภณ เริงสำราญ, 85 หน้า, ISBN 974-03-1310-8

งานวิจัยนี้ได้เตรียมจาระบีโดยใช้น้ำมันปาล์มเป็นน้ำมันหล่อลื่นพื้นฐานและสบู่แคลเซียมหรือสบู่ลิเทียมเป็นสารทำให้ข้นเหนียว โดยทำการเปรียบเทียบจาระบีที่ประกอบด้วย 22% โดยน้ำหนักของสบู่แคลเซียมหรือสบู่ลิเทียม ซึ่งเตรียมจากน้ำมันปาล์มและน้ำมันปาล์มอิพอกซิไดซ์กับจาระบีทางการค้าที่ประกอบด้วยสบู่แคลเซียมหรือสบู่ลิเทียมจากกรดไฮดรอกซีสเตียริกหรือกรด สเตียริก พบว่าจาระบีที่เตรียมได้ มีคุณสมบัติที่ใกล้เคียงกับจาระบีทางการค้า คือ มีค่าความอ่อนแข็งประมาณ 261 และ 237 และค่าจุดหยดประมาณ 101 °C และ 189 °C สำหรับจาระบีที่ใช้สบู่แคลเซียมและสบู่ลิเทียมของน้ำมันปาล์มอิพอกซิไดซ์เป็นสารทำให้ข้นเหนียว ตามลำดับ อย่างไรก็ตามจาระบีที่เตรียมจากสบู่ของน้ำมันปาล์มและน้ำมันปาล์มอิพอกซิไดซ์ มีราคาถูกกว่าจาระบีทางการค้าจากสบู่ของกรดไฮดรอกซีสเตียริกและกรดสเตียริก นอกจากนี้สมบัติอื่น ๆ ของจาระบีที่เตรียมจากสบู่ของน้ำมันปาล์มอิพอกซิไดซ์เป็นไปตามมาตรฐานผลิตภัณฑ์อุตสาหกรรม 713-2541 ดังนั้นจาระบีที่เตรียมจากสบู่ของน้ำมันปาล์มและน้ำมันปาล์มอิพอกซิไดซ์อาจจะนำไปใช้ทดแทนจาระบีทางการค้าได้

หลักสูตร...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... **ลายมือชื่อนิสิต**..
สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... **ลายมือชื่ออาจารย์ที่ปรึกษา**..............................
ปีการศึกษา..........2544..........

4272456723 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD : EPOXIDIZED PALM OIL/ GREASE/ PALM OIL

SUWITANAN BOONSRI: PREPARATION OF THICKENING AGENTS FOR GREASE FROM EPOXIDIZED PALM OIL,
THESIS ADVISOR : ASSOC. PROF. SOPHON ROENGSUMRAN, Ph.D., 85 PAGES, ISBN 974-03-1310-8

Greases were prepared using palm oil as base oil and calcium or lithium soap as a thickening agent. The greases containing 22 % wt/wt of calcium or lithium soap prepared from palm oil and epoxidized palm oil were compared with those containing commercial calcium or lithium soaps prepared from 12-hydroxystearic acid or stearic acid. The prepared greases were found to have similar properties as the commercial greases, with penetration values of ~261 and ~237 and dropping point values of ~101 °C and ~189 °C for greases containing calcium and lithium-epoxidized palm oil soaps used as thickening agent, respectively. However, the prepared greases from palm oil and epoxidized plam oil soaps are cheaper than commercial greases from 12-hydroxysteric acid and steric acid soaps. The other properties of epoxidized palm oil were within the specification of TIS 713-2541. Therefore, the prepared greases from palm oil and epoxidized plam oil soaps may be replaced the commercial greases.

Program ……Petrochemistry and Polymer Science…… Student's signature……………………………

Field of study ……Petrochemistry and Polymer Science…… Advisor's signature……………………………

Academic year…………………2001……………..

ACKNOWLEDGEMENT

I wish to express my sincere thank to my advisor, Associate Professor Dr. Sophon Roengsumran, for his assistance and helpful suggestions of valuable points of the experiments, for his kindness, encouragement and guidance throughout the course of this thesis. I am also highly grateful to Professor Dr. Pattarapan Prasassarakich, Associate Professor Dr. Amorn Petsom, Associate Professor Dr. Somchai Pengprecha, Assistant Professor Dr. Warinthorn Chavasiri for serving as chairman and members of thesis committee, respectively, whose comments have been specially valuable.

I am very grateful to the PTT Public Company Limited for the use of their equipments and their excellent facilities.

I also thank for the Department of Chemistry and the Program of Petrochemistry and Polymer Science and the Graduate School, Chulalongkorn University for the provision of experimental facilites and granting partial financial support throughout this research.

Lastly, I would like to thank everyone who has contributed suggestions and supports throughout this research.

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ABBREVIATIONS

ASTM = American Society for Testing and Materials

BT = Block temperature when the drop falls

^{13}C-NMR = Carbon-13 Nuclear Magnetic Resonance

^{o}C = Degree celsius

cm^{-1} = Unit of wave number

DP = Dropping point

FT-IR = Fourier-Transform Infrared Spectrophotometer

g = Gram

^{1}H-NMR = Proton Nuclear Magnetic Resonance

min = Minute

ml = Milliliter

NLGI = The National Lubricating Grease Institute

no. = Number

ODP = Thermometer reading when first drop reaches the bottom of the test tube

TIS = Thailand Industrial Standard

W = Mass of samples after test

W$_{L}$ = Evaporation loss percentage

W$_{S}$ = mass of samples before test

% = Percent

CHAPTER I

INTRODUCTION

1.1 Introduction

Lubricating greases containing of olive oil and lime were already used by the Egyptians in ca. 1400 B.C. for the lubrication of their wooden carriage axles. The development of modern greases has followed the development of the industrial age, passing from sodium greases to calcium and aluminum greases, lithium greases, and calcium complex soap greases. The first aluminum, barium and lithium complex soap greases were patented in 1952. A large number of patents have been granted since then, reflecting the great variety of the thickeners, oils and additives used and of the manufacturing procedures proposed [1].

Lubricating grease is a vital part of a great number of machine components. Grease may be used in preference to oil in applications where they can be expected to give satisfactory lubrication for long periods without the need for elaborate seals, pumps, or reservoirs. The flow pattern of grease within a baring and the small quantity directly involving with lubrication result in little or no cooling effect. This is the main limitation to the use of grease as a bearing lubricant. By the proper selection of raw materials, grease can be made which will satisfy applications ranging from bearings operating in the hard vacuum of outer space to the teeth of gears in a brick work. An acceptable grease life may be a few hours or several years [2].

The American Society for Testing and Materials (ASTM) D 288, "Standard Definitions of Terms Relating to Petroleum," defines a lubricating grease as a solid to semiliquid product of dispersion of a thickening agent in liquid lubricant (base oil) [2]. The use of grease is advantageous in the following types of applications and for the following reasons [3]:

(i) It decreases the dripping and spattering of the lubricant used by acting as an additional seal to reduce leakage.

(ii) It decreases the frequency of lubrication in some cases. Grease will stay in an application where some oils may leak out.

(iii) It helps seal out contaminants such as water and dirt. In corrosive atmospheres, it helps seal out those corrosive elements.

(iv) It hangs on the application in an intermittent operation where oil would drain away.

(v) It can suspend solids, such as moly, graphite, and zinc oxide, much better than oil. In certain applications, the addition of solids can be beneficial.

Nowadays, the popular thickening agent is metal 12-hydroxystearate. It has an excellent mechanical stability. The fatty acid is a castor oil derivative, being a natural (vegetable) raw material but more expensive, and must be imported. Then, mineral oil based grease is found in wide scale usage. A disadvantage of the known grease compositions is that they contain large amounts (in general 80-90%) of mineral lubricating oils. Mineral oils are not readily biodegradable. When using such a grease composition, comparatively large amounts of the relatively non-degradable mineral oil component will pass into the sanitary sewage system as a result of rain or when the streets are cleaned by washing thus creating a serious contamination problem. Environmental has also arisen when the grease of optionally tracked rubbish excavators, or excavator cables, links and other similarly lubricated parts comes into direct contact with or contaminates the soil and/or surface waters. Normally, waste greases respond to separate from water, and thus there should be necessity for supplying biodegradable products. Next, the development of biodegradable grease is composed of essentially the same chemicals as non-biodegradable products. Biodegradable and nontoxic esters such as vegetable oil, synthetic ester and polyglycol, may be used as the base oil for production of grease. The most popular base oil is vegetable oil because they are relatively inexpensive compared to synthetic oil, and are made from natural renewable resources and, therefore, in plentiful supply.

1.2 Objectives and scope of the research

1.2.1 Objectives

1. To synthesize epoxidized palm oil.
2. To prepare thickening agents from the epoxidized palm oil.
3. To prepare greases and study the properties of prepared greases.

1.2.2 Scope of the research

This study relates to the environmentally friendly greases composition that are made from palm oil. The thickening agents are lithium and calcium soap of epoxidized palm oil. The procedures are as follows:

1. Literature survey of relevant research works and preparation of chemicals and equipment.
2. Synthesis and characterization of the epoxidized palm oil by Nuclear Magnetic Resonance (NMR) and Infrared Spectroscopy (IR).
3. Preparation of thickening agents from reaction of calcium and lithium hydroxide with
    - Epoxidized palm oil
    - Palm oil
    - 12-Hydroxystearic acid
    - Stearic acid
4. Preparation of grease from prepared thickening agents.
5. Investigating the properties of epoxidized palm oil grease using.
    - Scanning electron microscopy (SEM)
    - Penetration (ASTM D 217)
    - Dropping point (ASTM D 2265)
    - Copper strip corrosion (JIS K 2220 Method A)
    - Water washout (ASTM D 1264)
    - Ash (ASTM D 128)
    - Determination of water (TIS 1182)
    - Evaporation loss (JIS K 2220)
6. Summarizing of the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Definition of Lubricating Grease

A lubricating grease is a solid to semifluid mixture of a liquid lubricant and a thickening agent. Additives to impart special properties or performance characteristics may be incorporated. The liquid component may be a mineral (petroleum) oil or a synthetic liquid; the thickener may be a metallic soap or soaps or a nonsoap substance such as an organophilic modified clay, a urea compound, carbon black, or other material. The viscosity of the fluid, the thickener concentration, and the chemical nature of the thickener may vary widely. The properties of the finished grease are influenced by the manufacturing process as well as by the materials used [4].

As previous mentional grease is basically used in applications in which an oil lubricant would leak out, could not properly seal the lubricated part, and would fall away or not reach the point of application. Grease is used where oil will not stay [3].

2.2 Basic Performance Requirements

Greases are most often used instead of fluids where a lubricant is required to maintain its original position in a mechanism, especially where opportunities for frequent relubrication may be limited or economically unjustifiable. This requirement may be due to the physical configuration of the mechanism, the type of motion, the type of sealing, or to the need for the lubricant to perform all or part of any sealing function in the prevention of lubricant loss or the entrance of contaminants. Because of their essentially solid mature, greases do not perform the cooling and cleaning functions associated with the use of a fluid lubricant. With these exceptions, greases are expected to accomplish all other functions of fluid lubricants [4].

A satisfactory grease for a given application is expected to:

(i) provide adequate lubrication to reduce friction and to prevent harmful wear of bearing components.

(ii) protect against corrosion.

(iii) act as a seal to prevent entry of dirt and water.

(iv) resist leakage, dripping, or undesirable throw off from the lubricated surfaces.

(v) resist objectionable change in structure or consistency with mechanical working (in the bearing) during prolonged service.

(vi) not stiffen excessively to cause undue resistance to motion in cold weather.

(vii) have physical characteristics suitable for the method of application.

(viii) be compatible with elastomer seals and other materials of construction in the lubricated portion of the mechanism.

(ix) tolerate some degree of contamination, such as moisture, without loss of significant characteristics.

(x) have suitable oxidation and thermal stability for the intended application.

2.3 Classification of Greases.

Based on their many fold applications and different compositions, the lubricating greases are classified according to various criteria [1]:

- The machinery and machine elements to be lubricated: greases for antifriction, jounal and wheel bearings, joints, gears, sinter strips etc.
- The industries which use them: greases for the automobile industry, railways, steel mills, the food industry, aviation, etc.
- The temperature of application: low-temperature, normal and high-temperature greases.
- The range of application: multi-purpose, special and normal greases.
- The composition: the group of soap-free greases, which is small with respect to the quantities produced but contains a large variety of greases, is distinguished from the group of soap-containing greases, which is large with respect to the quantity produced but small with respect to the number of different greases. Soap-containing greases are divided into simple and complex soap greases which are both named according to the cation on which the soap is based (e.g. lithium, sodium, calcium, barium and aluminum soap grease). This classification according to the soap cation is particularly explicit, since important properties are related to the cation: e.g. the dropping point of lime soap greases is ca. 100°C, of lithium soap greases ca. 180°C. Greases which contain two or more cations are called mixed soap greases.
- The base oil: greases based on synthetic or mineral oils, since some important properties of the greases depend on the oil component.
- The loading level: EP (extreme-pressure) greases and greases for normal bearing

- The deformability: an old, widely used and standardized classification divides the greases on the basis of their deformability (worked penetration) into NLGI consistency grades from 000 to 6 (NLGI: National Lubrication Grease Institute). This classification which grades the greases from very soft to very hard is based, however, solely on the worked penetration at 25 ^{o}C and neglects other material parameters.

2.4 Grades of grease

Greases are available in different grades or consistencies. The grade number is determined by a special instrument called a “penetrometer.” It consists of a calibrated metal cone and a special container into which the grease is packed, and held at a constant temperature. The cone is placed on the grease, point down. The grade is determined by how far the cone penetrates the grease in accordance with standards established by the National Lubricating Grease Institute (NLGI) [5].

If the grease is relatively hard, the cone will not penetrate very far. If the grease is soft, the cone will penetrate to a greater depth.

The amount of penetration indicates the grade number as shown in Table 2.1. Most manufacturers recommend either No.1 or No.2 grade.

Table 2.1 Classification of grease into NLGI consistency grades according to DIN 51 818 [1, 11]

NLGI No.	Worked penetration (0.1mm)	Visual assessment of deformability	Applications
000	445-475	Very fluid	Gear greases
00	400-430	Fluid	
0	355-385	Semifluid	Greases for antifriction bearings
1	310-340	Very soft	
2	265-295	Soft	
3	220-250	Semifirm	
4	175-205	Firm	Water pump greases
5	130-160	Very firm	Black greases
6	85-115	Hard	

2.5 Components and their Influence on the Properties of the Grease

2.5.1. Base Oils

Mineral and synthetic oils are suitable as base oils for greases. They can represent 65-95% of the mass of a grease. Oils with different qualities are used to satisfy the great number of grease applications and to give economic reasons. Some properties of the greases are mainly governed by the kind and viscosity of the base oil. An increase in viscosity reduces the evaporation losses, and improves the adhesive and corrosion protection properties, noise suppression and water resistance. On the other hand, an increase in viscosity give a negative effect on the cold properties and the transportability of the greases in central lubrication installations. The effect of greases on sealing materials (swelling and tensile strength) depends largely on the chemical composition of the base oil. The oxidation stability and decomposition temperature of the base oil provide a decisive influence on the maximum working temperature and service life of the greases in antifrication bearings. Oil separation increases from aromatic to naphthenic to paraffinic oils; on the other hard, it first decreases then again increases with increasing viscosity. The kind of base oil used determines the structural stability, the VT characteristics, the thickening power, the manufacturing procedure and partly the raw material costs.

2.5.1.1 Mineral Oils

Besides naphthenic oils, paraffinic and aromatic base oils are also used for the manufacture of lubricating greases. The preparation of simple lime soap greases with paraffinic oils is difficult. Base oils with low to medium viscosity indexes are preferred, since oils with low VI values usually require less thickener. Paraffinic base oils with high VI give greases which can be used over a wider temperature range than the greases based naphthenic oils.

In order to satisfy the different requirements, oils with viscosities in a range of 20 to 3400 mm^2/s at 20^oC are used. Oils with low viscosities give the greases good low-temperature properties, good transportability and low yield pressure; they provide low working temperatures in plain bearings and joints and allow low equilibrium temperatures and high speeds in antifriction bearings. Base oils with high viscosities are suitable for the preparation for the preparation of greases used for slow-running bearing and gears, high loads and temperatures; they also reduce oil separation and evaporation losses and give the grease good adhesive properties and water resistance.

2.5.1.2 Synthetic Oils

In comparison with mineral oils, the cost of synthetic oils is very high For this reason, synthetic oils are used for the manufacture of greases only where lubricating properties are required which cannot be achieved with a mineral oil.

Of importance for the manufacture of greases are diester oils, polyglycol ethers, silicones, phosphoric acid esters, perfluoro- and chlorofluoroalkyl ethers and hydrocarbons. These synthetic oils are available in different viscosity grades and possess excellent VT and low-temperature characteristics; however, they also have some negative properties, such as high pour point (polyphenyl ethers) or a strong creeping tendency on metal surfaces (silicones). Special greases with such fluid components represent less than 1% of the total grease production, and are applied mostly in aviation and space travel [1].

2.5.1.3 Natural Oils

Natural oils or vegetable oils are used by several manufacturers for greases. Of the vegetable oil triglycerides and the synthetic triglycerides, preferred are vegetable oil triglycerides. The preferred vegetable oils are palm, soybean, rapeseed, sunflower, coconut, lesquerella, canola, peanut, safflower and castor oils. The reasons for their popularity are that (i) they are nontoxic and highly biodegradable, (ii) they are relatively inexpensive compared to synthetic fluids (iii) they are made from natural renewable resources and, therefore, in plentiful supply, and (iv) some vegetable oils offer excellent lubricating properties [6].

Palm oil

The oil palm fruit is unusual in that it yields two distinct oils: palm kernel oil is obtained from the kernel and palm oil from the pulp (about 50% oil).

Palm oil is colored deep orange-red by the large amount of carotene (0.05-0.20%). The color is not much affected by alkali refining, but palm oil is bleached to a yellow color similar to that of other vegetable oils by hydrogenation. Palm oil has a pleasant, characteristic odor, is very stable to oxidation, and has no drying properties. At ordinary temperatures of 20-25 ^{o}C, it is semisolid. Its consistency and melting point depend on its content of free fatty acids because the free acids has melting point higher than the glycerides. The commercial palm oil with a relatively low free fatty acid content are known as soft oils, whereas those with high acidity are termed hard oils [7].

The triglyceride composition of palm oil evidently does not adhere to the random or even theories of distribution. Typically, palm oil has32-47 % palmitic acid and 40-52 % oleic acid in its triglycerides, and is thus more unsaturated. Fatty acid content of palm oil is shown in Table 2.2 .

Table 2.2 Fatty acid composition of palm oil

Component acids	Amount of fatty acid composition (wt%)
Saturated acids	
Lauric acid	0.1-1.0
Myristic acid	0.9-1.4
Palmitic acid	37.9-41.7
Stearic acid	3.0-5.0
Unsaturated acids	
Oleic acid	40.7-44.0
Linoleic acid	10.4-14.0
Linolenic acid	0.1-0.6

2.5.2 Soap

2.5.2.1 Simple soaps

Simple-soap greases represent the major fraction of lubricating greases manufactured on the industrial scale. They contain of three groups of components; 4-20 wt % soap, 75-96 wt % oil and 0-5 wt % additives; the soap content of special greases can be as high as 40 wt %. The soaps are produced from carboxylic acids or their glycerides (fats and oils) and alkali or alkaline earth hydroxides and alcoholates and are present in the greases in the form of characteristic fiber structures. The soap cations and anions are responsible for essential properties of soap grease.

The cation governs thickening ability, water resistance, melting point and thus dropping point. The consistency of the grease increases with increasing soap content. The chain length of the fatty acids has an influence on the solubility and the surface properties of the soaps in the oils. Very long as well as short fatty-acid chains affect negatively the thickening ability of soap: in the case of long-chain fatty acids, this is due to the good solubility of the soaps, in the case of the short-chain acids to the poor solubility of the soap. Maximum thickening is generally achieved with fatty acids with 18 C atoms. Branching of the alkyl chain in the fatty acid molecule lowers the melting point of the soaps and thus reduces the thickening effect; on the other hand, due to their high polarity and depending on their position in the molecule, hydroxy groups increase the melting points and thus the thickening effect.

Soaps of unsaturated fatty acids are better soluble in mineral oils, and thus reduce thickening effect and dropping point. The lower oxidation stability of the unsaturated fatty acids limits their applications. Today, the most important greases are those based on calcium and lithium soaps, while an importance of aluminum, barium and sodium-soap greases has decreased.

2.5.2.2 Mixed soap greases

Mixtures of simple soap greases with different cations, e.g. sodium/calcium, lithium/calcium or sodium/lithium/calcium, are known as mixed soap greases. Their properties depend on proportions of components in the mixture. Thus, an addition of calcium soaps to sodium soap greases improves poor water resistance of the sodium soap greases, and reduces the cost. Ca-Na soap greases can be used at higher temperatures than the calcium soap greases. Li-Ca soap greases have a better water resistance than the pure lithium soap greases, and their raw material costs are lower. The dropping point of 150 ^{o}C is significantly higher than that of the calcium soap grease. The effect of the mixing ratio of the soaps on properties (e.g. dropping point) must be taken into account when formulating such greases.

In the manufacture of mixed soap greases, one base is usually reacted *in situ* with fatty acids after which the others are added, the soaps obtained in this way are then dissolved in the oil by further heating. Simple mixing of finished simple soap greases at room temperature gives greases with less stable properties.

2.5.2.3 Complex soaps

According to ASTM, the soap crystals or soap fibers in a complex soap are formed by co-crystallization of two or more compounds. Metal soaps of the higher fatty acids (e.g. metal stearate) can form so-called complex soaps with the metal salts of short-chain organic acids (e.g. acetic acid) or inorganic salts (e.g. carbonates). This reaction alters typical grease parameters, and usually manifests itself by a considerable rise of the dropping point.

Lubricating greases containing of complex metal soaps, synthetic oils or mineral oils and additives are prepared by various procedures. They represent a significant progess in grease technology since they can satisfy difficult requirements better than the conventional greases, particularly at high temperatures.

Among the multitude of the theoretically possible complex soap greases, those with thickener systems based on complex aluminum, barium, calcium, lithium and sodium soaps have gained prominent importance.

2.5.2.4 Other thickeners

A multitude of lubricating greases are available with thickeners other than those described above; they are characterized in the first approximation by the thickeners used.

(i) Synthetic soap-like salts: alkali and alkaline earth salts of terephthalic acid, sodium salts of sebacic acid N-laurylamide, N-octadecyl terephththalate or N-lauroyl-6-aminocaproate.

(ii) Salts of acids that contain no carboxyl groups: calcium salt of N-stearoylsulfanilic acid, lithium propylphosphate, lithium stearamidomethane phosphonate. Some metal alkylthiophosphates serve as thickeners as well as EP additives.

(iii) Inorganic thickeners; silica (precipitated or finely dispersed from the gas phase), e.g. Aerosil which can be rendered hydrophobic by treatment with diisocyanates or epoxides to improve its water resistance. Organophilic bentonites (montmorillonite, hectorite), obtained by exchange of Na ions with quaternary ammonium ions.

(iv) Pigments; alizarin, anthraquinone, indigo, azo, indanthrene and phthalocyanine dyestuffs and ultramarine blue are used mainly for silicone greases.

(v) Polymers: linear, branched and partially branched polyethylenes, isotactic polypropylenes, poly-1-butenes and poly-(4-methyl-1-pentenes), alkyl-acrylate-acrylamide copolymers, condensation products of alkylphenol, fatty acid and formaldehyde, alkylhydroxyethyl cellulose and polyureas.

At present, the greatest attention is paid to the organophilic bentonites and polyureas; greases based on these products and mineral or synthetic oils are particularly suitable for use at high temperatures where they can be superior to the normal greases. Greases prepared with carbon black or colloidal silica serve for the lubrication of hot, dust-exposed open gears (e.g. rotary tubular kilns). Organic thickeners are used in silicone oils for the manufacture of high temperature greases; however, they can easily cause fouling of machine parts [1].

2.5.3 Additives

Additives are used to a limited extent in greases. Two common are rust inhibitors and anti-oxidants. Some greases have very little natural rust-preventive properties unless an inhibitor is added. Oxidation is the worst enemy of grease. At low temperatures, oxidation is slow, and a grease retains its lubricating ability for rather long periods. As temperatures increase, however, the rate of oxidation increases, and the period of usefulness of the grease is decreased.

Many greases may also contain extreme-pressure or anti-wear additives to improve their performance under extreme conditions [5].

2.6 Manufacturing processes

Most greases are made by a batch production technique in kettles ranging in size from half a ten tons. Modern kettles are jacketed vessels with provision for heating and cooling the contents. They contain stirring and scraping paddles, and are often fitted with an external pumping system to give bottom to top circulation, thus ensuring good mixing, and heat transfer from the kettle walls to the contents. The whole manufacturing process can be performed in an open kettle at atmospheric pressure, but it is more common to use closed kettles (autoclaves), operating at up to

10 bars, for the saponification stage, then to transfer the product to open kettles for cooling. This is a much quicker method of manufacture, and one autoclave can frequently be used in conjunction with several open kettles. A grease plant of this type is shown in Figure 2.1 .

Recently, continuous production techniques have been developed for soap thickened grease manufacture. In one process, all the heat required is supplied to the oil alone. The saponification takes place in a reaction vessel subject to expansion chamber to flash off the water. Subsequent cooling is achieved by final products tends to contain very little air compared with conventionally made grease. This manufacturing process is illustrated in Figure 2.2. It is attractive because the system holds only a small quantity of grease, and switching from one type to another entails much smaller cleaning losses than in batch production.

Mills and homogenizers improve the distribution of the thickener in the oil, and help to produce a smooth and uniform material. In principle they function by forcing the grease through a narrow aperture at a high shear rate. High speed mills have a gap of up to 600 μm between a stator and a rotor which rotates at 2000 to 3000 rev/min. Homogenizers are reciprocating pumps which are used to force the grease through narrow orifices at pressures up to 200 bars [3].

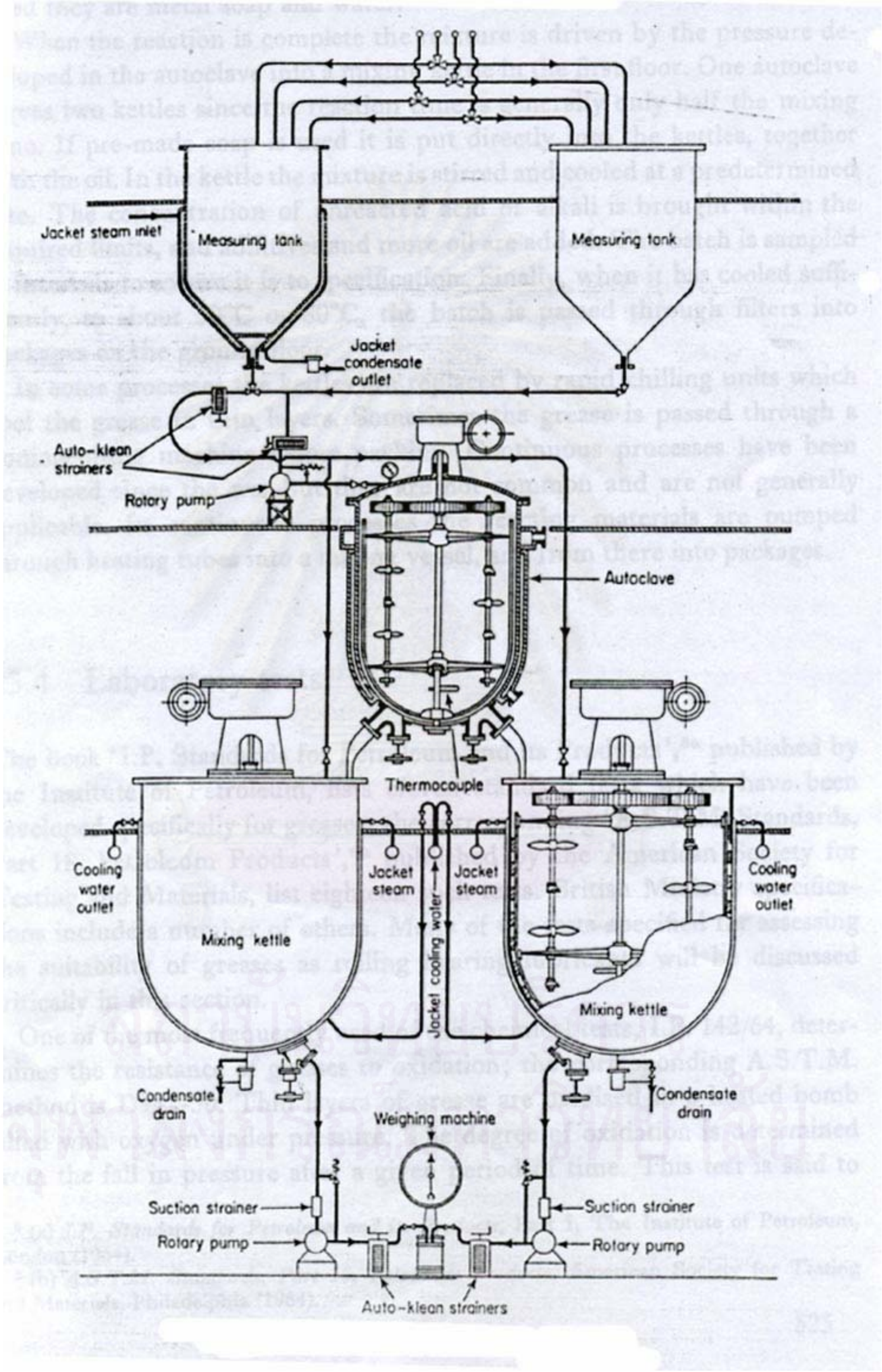


Figure 2.1 Typical layout of grease plant [20]

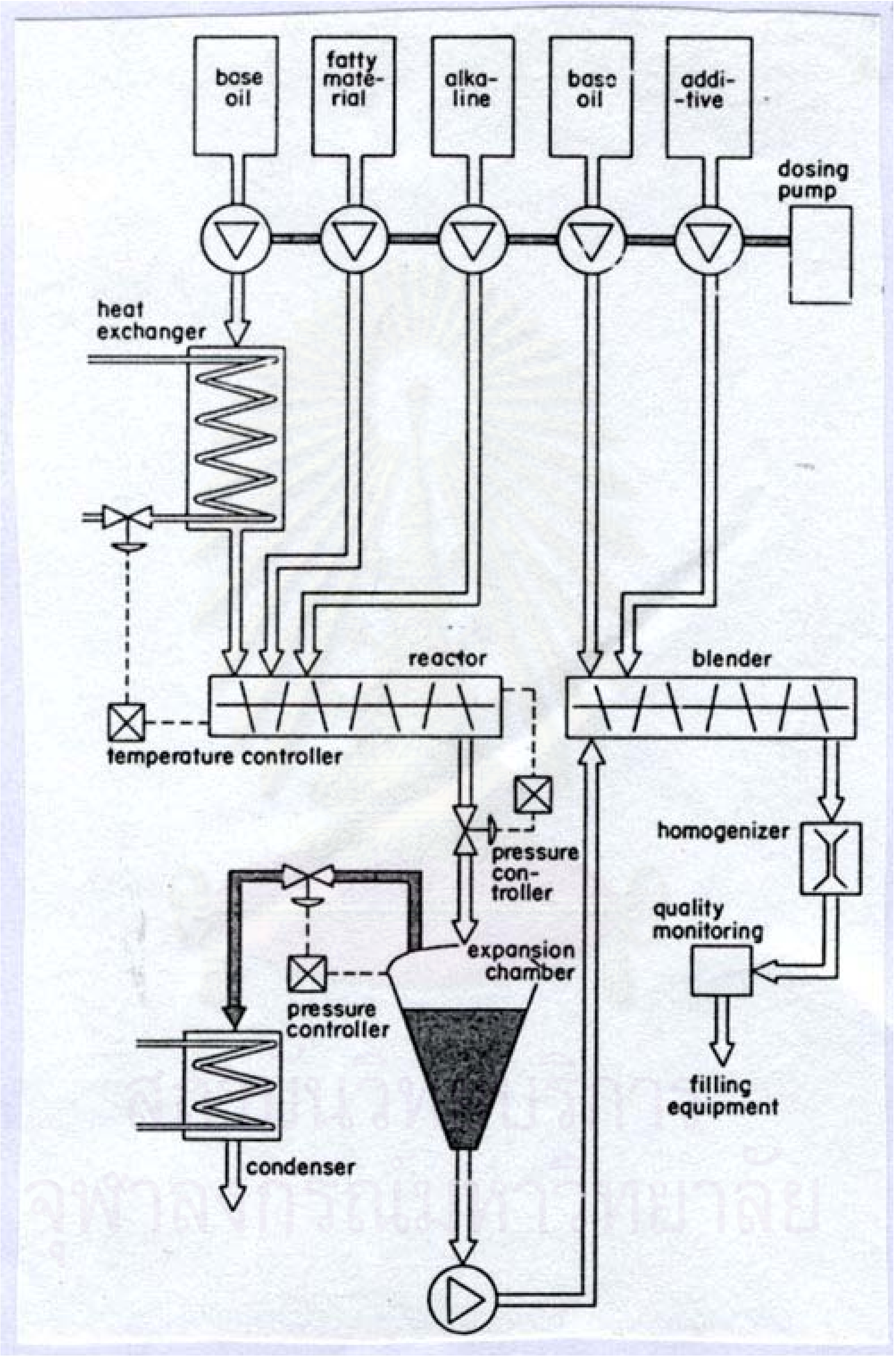


Figure 2.2 Continuous unit flow diagram [2]

2.7 Texture and structure

The flow characteristics of lubricating greases can be related to differences in the structure. In order to obtain a grease structure, the thickener must not be truly dissolved in the oil nor form a colloidal dispersion; it must be present as a separate phase with a special network [1].

Textures like the appearance and feel of greases. A grease may be described as smooth, buttery, fibrous, long- or short-fibered, stringy, tacky, etc. which can be seen under an electron microscope as shown in Table 2.3 and Figures 2.3-2.6. These characteristics are influenced by the viscosity of the fluid, types of thickener, proportion of each component, the presence of certain additives, and process of manufacturing. There are no standard test methods for quantitative definition of these properties. Texture and structure are factors in the adhesiveness and ease of handling of a grease [4].

Soap thickened greases contain a network of randomly oriented fibers up to 25 µm long. The fibers are formed by the controlled crystallization of soap prepared by reacting alkali or alkaline earth metal with a fatty acid. Oil is retained within this structure mainly by capillary forces in the interstices between the fibers. The alkali component may be calcium, sodium, lithium, barium, or aluminium, whilst the fatty acids are usually in the C_{10}-C_{30} range, and include mono-, di- and tri-unsaturated acids.

Some non-soap grease thickeners are particulate materials such as carbon blacks, organobentonites, silicas, terephthalamates, phthalocyanine, and other organic dyes. The particles of these materials have large surface-to-weight ratios, and retain the oil by surface forces. Other non-soap thickeners are polymers such as polyethylene, polypropylene, and polyureas. There are believed to thicken by a fiber structure similar to soaps [2].

Table 2.3 Microstructures of grease thickeners [1]

Thickener	Mean Dimensions Diameter × Length(10^{-12}m)	Appearance	
		microscopic	macroscopic
Na soaps	1×100	Long fibers	Long fibers, stringy
	0.15×1.5	Short fibers, short threads	Short fibers, smooth
Li soaps	0.2×25	Long fibers; spirals, mostly double	Medium fibers
	0.2×2	Short fibers, rod clusters	Short fibers, smooth
Ca soaps	0.1×1	Fine threads, short rings	Short fibers, smooth
Al soaps	0.1	Spheres	Short fibers, smooth
Organophilic bentonites	0.1×0.5	Platelets, card house structure	Short fibers, smooth

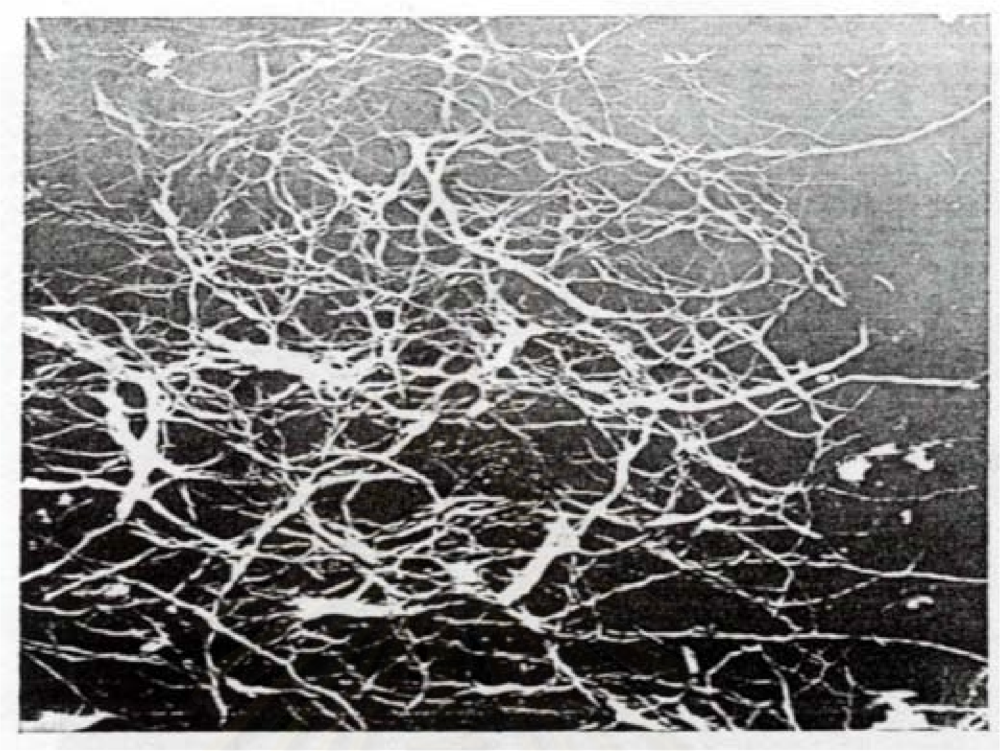


Figure 2.3 Electron micrograph of a lithium hydroxystearate grease [20]

Figure 2.4 Electron micrograph of a calcium stearate showing flat and spiral fibers [20]

Figure 2.5 Electron micrograph of an aluminium stearate grease [20]

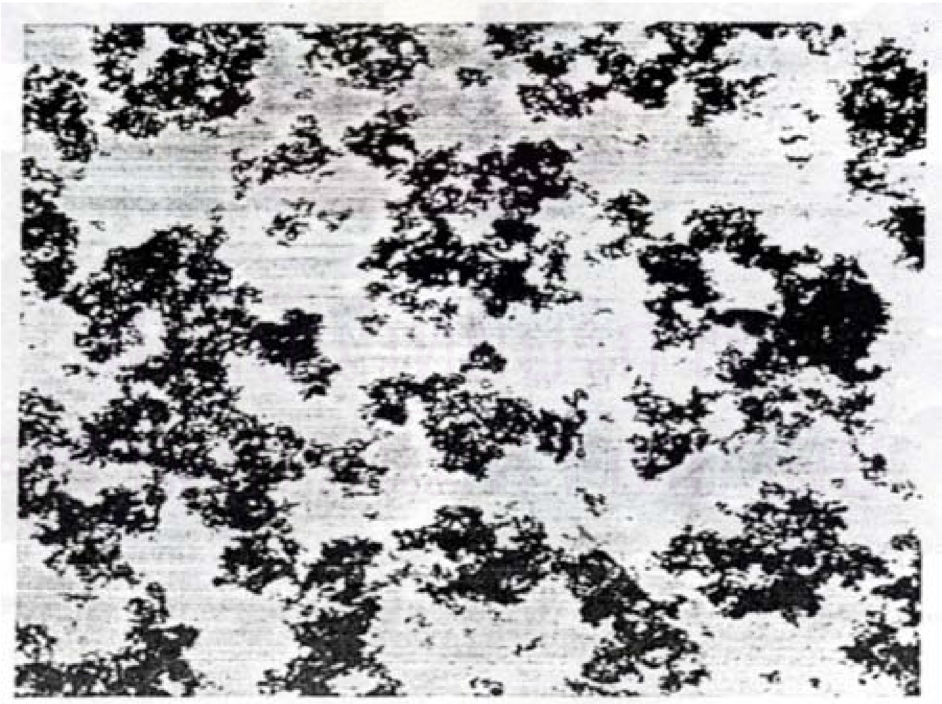


Figure 2.6 Electron micrograph of a silica microgel grease [20]

2.8 Grease testing

Many of the previous grease properties are determined by methods which have been standardized or otherwise accorded with industrial recognition. These, in conjunction with simulated performance tests, permit some approximate judgment for the proper selection of greases for a given application. They are, however, not considered to be replacements for, or equivalent to, longtime service tests [4].

Appendix A shows some of the more important tests identified as to sponsor and title [1]. An idea of the usable temperature range of average lubricating greases containing different thickening agents is given in Table 2.4 [8].

Table 2.4 Performance characteristics of different type of lubricating greases [8]

Type of thickener	Max cont. usable temp,^{o}F	Pump ability at 32^{o}F	Low-temp starting torque	Water resistance	Worked stability	Service life
Soap base:						
Al	175	Fair	Medium	Fair	Poor	Short
Br	350	Fair	Medium	Good	Good	Moderate
Ca	175	Good-fair	Medium-low	Good	Fair	Moderate
Ca complex	250	Fair	Medium-low	Good	Fair	Moderate
Li	300	Good or fair	Medium-low	Good	Excellent-fair	Moderate-long
Na	250	Good-poor	High-low	Poor	Excellent-poor	Moderate-long
Na-Ca	250	Good-fair	Medium-low	Fair-poor	Excellent-poor	Moderate-long
Nonsoap base:						
Bentonite	250	Good-fair	Medium-low	Good-fair	Poor	Moderate-short
Fine silica	250	Good-fair	Medium-low	Goor-fair	Poor	Moderate
Organic compounds	300	Good-fair	Medium-low	Good	Good	Moderate-long

2.9 Biodegradable grease

In view of stringent regulation, in some countries, as to discharge or plant wastes containing emulsified greases and oils, suggestions have been made that lubricating greases for some applications be biodegradable. Normally, waste lubricating grease will respond to separation from water, and thus there should be little necessity for supplying biodegradable products [9].

Biodegradation is defined as the chemical breakdown or transformation of a substance caused by organisms or their enzymes [6].

The grease and the environment working group within the European Lubricating Grease Institute (ELGI) developed a test specification for measuring grease biodegradability. This test is referred to as CEC L-33-A-94.

CEC L-33-A-94

A recent survey of so-called “biodegradable” lubricants indicated that the majority of lubricants manufacturers use the CEC L-33-A-94 (formerly CEC L-33-T-82) to justify their biodegradability claim. The test was designed by the Coordinating European Council (CEC) for “Biodegradability of Two-Stroke Cycle Engine Oils in Water”, and interestingly is only for determining primary biodegradation, as compared to ultimate biodegradation. For a test, infrared spectroscopy is used to measure the disappearance of certain hydrocarbons over a 21 days period when the lubricant is mixed with inoculum containing microorganisms [10]. Table 2.5 shows biodegrability of different oils.

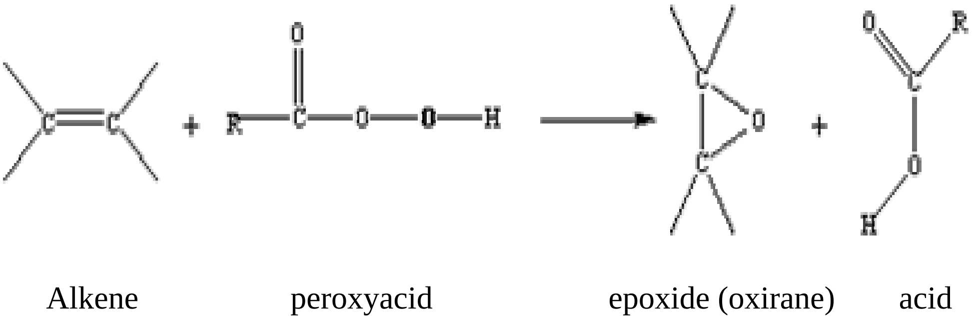
Table 2.5 CEC L-33T-82 test results for common oils

Oil type	Amount biodegraded (%)
Mineral oil	15-35
White oil	25-40
Natural & vegetable oil	70-100
PAO	5-30
Polyether	0-25
PIB	0-25
Phthalate & trimellitate esters	5-80
Polyols & diesters	55-100

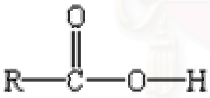
S. Harold, *Biodegradability: Review of the Current Situation*, 1993, The Lubrizol Corporation, p.4.

2.10 Epoxidation

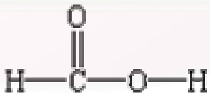
When speak into the oxidation of alkenes, we usually mean the reactions of alkenes that form carbon-oxygen bonds. These reactions are particularly important because many of the common functional groups contain oxygen, and alkene oxidations are some of the best methods for introducing oxygen into organic molecules. We consider methods for epoxidation, hydroxylation, and oxidative cleavage of the double bonds of alkenes.



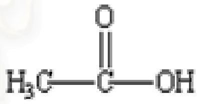
An epoxide is a three-membered cyclic ether, sometimes called an oxirane. Epoxides are valuable synthetic intermediates, used to convert alkenes to a variety of other functional groups. An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a -O-O- (peroxy) linkage. The epoxidation of an alkene is clearly an oxidation since an oxygen atom is added. Some commom peroxyacids (sometimes called peracids) and their corresponding carboxylic acids are shown below.


$R-\overset{\overset{O}{\|}}{C}-O-H$

carboxylic acid


$H-\overset{\overset{O}{\|}}{C}-O-H$

formic acid


$H_3C-\overset{\overset{O}{\|}}{C}-OH$

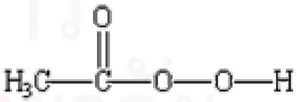
acetic acid


$R-\overset{\overset{O}{\|}}{C}-O-O-H$

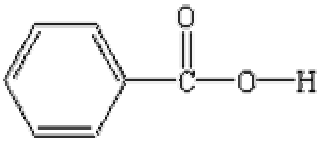
peroxyacid


$H-\overset{\overset{O}{\|}}{C}-O-O-H$

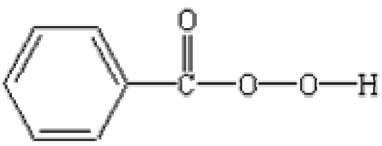
peroxyformic acid


$H_3C-\overset{\overset{O}{\|}}{C}-O-O-H$

peroxyacetic acid

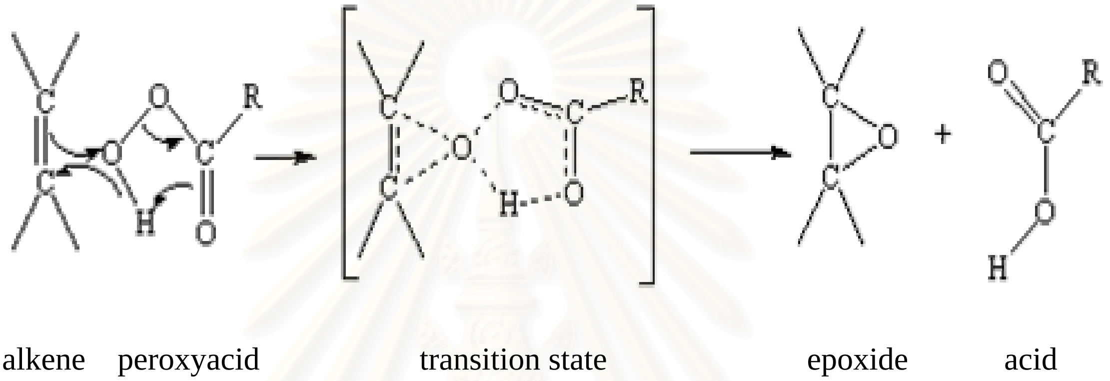


benzoic acid



peroxybenzoic acid

A peroxyacid epoxidizes an alkene by a concerted electrophilic reaction where several bonds are broken and several bonds are formed at the same time. Starting with the alkene and the peroxyacid, a one-step reaction gives the epoxide and the acid directly.



Synthesis and reactions of epoxides are unlike those of other ethers. Here we review the epoxidation techniques already covered, and see how the Williamson ether synthesis is applied to the synthesis of epoxides.

Peroxyacids are used to convert alkenes to epoxides. Since the peroxyacid is strongly acidic, the epoxide opens to a glycol. Therefore, a weak peroxyacid is used to make an epoxide

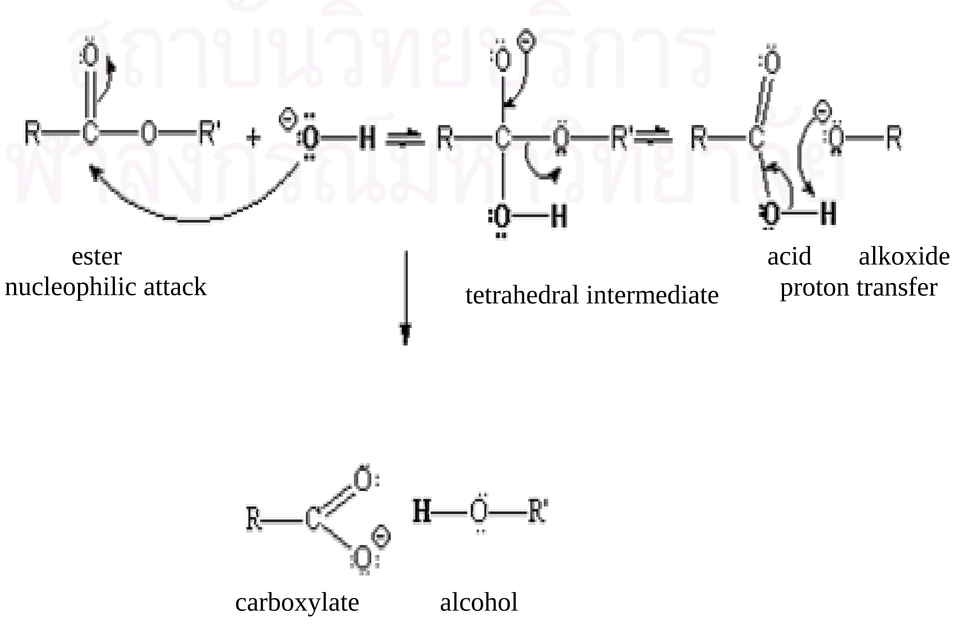
The epoxidation takes place in a one-step, concerted reaction that maintains the stereochemistry of any substituents on the double bond.

2.11 Saponification

Saponification was discovered, when it was found that a curdy material resulted when animal fat was heated with wood ashes. Alkaline substances in the ashes promoted hydrolysis of the ester linkages in the fat. Soap is currently made by boiling animal fat or vegetable oil with a solution of sodium hydroxide.

The term saponification (Latin, saponis, “soap”) literally means “the making of soap.” Soap is made by the basic hydrolysis of fats, which are esters of long-chain carboxylic acids (fatty acids) with the triol glycerol. When a fat is hydrolyzed by sodium hydroxide, the resulting long-chain carboxylate salts are what we know as soap.

The basic hydrolysis of esters, called saponification, avoids the equilibrium of the Fischer esterification. Hydroxide ion attacks the carbonyl group to give a tetrahedral intermediate. Expulsion of an alkoxide ion gives an acid, and a fast proton transfer gives an carboxylate ion and an alcohol. This strongly exothermic proton transfer drives the saponification to completion. Notice that a full mole of base is consumed to deprotonate the acid [12].



2.12 Literature reviews

In 1978, Grasshoff [13] studied biodegradable lubricating grease composition comprising an emulsion of vegetable-derived gel, water and a lubricant from the class of natural oils and fats.

In 1986, Iseya et al. [14] studied a lithium-soap grease which comprises: adding a hydroxy-fatty acid having from 12 to 24 carbon atoms, and a dicarboxylic acid having from 8 to 10 carbon atoms to a base oil (I) having an aniline point of from 110 to 130°C. at a temperature less than 100°C. with stirring to prepare a uniform dispersion of said acids in the base oil (I); adding lithium hydroxide to said uniform dispersion with stirring; reacting said acids and tithium hydroxide and dehydrating by heating to a temperature of 195 to 210°C.; cooling the reaction mixture to a temperature not higher than about 160°C. at a cooling rate of from about 20 to 80° C./hour; and adding a base oil (II) having an aniline point of from 130 to 140° C. to the reaction mixture for a period of from 10 seconds to 30 minutes in an amount so that the weight ratio of the base oil (I) to the base oil (II) is from 30:70 to 60:40 and the resulting mixture of the base oils (I) and (II) has a dynamic viscosity as determined at 100°C. of from 5 to 50 centistokes and an aniline point of from 125 to 135° C. to produce said lithium-soap grease.

In 1996, Moore [15] studied an optical fibre cable comprises a vegetable oil grease as a water blocking agent. The oil may be palm, corn, linseed, sunflower, coconut, olive or castor oil. The oil may be mixed with a gelling agent eg. silica or powdered clay to make the grease. The cable may comprise a tube or sheath of polyethylene or polypropylene or an elongate core having slots for optical fibres.

In 1997, Wiggins [16] studied environmentally friendly lubricating grease composition as well as several processes for preparing the grease composition is described which comprises (A) a base oil wherein the base oil is a natural oil synthetic triglyceride wherein alkyl group are aliphatic groups that contain from about 7 to about 23 carbon atoms and (B) a thickener wherein the thickener (B) is a reaction product of (B1) a metal based material and (B2) a carboxylic acid or its ester, wherein the metal based material (B1) comprises a metal oxide, metal hydroxide, metal carbonate or metal bicarbonate, wherein the metal is an alkali or alkaline earth metal and wherein the carboxylic acid (B2) is of the formula $R^1(COOR^2)_n$ where R^1 is an aliphatic or hydroxy substituted aliphatic group that contains from 4 to about 29 carbon atoms, R^2 is hydrogen or an aliphatic group containing from 1 to 4 carbon atoms and n is an integer of from 1 to 4, wherein the equivalent ratio of (B1):(B2) is from about 0.70-1.10 and wherein the weight ratio of the base oil to the sum of the metal based material and the carboxylic acid is from 50:50 to 95:5.

In 1997, Wiggins [17] studied an enhanced biodegradable grease composition that is environmentally friendly, as well as several processes for preparing the grease composition is described which comprises (A) a base oil wherein the base oil is a natural oil or synthetic triglyceride wherein alkyl groups are aliphatic groups that contain from about 7 to about 23 carbon atoms; (B) at least one performance additive comprising an alkyl phenol, a benzotriazole, or an aromatic amine; and (C) a thickener wherein the thickener (C) is a reaction product of (C1) a metal based material and (C2) a carboxylic acid or its ester. The enhanced biodegradable lubricating grease may also contain (D) a viscosity modifier, (E) a pour point depressant, or mixtures of (D) and (E).

In 1997, Eugene [18] studied lubricant compositions comprising biodegradable ester base stocks which are provided for water-cooled or air-cooled two-cycle engines. Grease compositions comprising biodegradable ester base stocks are provided for a wide variety of machinery including chain saws, truck chassis, and the rail, wheel flanges and switches on the railroads.

CHAPTER III

EXPERIMENTAL

3.1 Apparatus and Equipments

1. Fourier-Transform NMR Spectrometer Model AC-F 200 (200MHz); Bruker Spectrospin
2. Fourier-Transform Infrared Spectrophotometer; Model Impact410; Nicolet
3. Penetrometer; Stanhope-Seta Limited, England.
4. Dropping point tester; Petrotest
5. Water washout tester; Stanhope-Seta Limited, England.
6. Evaporation loss tester; Petrotest
7. A variable-speed stirring motor fitted with a four-blade stirring shaft; Kika Labortechnik RW 16 basic
8. Hotplate magnetic stirrer; Jenway 1100
9. Scanning electron microscope; JSM-5410 LV, Japan
10. Box Furnace; Gallenkamp size 2
11. Rolling

3.2 Chemicals

1. Commercial palm oil
2. 50% Hydrogenperoxide; Fluka
3. Glacial acetic acid; Merck
4. 98 % Sulfuric acid; Merck
5. Hexane; J.T. Baker
6. Anhydrous sodium sulfate: analytical grade; Merck
6. Calcium hydroxide; BDH
7. Lithium hydroxide; Fluka
8. Stearic acid: BHD
9. 12-Hydroxystearic acid; Fluka
10. Chloroform-d, analytical grade; Merck
11. 95% Ethanol
12. 95% Isooctane; Merck

3.3 Experimental procedures

3.3.1 Preparation of epoxidized palm oil

3.3.1.1 Synthesis of epoxidized palm oil [19]

Palm oil (150 g) were placed in a three-neck flask fitted with a reflux condenser and thermometer. Hexane (150 g), glacial acetic acid (21.30 g) and 50% sulfuric acid (3.15 g) were added, and the mixture was heated under constant stirring at 55 to 65 °C. Then 50% hydrogenperoxide (57.88 g) was slowly added over 1 hour period. The temperature was maintained at 60 to 65 °C for 6 hours. To stop the reaction, the phases were allowed to separate. The oil layer was washed with warm water until free of acetic acid. The oil layer was dried using anhydrous sodium sulfate, and then filtered. Hexane was removed by using a rotary evaporator. Epoxidized palm oil (132.93 g) as the clear yellow liquid was obtained. If left overnight, the epoxidized palm oil became white wax.

3.3.1.2 Characterization of epoxidized palm oil

The product, epoxidized palm oil, was a clear yellow liquid. The characterization of epoxidized palm oil was carried out by FT-IR, ^{1}H-NMR and ^{13}C-NMR. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording NMR spectra.

3.3.2 Preperation of thickening agents

3.3.2.1 Calcium epoxidized palm oil soap

Epoxidized palm oil (20 g) and a solution of calcium hydroxide (5 g) dissolved in a mixture of 20 ml water and 20 ml ethanol (cosolvent) were placed in a 100-ml bottom flask. The reaction mixture was refluxed with stirring for 1.5-2 hours. The reaction was stopped, collected the soap by filtration. The soap was washed with water and ethanol, and dried overnight to give yellowish solid (94% yield).

3.3.2.2 Calcium palm oil soap

Palm oil (20 g) and a solution of calcium hydroxide (5 g) dissolved in a mixture of 20 ml water and 20 ml ethanol (cosolvent) were placed in a 100-ml bottom flask. The reaction mixture was refluxed with stirring for 1.5-2 hours. The reaction was stopped, collected the soap by filtration. The soap was washed with water and ethanol, and dried overnight to give yellowish solid (92% yield).

3.3.2.3 Calcium 12-hydroxysterate soap

12-Hydroxystearic acid (13.42 g) was melted and added to a 25% solution of calcium hydroxide (1.80 g). The reaction mixture was heated and stirred with a mechanical stirring at over 100°C and water was removed over 30 min to give yellowish solid (94% yield).

3.3.2.4 Calcium stearate soap

Stearic acid (13.38 g) was melted and added to a 25% solution of calcium hydroxide (1.90 g). The reaction mixture was heated and stirred with a mechanical stirring at over 100°C and water was removed over 30 min to give yellowish solid (96% yield).

3.3.2.5 Lithium epoxidized palm oil soap

Epoxidized palm oil (20 g) and a solution of lithium hydroxide (3 g) dissolved in a mixture of 20 ml water and 20 ml ethanol (cosolvent) were placed in a 100-ml bottom flask. The reaction mixture was refluxed with stirring for 1.5-2 hours. The reaction was stopped, collected the soap by filtration. The soap was washed with water and ethanol, and dried overnight to give white solid (94% yield).

3.3.2.6 Lithium palm oil soap

Palm oil (20 g) and a solution of lithium hydroxide (3 g) dissolved in a mixture of 20 ml water and 20 ml ethanol (cosolvent) were placed in a bottom flask. The reaction mixture was refluxed with stirring for 1.5-2 hours. The reaction was stopped, collected the soap by filtration. The soap was washed with water and ethanol, and dried overnight to give white solid (93% yield).

3.3.2.7 Lithium 12-hydroxysterate soap

12-Hydroxystearic acid (14 g) was melted and added to a 25% solution of lithium hydroxide (1.16 g). The reaction mixture was heated and stirred with a mechanical stirring at over 100°C and water was removed over 30 min to give white solid (96%).

3.3.2.8 Lithium stearate soap

Stearic acid (14.02 g) was melted and added to a 25% solution of lithium hydroxide (1.22 g). The reaction mixture was heated and stirred with a mechanical stirring at over 100°C and water was removed over 30 min to give white solid (97% yield).

3.3.4 Preparation of grease

3.3.4.1 Grease from calcium epoxidized palm oil soap

Palm oil (50 g) and calcium epoxidized palm oil soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to over 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain light yellow semifluid.

3.3.4.2 Grease from calcium palm oil soap

Palm oil (50 g) and calcium palm oil soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to over 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain light yellow semifluid.

3.3.4.3 Grease from calcium 12-hydroxystearate soap

Palm oil (50 g) and calcium 12-hydroxystearate soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to over 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain light yellow semifluid.

3.3.4.4 Grease from calcium stearate soap

Palm oil (50 g) and calcium stearate soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to over 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain light yellow semifluid.

3.3.4.5 Grease from lithium epoxidized palm oil soap

Palm oil (50 g) was used as base oil and lithium epoxidized palm oil soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour.

The temperature was quickly raised to about 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain brownish red semifluid.

3.3.4.6 Grease from lithium palm oil soap

Palm oil (50 g) and lithium palm oil soap (14.29 g) were heated with and stirred a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to about 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain brownish red semifluid.

3.3.4.7 Grease from lithium 12-hydroxysterate soap

Palm oil (50 g) and lithium 12-hydroxystearate soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to about 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain brownish red semifluid.

3.3.4.8 Grease from lithium stearate soap

Palm oil (50 g) and lithium stearate soap (14.29 g) were heated and stirred with a mechanical stirring at 100°C for 1 hour. The temperature was quickly raised to about 200°C and water was removed until the mixture was a clear brown liquid; then it was cooled. The grease was formed and milled to obtain brownish red semifluid..

3.3.5 Investigation of properties

3.3.5.1 Scanning electron microscopy (SEM)

The thickening agents and greases were visually observed for their physical appearances. The fibers of the thickening agents and greases were observed using scanning electron microscopy (SEM).

Before SEM observation, the oil component (in grease) was removed by volatile solvent (pentane, petroleum ether), and their surface was subjected to gold coating by the use of an ion sputtering device after fixing on the specimen stub. Then, photographs of coated samples were taken using SEM. Properties of greases were measured by following the test methods as shown in Table 3.1 .

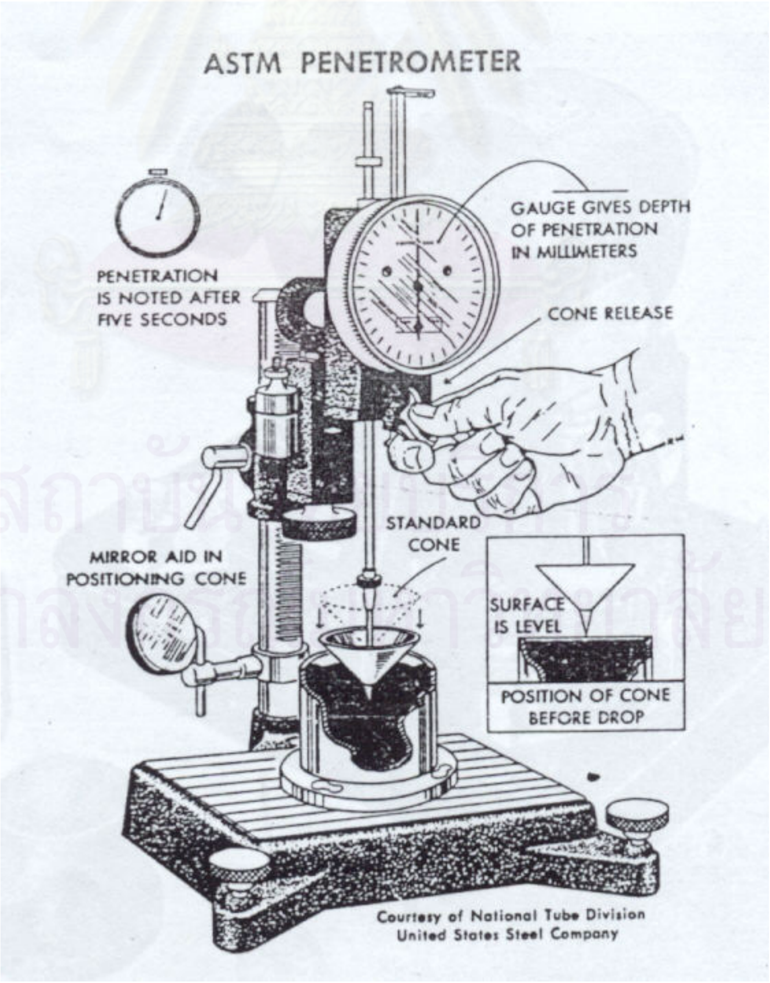
Table 3.1 Testing method of greases

Testing Method	Standard	Ca Grease	Li Grease
Penetration	ASTM D 217	3	3
Dropping Point	ASTM D 2265	3	3
Copper Strip Corrosion	JIS K 2220 Method A	3	3
Water Washout	ASTM D 1264	3	3
Ash	ASTM D 128	3	-
Determination of Water	TIS 1182	3	-
Evaporation Loss	JIS K 2220	-	3

3.3.5.2 Penetration

The greases were measured for their consistency by worked penetration for classified greases according to the National Lubricating Grease Institute (NLGI).

For worked penetration, about 500 g of greases were brought to 25 °C and placed in a worker cap. The greases were subjected to 60 double strokes in the grease worker. The penetration was determined immediately by releasing a cone assembly from the penetrometer and allowing the cone to drop freely into the greases for 5 second. The penetration value of each grease sample was determined in triplicate, and the average value was reported.



Courtesy of National Tube Division
United States Steel Company

Figure 3.1 Penetrometer

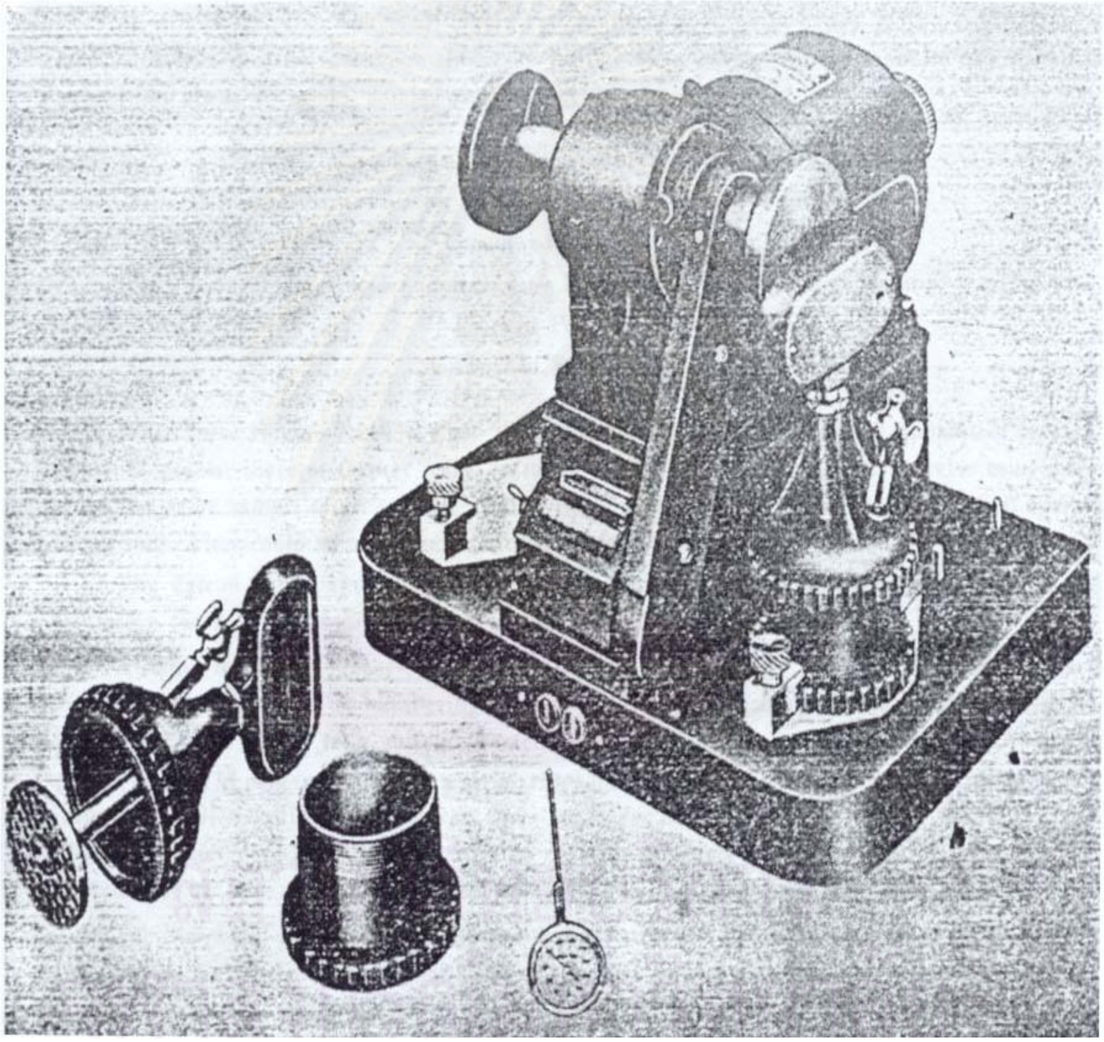


Figure 3.2 Grease worker

3.3.5.3 Dropping Point

The greases in a grease test cup was supported in a test tube placed in an aluminum block oven at a preset constant temperature. A sample thermometer was placed in the tube and so positioned that it measures the temperature in the sample cup without coming in contact with the greases.

As the temperature increased, at some point a drop of material will fall from the cup to the bottom of the test tube. The reading on the sample thermometer was recorded to the nearest degree as the observed dropping point. At the same time, the temperature of the aluminum block oven was also recorded to the nearest degree.

One third of the difference between the two values is the correction factor which is added to the observed value and recorded as the dropping point of the greases.

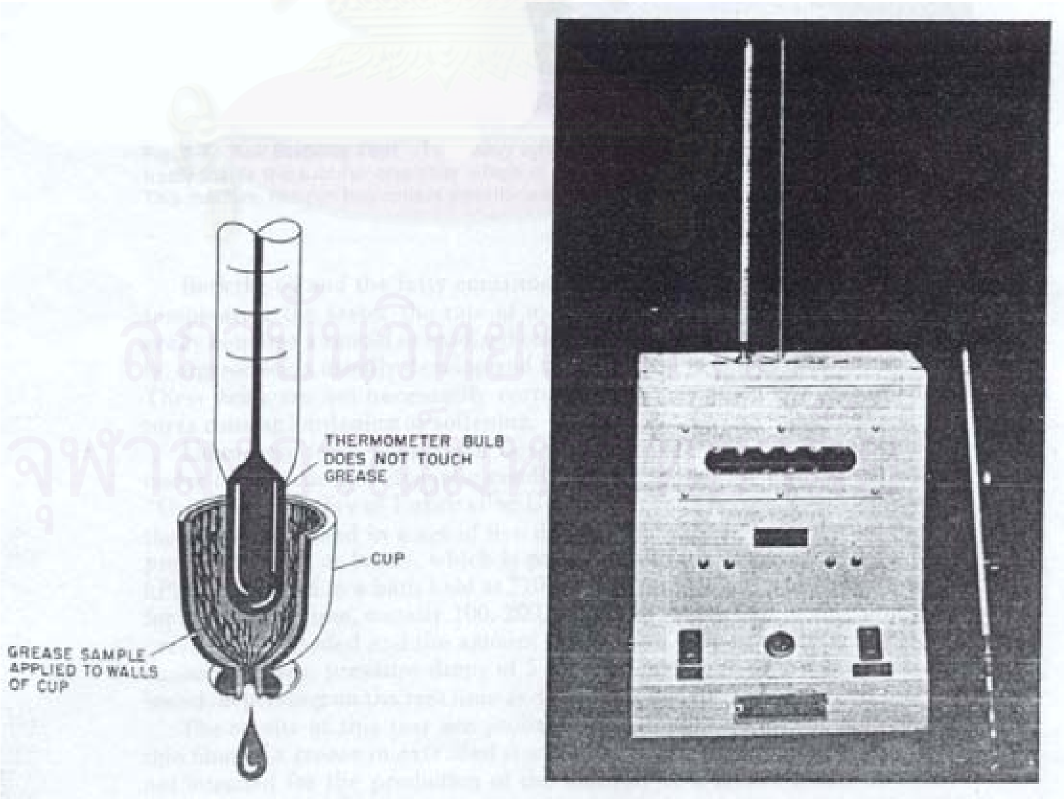


Figure 3.3 Dropping point tester

3.3.5.4 Copper Strip Corrosion

A polished copper plate was immersed in the epoxidized palm oil greases and, examined in the presence of a change in color to green or black or discoloration on the copper plate after keeping for 24 hours at room temperature.

3.3.5.5 Water Washout

The epoxidized palm oil greases were packed in a ball bearing. The bearing was then inserted in a housing with specified clearances, and rotated at 600 ± 30 rpm. Water, controlled at specified test temperature, impinges on the bearing housing at a rate of 5 ± 0.5 ml/s. The amount of grease washed out in 1 hour is a measure of the resistance of the grease to water washout.

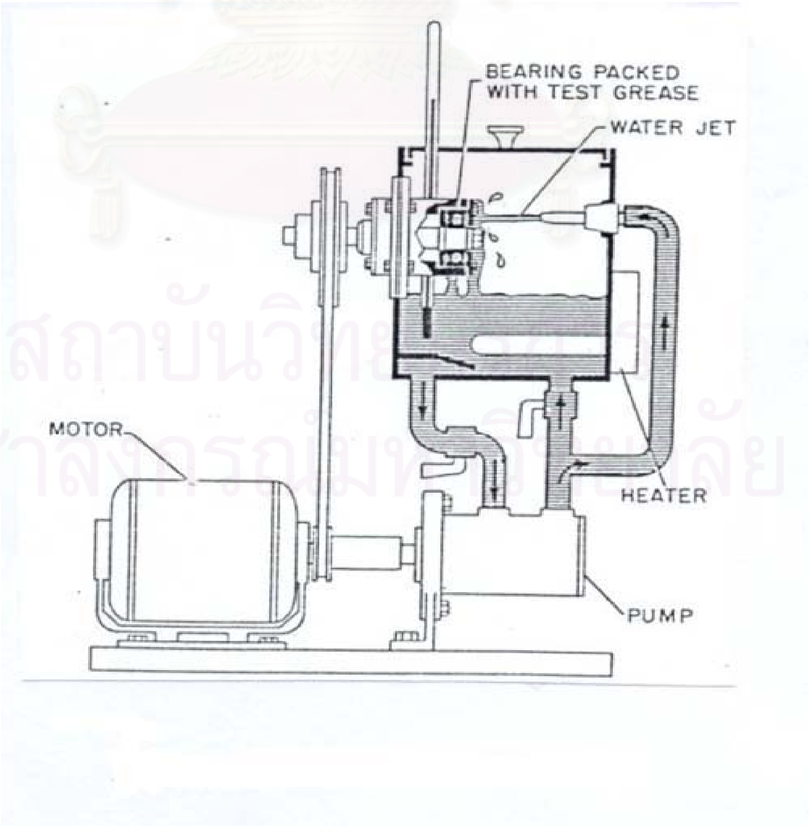


Figure 3.4 Water washout tester

3.3.5.6 Ash

The epoxidized palm oil calcium-grease 2 to 5 were placed in a weighed porcelain crucible and weighed the sample to the nearest 0.1 g. Slowly burned off the combustible matter, and finally ignited the residue until the ash was free of carbonaceous matter. The sample crucible was cooled and contented in a desiccator and weighed, reported the result as percentage of ash.

3.3.5.7 Determination of Water

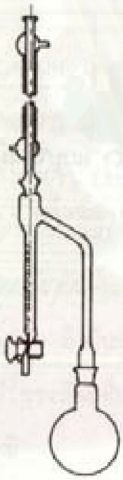


Figure 3.5 Distillation apparatus in determination of water.

The epoxidized palm oil calcium-grease (25 g) and 100 ml of isooctane were used. The amount of water was determined by distilling the mixture, the water being condensed and collected in a trap graduated from 0 to 10 ml in 0.1 ml division. In the latter instance, the reading gives the percent of water by volume directly, while with grease the reading multiplied by TIS 1182 gives the percent water by weight.

3.3.5.8 Evaporation Loss

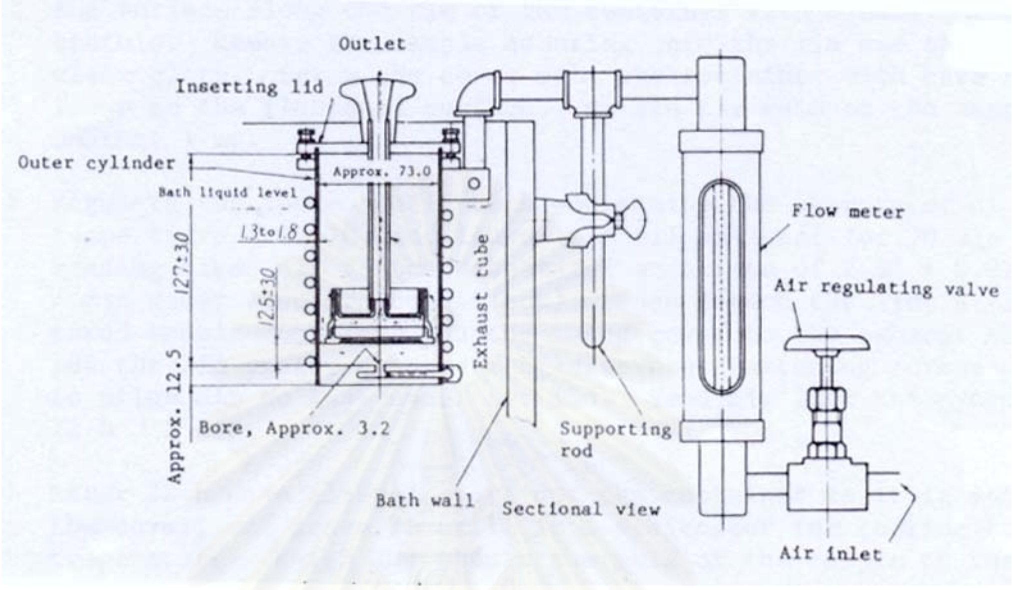


Figure 3.6 Evaporation loss tester

Hot air was applied to the surface of the epoxidized palm oil lithium-grease for 22 hours in a bath kept at a specified temperature (99^{o}C). The evaporation loss from the loss was calculated in the mass of the sample.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of epoxidized palm oil

4.1.1 Synthesis of epoxidized palm oil

Epoxidized palm oil could be synthesized by epoxidation of palm oil with peroxyacetic acid using 50% sulfuric acid as a catalyst. In this study, the product (89% yield) obtained was a clear yellow liquid.

4.1.2 Characterization of epoxidized palm oil

Epoxidized palm oil was characterized by infrared spectrophotometry (IR) and nuclear magnetic resonance spectroscopy (NMR).

4.1.2.1 FT-IR Spectra

FT-IR spectra of palm oil and epoxidized palm oil are shown in appendix B (Figures B-1 – B-2). Table 4.1 lists important absorption peaks and their assignments. In a comparison of the IR spectra of epoxidized palm oil and palm oil, the absorption peak at wave munber 834 cm^{-1} for epoxidized palm oil was observed due to the presence of epoxy ring, while there was no peak at this wave number for palm oil. The peak a ~1650 cm^{-1} for palm oil was observed due to the presence of double bond, while no peak at ~1650 cm^{-1} epoxidized palm oil.

Table 4.1 FT-IR data of palm oil and epoxidized palm oil

Vibration Assignments	Wave number (cm^{-1})	
	Palm oil	Epoxidized palm oil
CH_2 rock	721	721
Epoxide ring	-	834
C-O stretch	1160	1160
CH_3	1376	1376
CH and CH_2	1461	1466
C=C stretch	1650	-
C=O stretch	1744	1744
C-H stretch	2856	2847
	2922	2931

4.1.2.2 ^{1}H-NMR Spectra

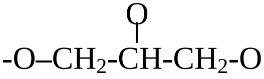
^{1}H-NMR spectra of palm oil and epoxidized palm oil are shown in Appendix B (Figure B-3 – B-4).

Signals between δ_H 0.81 to δ_H 2.31 ppm are belong to protons of long chain fatty acid of triglyceride. Signals between δ_H 4.00 to δ_H 4.30 ppm are belong to protons of glycerol moiety of triglyceride, and between δ_H 5.20 to δ_H 5.40 ppm are belong to HC=CH protons of long chain fatty acid groups.

For epoxidized palm oil in deuterated chloroform, the ^{1}H-NMR spectrum was nearly the same as that of palm oil; but the signals between δ_H 5.20 to δ_H 5.40 ppm belonged to HC=CH protons of long chain fatty acid are absent due to displacement of signals between δ_H 2.80 to δ_H 3.10 ppm which belonged to protons in epoxide group.

4.1.2.3 ^{13}C-NMR Spectra

^{13}C -NMR spectra of palm oil and epoxidized palm oil are shown in Appendix B (Figure B-5 – B-6).

The ^{13}C -NMR spectrum of palm oil in deuterated chloroform indicated the signals between δ_C 14.00 to 34.11 ppm which are belong to carbons of long chain fatty acid groups of triglyceride. The signals at δ_C 62.01 and δ_C 68.85 ppm referred to  $-O-CH_2-\overset{\overset{\displaystyle O}{|}}{C}H-CH_2-O$ carbons in the glycerol moiety of triglyceride. The signals between δ_C 127.83 to δ_C 130.05 ppm referred to C=C of long chain fatty acid groups and at δ_C 172.64 and δ_C 173.05 ppm referred to –COO- group in triglyceride.

For epoxidized palm oil in deuterated chloroform, its ^{13}C-NMR spectrum was nearly the same as that of palm oil, but the signals between δ_C 127.83 to δ_C 130.05 ppm referred to C=C in long chain fatty acid groups are absent due to displacement of epoxide groups at δ_C 54.04 and δ_C 61.96 ppm.

4.2 Preparation of thickening agents

Thickening agents of epoxidized palm oil were prepared by saponification of metal (Li and Ca) hydroxide with epoxidized palm oil.

Visual characteristics and scanning electron micrograph of thickening agents of epoxidized palm oil are summarized in Table 4.2. The results of visual characteristics indicate that the thickening agent prepared by calcium hydroxide appeared as yellowish soap as shown in Figure 4.1. The thickening agent prepared from lithium hydroxide resulted in white soap similar to that of calcium soap as shown in Figure 4.2.

Figure 4.1 Photograph of epoxidized palm oil calcium soap

Figure 4.2 Photograph of epoxidized palm oil lithium soap

4.3 Preparation of grease

Greases were prepared by blending of palm oil and 22% thickening agents. Greases obtained were yellow to brown semifluid.

4.4 Investigation of the grease properties

4.4.1 Scaning Electron Microscopy

Visual characteristics of epoxidized palm oil greases and scanning electron micrograph of thickening agents and epoxidized palm oil greases are summarized in Table 4.2.

The epoxidized palm oil grease prepared by calcium soap appeared as light yellow smooth and buttery semifluid as shown in Figure 4.3, and that of lithium soap appeared as reddish brown and buttery semifluid as shown in Figure 4.4. The results of scanning electron micrograph of the thickening agents which was spongy-like are shown in figures 4.5-4.6, and the epoxidized palm oil greases which were fibers are shown in Figures 4.7-4.8. These results of scanning electron micrograph were consistent with the lubricating greases reported by Mr R. J. Bird and Mr G. Rooney of Thornton Research Center that the fiber of lithium hydroxystearate grease is stringy fibers and the fiber of calcium stearate is flat and spiral fibers [20]. The grease fiber depend on type of soap and grease manufacture.

Table 4.2 Summary of visual characteristics and scanning electron micrograph of thickening agents and greases of epoxidized palm oil.

Characteristics	Ca -epoxidized palm oil			Li-epoxidized palm oil		
	Color	Observation	SEM	Color	Observation	SEM
Thickening agents	Yellowish white	Granule-like	Spongy-like	White	Granule-like	Spongy-like
Grease	Light yellow	Smooth and buttery	Flat fibres	Brownish red	Buttery	Stringy-finer fibres

Figure 4.3 Photograph of epoxidized palm oil calcium grease

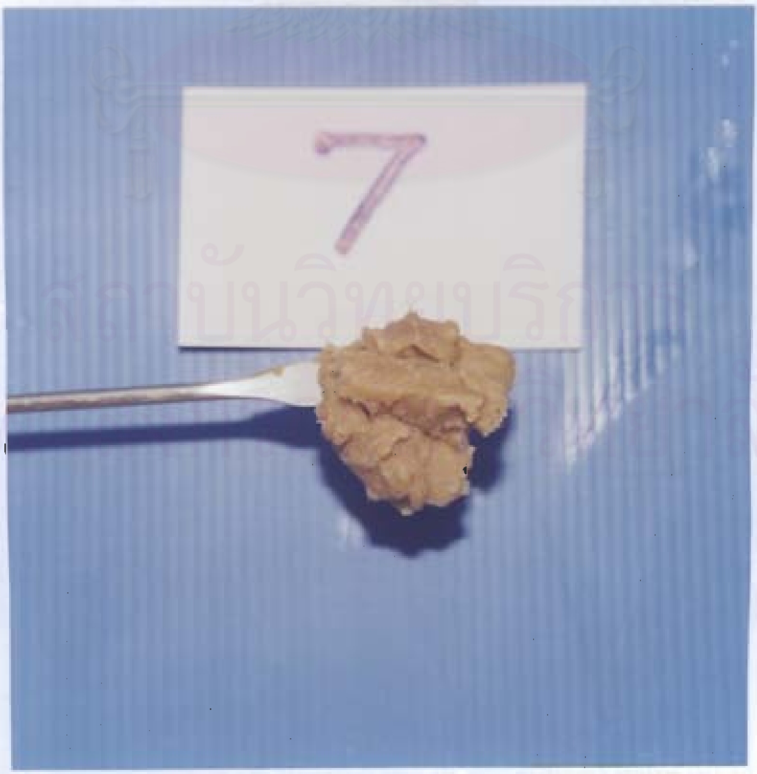


Figure 4.4 Photograph of epoxidized palm oil lithium grease

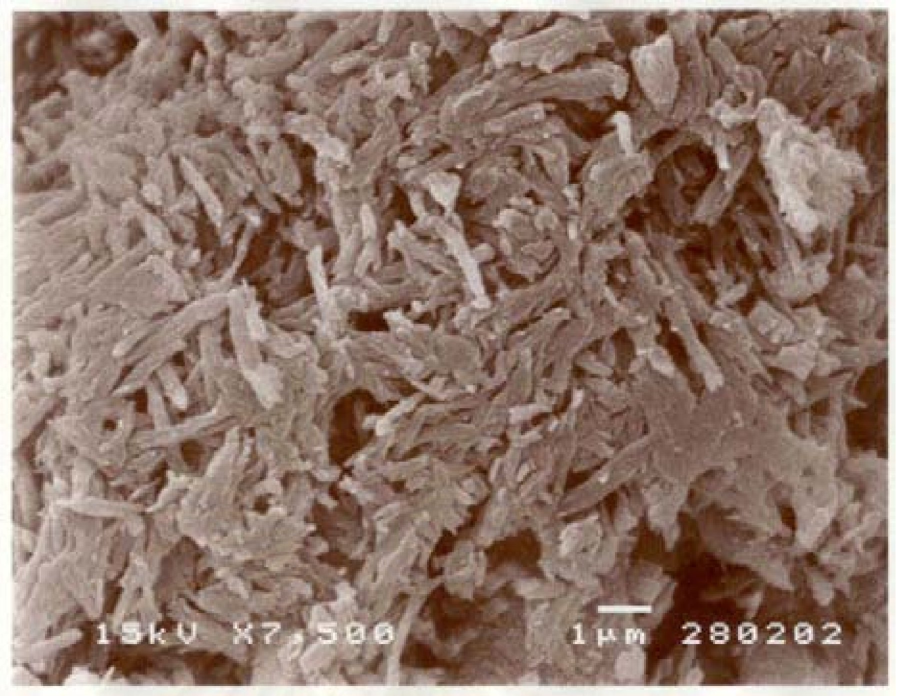


Figure 4.5 Scanning electron micrograph of epoxidized palm oil calcium soap

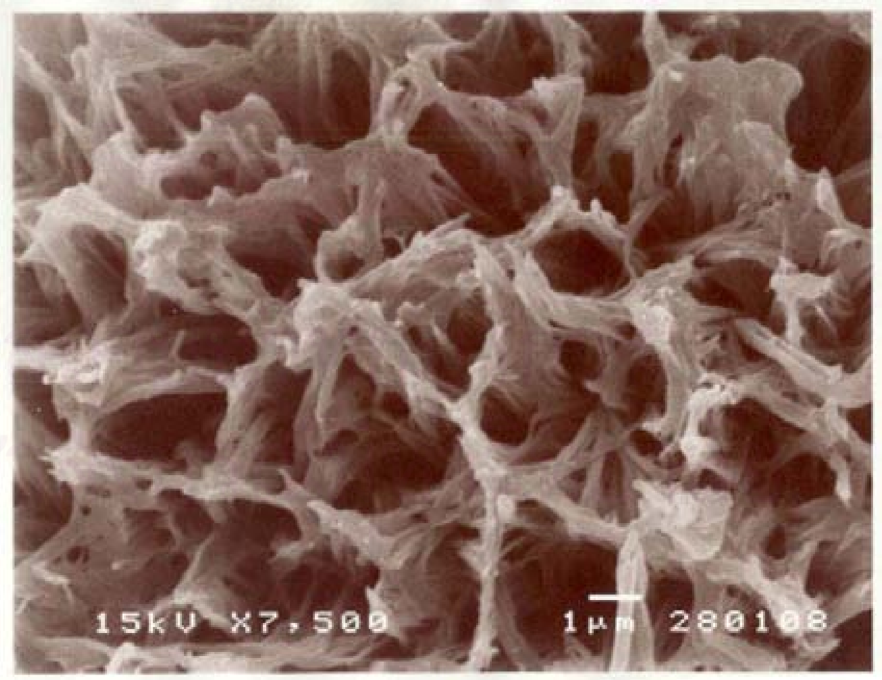


Figure 4.6 Scanning electron micrograph of epoxidized palm oil lithium soap

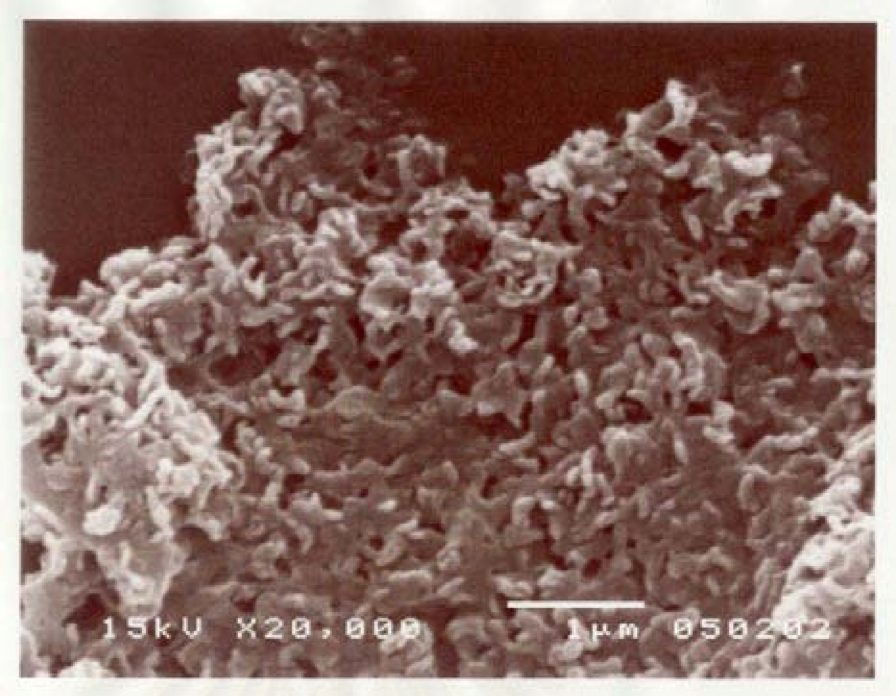


Figure 4.7 Scanning electron micrograph of epoxidized palm oil calcium grease

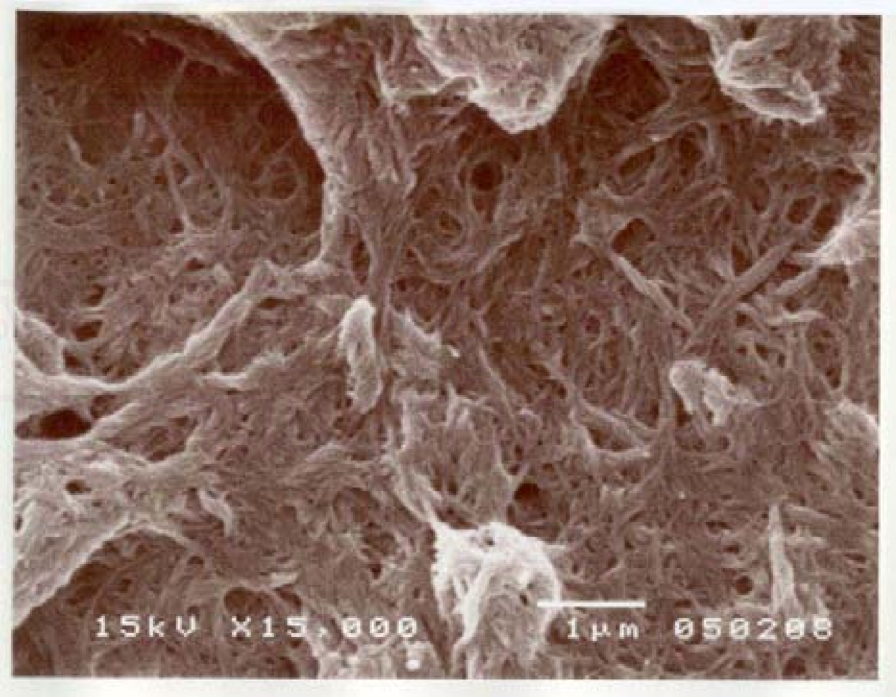


Figure 4.8 Scanning electron micrograph of epoxidized palm oil lithium grease

The Thai Industial Standard 713-2541 indicates the properties of grease which classified according to various uses. In this study, the properties of grease were compared with general greases obtained commercially using calcium soap and lithium soap . Properties are shown in table 4.3.

Table 4.3 The testing of greases follow TIS 713-2541

Testing Method	Standard	Ca Grease	Li Grease
Penetration	ASTM D 217	3	3
Dropping Point	ASTM D 2265	3	3
Copper Strip Corrosion	JIS K 2220 Method A	3	3
Water Washout	ASTM D 1264	3	3
Ash	ASTM D 128	3	-
Determination of Water	TIS 1182	3	-
Evaporation Loss	JIS K 2220	-	3

4.4.2 Penetration (ASTM D 217)

Consistency is defined as the degree to which a plastic material resists deformation under an application of a force. In the case of grease, it is a measure of the relative hardness or softness by the cone penetrometer after 60 double strokes. It is reported that the average value obtained in Tables 4.4-4.5 and Figure 4.1 as the worked penetration of the greases under test and classified according to NLGI Grade.

The greases have NLGI grade 1 to 3 (Figure 4.2) and the higher NLGI number is the lower the work penetration.

Table 4.4 Penetration of Ca grease

Ca Grease	Penetration				NLGI No.
	Unworked	Worked 1	Worked 2	Worked average	
12-Hydroxystearic acid	210	220	234	227	3
Epoxidized palm oil	226	257	265	261	2-3
Steric acid	258	272	287	279.5	2
Palm oil	287	313	317	315	1

Table 4.5 Penetration of Li grease

Li Grease	Penetration				NLGI No.
	Unworked	Worked 1	Worked 2	Worked average	
12-Hydroxystearic acid	218	223	247	235	3
Epoxidized palm oil	219	225	249	237	3
Steric acid	221	228	250	239	3
Palm oil	256	263	290	276.5	2

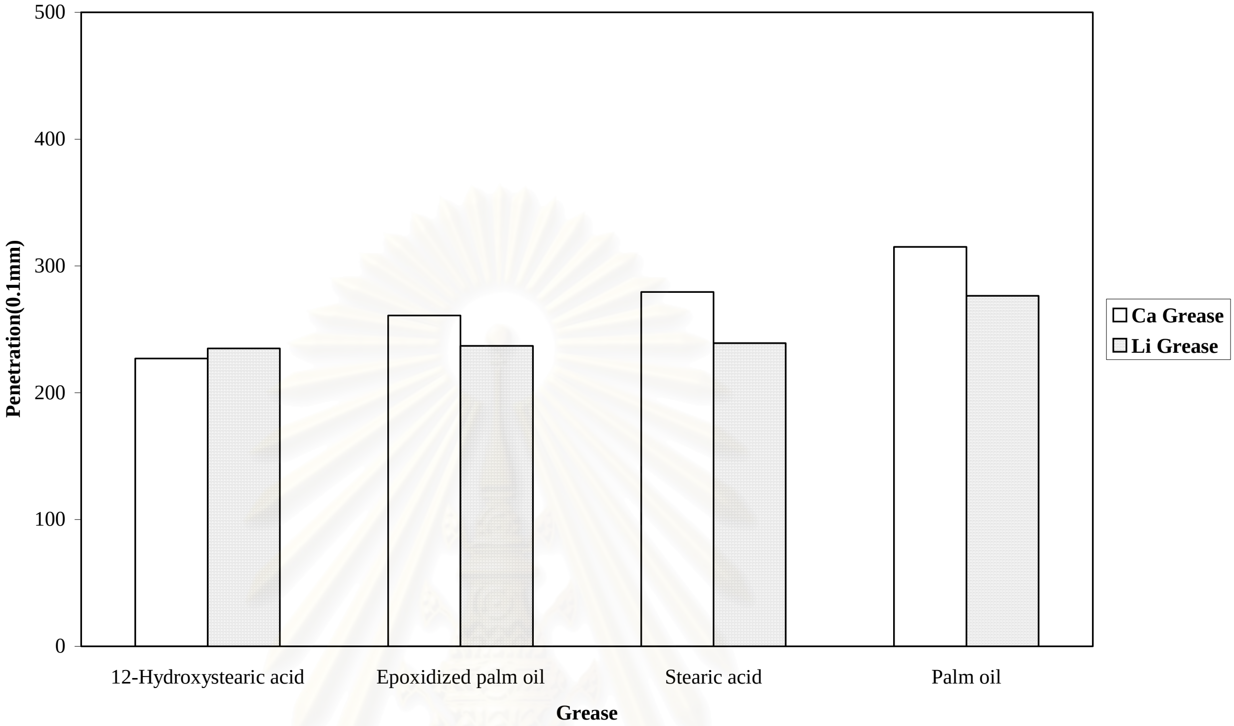
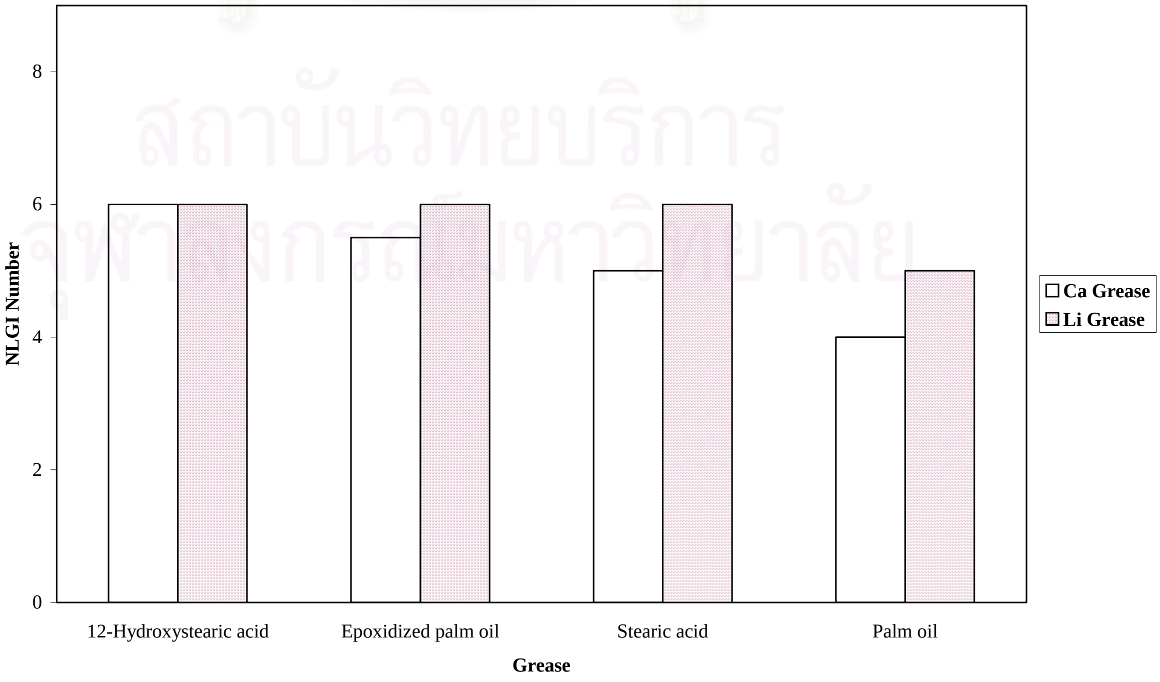


Figure 4.9 Worked penetration of epoxidized palm oil greases



In this study, the prepared greases are hard semifluid as minimum worked penetration as maximum NLGI number were arranged as follows 12-hydroxystearic acid, epoxidized palm oil, palm oil and stearic acid, respectively. The resulted calcium and lithium epoxidized palm oil greases were softer consistency than 12-hydroxystearic acid grease. This may be because the former two may contain some glycerol and mixed fatty acid soaps. However, the resulted calcium and lithium epoxidized palm oil greases were harder consistency than that of palm oil grease because they contained dihydroxy stearic acid. However, for the epoxidized palm oil calcium and lithium greases, the worked penetration were similar to those of the other greases. Thus, the epoxidized palm oil greases can be used similar to other prepared greases.

Figure 4.10 NLGI number of epoxidized palm oil greases

4.4.3 Dropping Point (ASTM D 2265)

The dropping point of a grease is the temperature at which it liquefied when heated and dropped from a cup through a bottom orifice. The dropping point of a grease is not considered to have any bearing on service performance other than that, at temperatures above the dropping point, the grease may be approached the operating limits of satisfactory performance. It is reported that the corrected dropping point and the aluminum block oven temperature immediately after the drop was observed and calculate for the dropping point as follows:

$$DP = ODP + [(BT - ODP) / 3]$$

Where:

DP = dropping point;

ODP = thermometer reading when the first drop reaches the bottom

of the test tube, and

BT = block temperature when the drop falls.

In this study, the calcium soap greases have dropping point range of 100-110 °C and the lithium soap greases have dropping point range of 189-205 °C as shown in Table 4.6-4.7 and Figure 4.3.

Table 4.6 Dropping point of Ca greases

Ca Grease	Dropping point						
	ODP 1	BT 1	DP 1	ODP 2	BT 2	DP 2	DP Av.
Stearic acid	107	120	111	102	120	108	109.5
Palm oil	94	121	103	94	121	103	103
12-Hydroxysteric acid	96	121	104	90	121	101	102.5
Epoxidized palm oil	95	120	103	90	120	100	101.5

Table 4.7 Dropping point of Li greases

Li Grease	Dropping point						
	ODP 1	BT 1	DP 1	ODP 2	BT 2	DP 2	DP Av.
Stearic acid	192	232	205	190	232	204	204.5
Palm oil	179	232	197	177	232	195	196
12-Hydroxysteric acid	170	232	190	171	232	191	190.5
Epoxidized palm oil	169	232	190	167	232	189	189.5

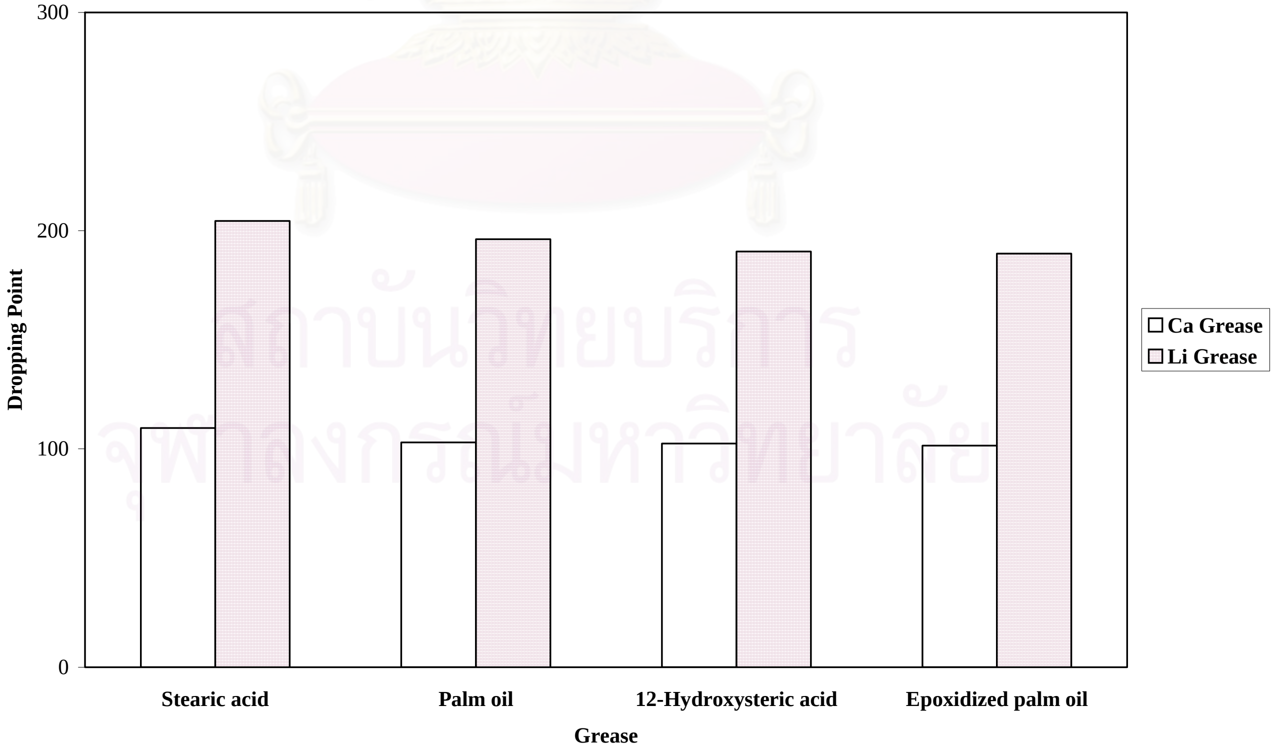


Figure 4.11 Dropping point of epoxidized palm oil greases

In this study, the results of dropping point at high temperature were arranged as follows: stearic acid, palm oil, 12-hydroxystearic acid and epoxidized palm oil, respectively. The cause is the difference of fatty thickener. However, the dropping point of calcium and lithium greases were similar to those of the other greases. Thus, the epoxidized palm oil greases can be in used similar application to that of the 12-hydroxystearic acid but the palm oil greases can be used in similar application to that of the epoxidized palm oil greases because of the near dropping point, easy preparation and low cost.

In this study, the epoxidized palm oil calcium and lithium greases were tested according to TIS 713-2541 (Table 4.3).

4.4.4 Copper Strip Corrosion (JIS K 2220 Method A)

A clean strip of mechanically polished pure copper sheet was submerged in the test material of epoxidized palm oil calcium and lithium soap, which was then maintained for 24 hours at room temperature.

The results of epoxidized palm oil calcium and lithium greases are the disappearance or unchange of the pure copper color to green or black on the copper plate in accordance with TIS 713-2541. Therefore, the greases are not corrosive with surface metal.

4.4.5 Water Washout (ASTM D 1264)

The amount of washed out grease in 1 hour was a measure of the resistance of the product. The test was determined for the ability of grease to remain in a bearing in the presence of water.

It is reported that the average of duplicate tests as the percentage weight of washed out greases at the test temperature which the bearing assembly and grease were dried. The results of epoxidized palm oil calcium grease was 1.06 % and lithium grease was 8.19 % . They were compared with TIS 713-2541 and it was found that the resistance of the washed out greases are quite low and within specification.

4.4.6 Ash (ASTM D 128)

The weight of the residue of epoxidized palm oil calcium grease is reported as percentage of ash was 1.38. The results of ash of epoxidized palm oil calcium grease was white because the ash contained alkaline earth metal and it was the most valuable indication of the presence of soap (or other additive material in the oil). The result was compared with TIS 713-2541, and it was not higher than specification

4.4.7 Determination of Water (TIS 1182)

It is reported that the amount of water was determined by distilling a mixture of the lubricant with a specified solvent. The water was condensed and collected in a graduated trap from 0 to 10 ml in 0.1 ml divisions.

Determination of water = $v/w \times 100$

Where, v : volume of storage (cm^3)

w : volume or mass of sample (cm^3 or g)

Normally, Ca grease contains water in its molecule and the excess water results in its stability, so it is necessarily to check the water content. The determination of water revealed that only trace of water is in epoxidized palm oil calcium soap, thus it has good stability when it was compared with specification in TIS 713-2541.

4.3.8 Evaporation Loss (JIS K 2220)

The result is calculated for the evaporation loss percentage according to the following formula and express as an average obtained by rounding off to two places of decimals from two test results of epoxidized palm oil lithium grease obtained as in table 4.8 for the same sample.

$$W_L = \frac{(W_S - W)}{W_S} \times 100$$

Where, W_L : evaporation loss percentage (mass%)

W_S : mass of samples before test (g)

W : mass of samples after test (g)

Table4.8 Evaporation loss of epoxidized palm oil lithium grease

Times	W_S	W	W_L
1	15.524	15.325	1.28
2	16.012	15.743	1.68
average			1.48

Normally, Li grease was used at high temperature condition, so it is necessary to check for the evaporation loss. The evaporation loss is 1.48%, therefore the epoxidized palm oil lithium grease is within the acceptable range of mass loss when it was compared with the specification in TIS 713-2541.

These properties of epoxidized palm oil calcium and lithium greases were compared with the specification in TIS 713-2541. It indicated that these greases were within the specification as shown in table 4.9-4.10.

Table4.9 The properties of calcium grease in TIS 713-2541

Testing Method	Calcium Grease	
	TIS 713	Results
1. Worked Penetration	No.2 (265-295)	No.2 (261)
2. Dropping Point	≥ 85°C	101°C
3. Copper Strip Corrosion	Disappearance	Disappearance
4. Water Washout	≤ 20 %	1.06 %
5. Determination of Water	≤ 2.5 %	Trace
6. Ash	≤ 3.5 %	1.38 %

Table4.10 The properties of lithium grease in TIS 713-2541

Testing Method	Lithium Grease	
	TIS 713	Results
1. Worked Penetration	No.3 (220-250)	No.3 (237)
2. Dropping Point	≥ 180°C	189.5°C
3. Copper Strip Corrosion	Disappearance	Disappearance
4. Water Washout	≤ 20 %	8.19 %
5. Evaporation Loss	≤ 2.0 %	1.48 %

The important properties, penetration and dropping point, were compared with the literature and commercial grease of PTT as shown in Tables 4.11 – 4.12.

Table 4.11 Comparison of the important properties of calcium greases

Ca Grease	Ref.17	Ref.18	Chasis	Result
Base Oil	Sunyl 80 oil	Blended rapeseed oil	Mineral oil	Palm oil
Thickener	12-hydroxystearic acid	12-hydroxystearic acid	Ca soap	Epoxidized Palm oil
Penetration(0.1mm)	260	254	-	261
NLGI Number	2-3	2-3	2	2
Dropping Point(^{O}C)	121	106	101	101

For the epoxidized palm oil calcium grease, the penetration and dropping point were found to be similar to those of the other literature and commercial greases. The different result of penetration of each grease was due to content of thickener. The penetration or NLGI number was not clearly related with dropping point. Similar to the epoxidized palm oil calcium grease, the epoxidized palm oil lithium grease gave the dropping point similar to that of the other literature and commercial greases but the penetration was quite different.

Table 4.12 Comparison of the important propertiesof lithium grease

Li Grease	Ref.17	Ref.18	Ref.19	Multipurpose	Result
Base Oil	Sunyl 80 oil	Blended sunyl 80 oil	Blended synthetic oil	Mineral oil	Palm oil
Thickener	12-Hydroxy stearic acid	12-Hydroxy stearic acid	12-Hydroxy stearic acid	Li soap	Epoxidized palm oil
Penetration(0.1mm)	331	279	420	-	237
NLGI Number	1	2	00	2,3	3
Dropping Point(^{O}C)	187	200	180	190	189.5

From Tables 4.11 – 4.12, the penetration and dropping point of epoxidized palm oil calcium and lithium greases were similar to those of the literature and commercial greases. In case of base oil, the literature and commercial greases used to blend base oil with additive but this study used palm oil, non-additive. In case of thickener, the literature and commercial greases used 12-hydroxystearic acid from hydrogenation of caster oil that must be imported material and expensive but this study used epoxidized palm oil from palm oil with locally available and low cost. Thus, the epoxidized palm oil grease can be use in similar application to that of the 12-hydroxystearic acid greases and the palm oil greases can be use in similar application to that of the epoxidized palm oil because they had the range of same penetration and dropping point.

CHAPTER V

CONCLUSIONS

From this study, epoxidized palm oil was synthesized from the epoxidation of palm oil with peroxyacetic acid using sulfuric acid as a catalyst. The epoxidized palm oil from the reaction was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR). The product was a clear yellow liquid and obtained in 89% yield.

The thickening agents were prepared from the saponification of epoxidizied palm oil with a 25% solution of metal hydroxide (calcium hydroxide and lithium hydroxide). The other thickening agents of palm oil, 12-hydroxystearic acid and stearic acid were prepared by the same procedures. The thickening agents of calcium soaps were yellowish solid (94% yield), and the thickening agents of lithium soaps were white solid (95% yield).

The thickening agents were blended with palm oil. The greases of calcium soap was light yellow semifluids, and the greases of lithium soap was brownish red semifluids.

Finally, the properties of the prepared epoxidized palm oil greases of calcium and lithium soaps were carried out according to TIS 713-2541 of general greases as worked penetration, dropping point, copper strip corrosion, water washout, ash, determination of water and evaporation loss. The properties of epoxidized palm oil greases of calcium and lithium soaps were found to be within the specification of the general grease of TIS 713-2541 and similar to those of the literatures and commercial greases that used palm oil as base oil and 12-hydroxystearic acid soap as thickener.

The prepared grease from the same soap of epoxidized palm oil, palm oil, 12-hydroxystearic acid and stearic acid, had the different results of penetration and dropping point due to each thickener, nevertheless, these results from the same soap were quite similar. Thus, the epoxidized palm oil greases can be used in similar application to those of the literatures and commercial greases.

SUGGESTIONS FOR FURTHER WORK

The greases using epoxidized palm oil soap should be further studied for the biodegradability of the greases.

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APPENDICES

APPENDIX A

GREASE TESTS

Table A-1 Procedures for the testing of lubricating greases

ASTM method number	Title
ASTM D 128	Analysis of lubricating greasse
ASTM D 217	Cone penetration of lubricating greases
ASTM D 566	Dropping point of lubricating greases
ASTM D 942	Oxidation stability of lubricating greases by the oxygen bomb method
ASTM D 1092	Appararent viscosity of lubricating greases
ASTM D 1263	Leakage tendencies of automotive wheel bearing greases
ASTM D 1264	Water washout characteristics of lubricating greases
ASTM D 1403	Cone penetration of lubrication grease using one-quarter and one-half scale cone equipment
ASTM D 1478	Low-temperature torque of ball bearing greases
ASTM D 1742	Oil separation from lubricating grease during storage
ASTM D 1743	Corrosion preventive properties of lubricating greases
ASTM D 1831	Roll stability of lubricating grease
ASTM D 2265	Dropping point of lubricating grease over wide temperature range
ASTM D 2266	Wear preventive characteristics of lubricating grease (Four-ball method)
ASTM D 2509	Measurement of load-carrying capacity of lubricating grease (Timken method)
ASTM D 2596	Evaporation loss of lubricating greases over wide-temperature range
ASTM D 3527	Life performance of automotive wheel bearing grease
ASTM D 4170	Fretting wear protection by lubricating greases
ASTM D 4289	Compatibility of lubricating grease with elastomers
ASTM D 4290	Leakage tendencies of automotive wheel bearing grease under acclerated conditions
ASTM D 4693	Low-temperature torque of greased-lubricated wheel beating s

APPENDIX B

SPECTRA OF EPOXIDIZED PALM OIL

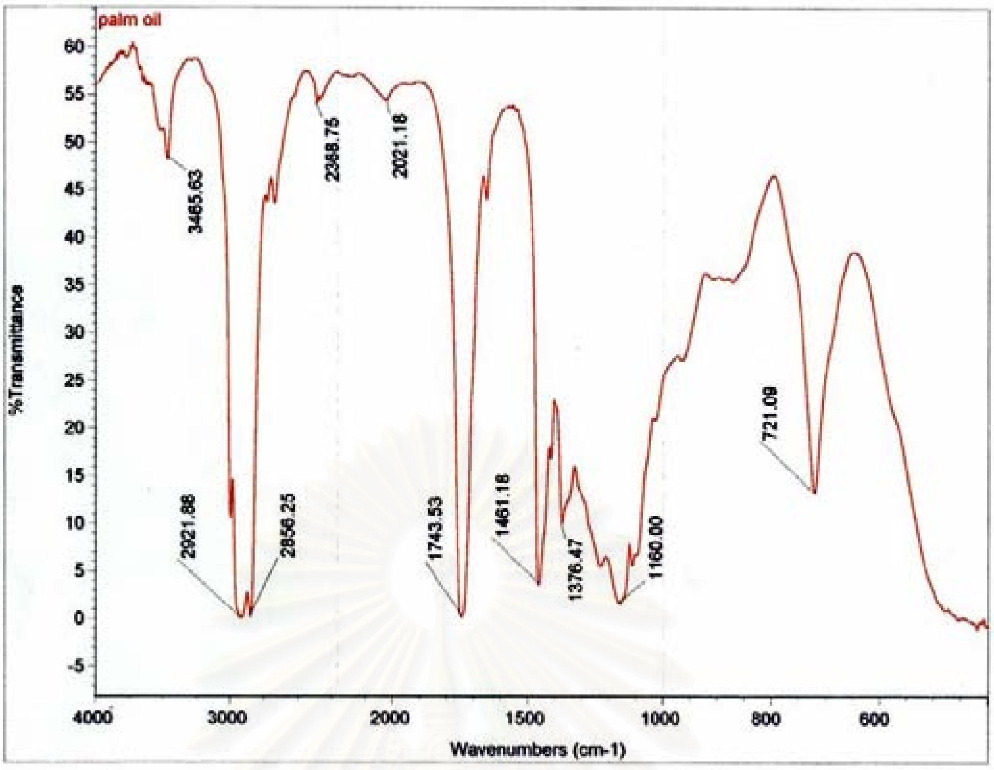


Figure B-1 FTIR spectrum of palm oil

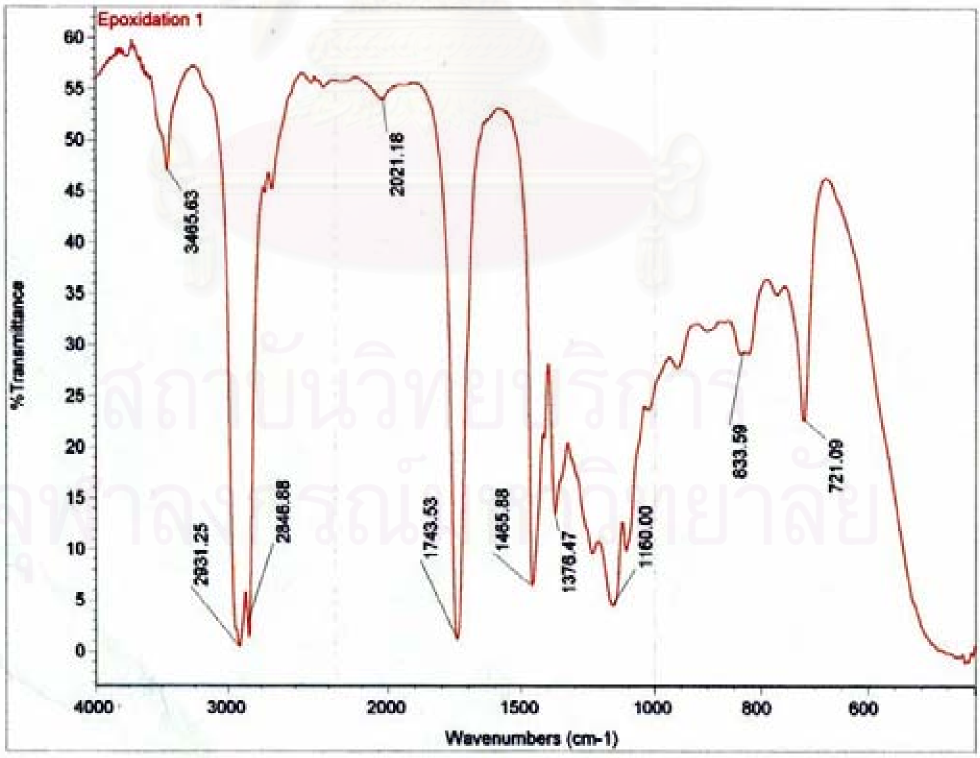


Figure B-2 FTIR spectrum of epoxidized palm oil

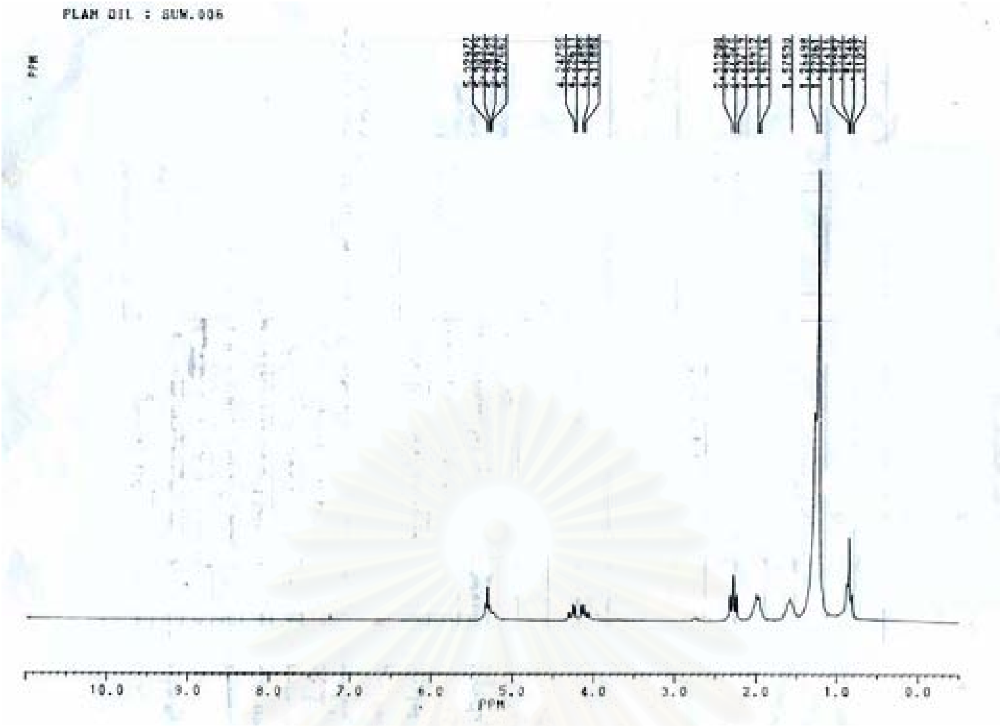


Figure B-3 ^{1}H-NMR spectrum of palm oil

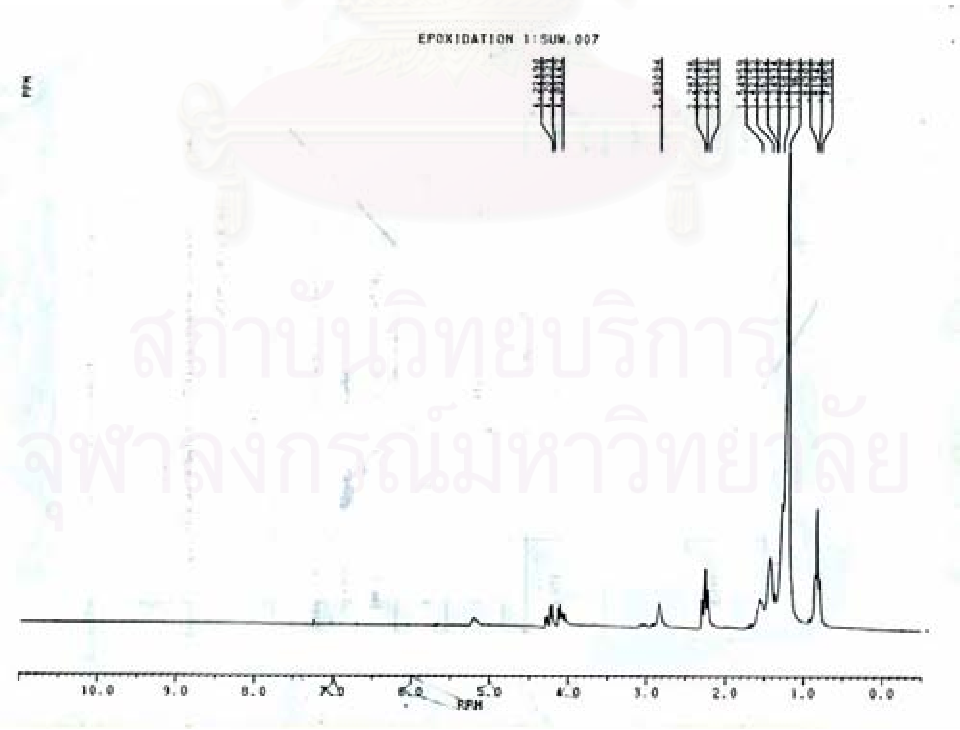


Figure B-4 ^{1}H-NMR spectrum of epoxidized palm oil

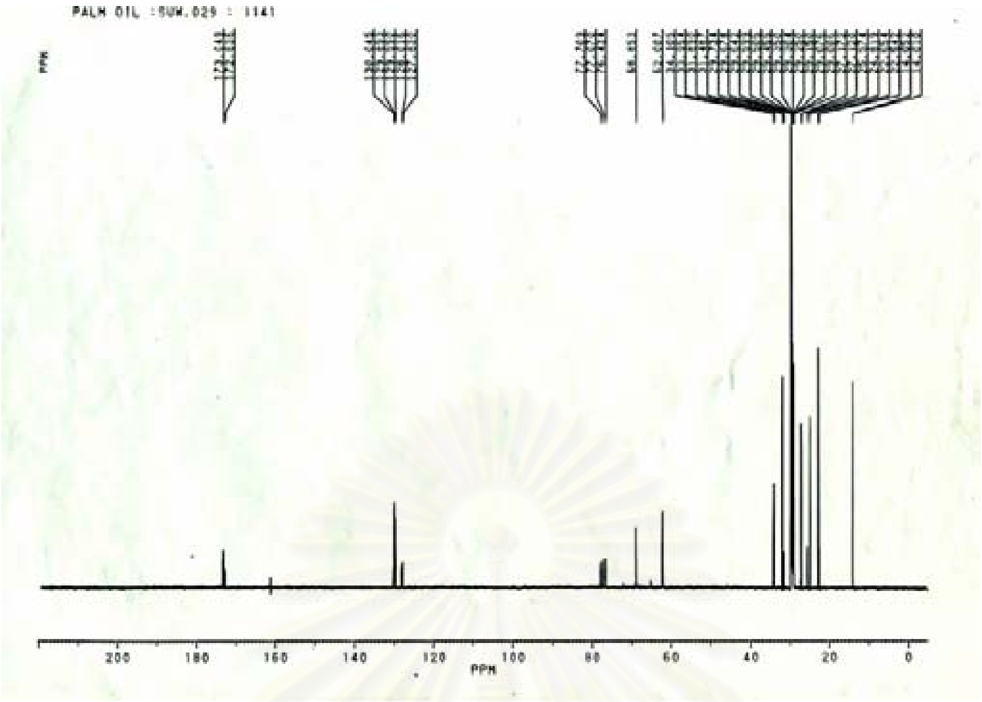


Figure B-5 ^{13}C-NMR spectrum of palm oil

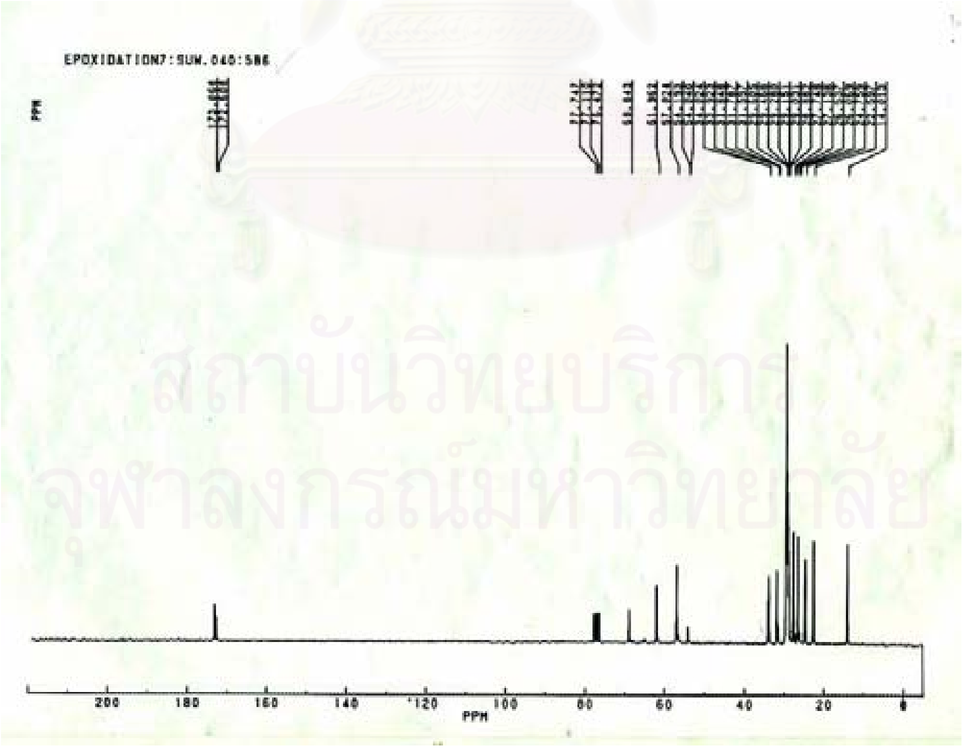
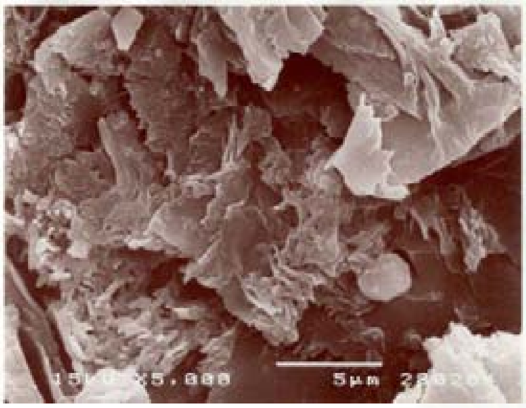


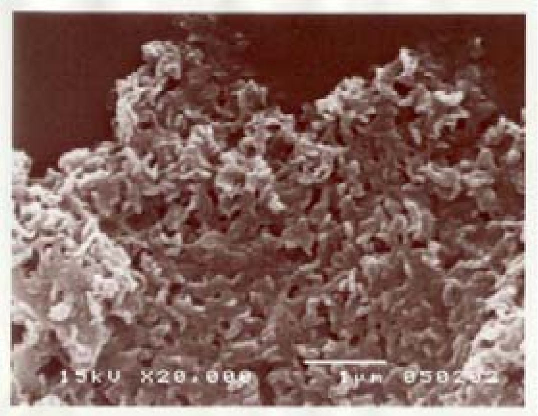
Figure B-6 ^{13}C-NMR spectrum of epoxidized palm oil

APPENDIX C

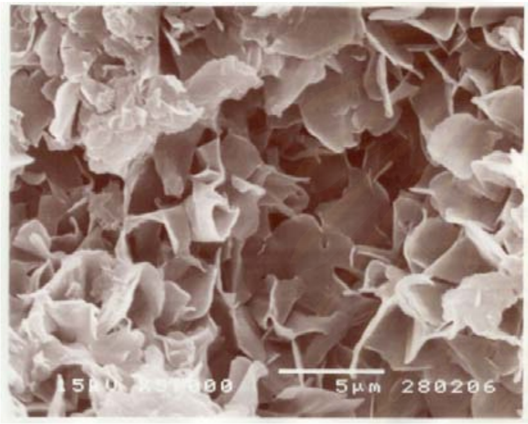
SCANNING ELECTRON MICROGRAPH
OF THE OTHER GREASES



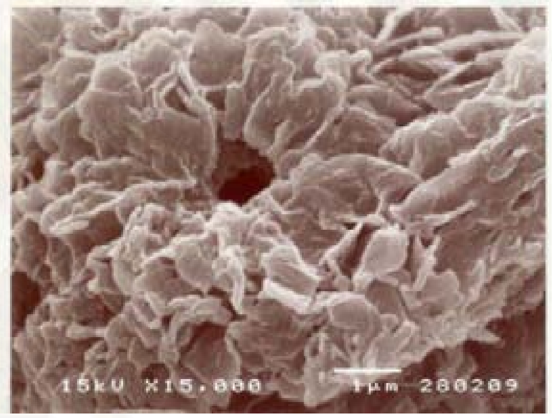
C-1 : Palm oil calcium soap



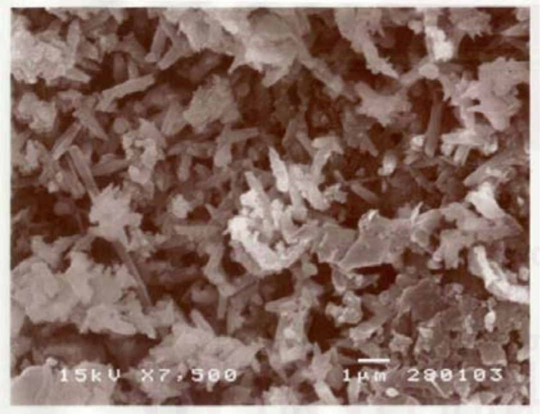
C-2 : Palm oil calcium grease



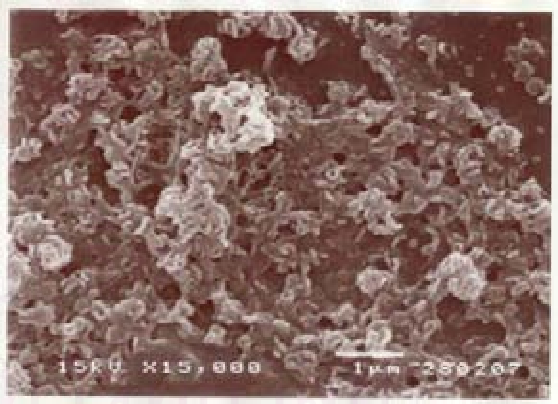
C-3 : 12-Hydroxystearic acid calcium soap



C-4 : 12-Hydroxystearic acid calcium grease

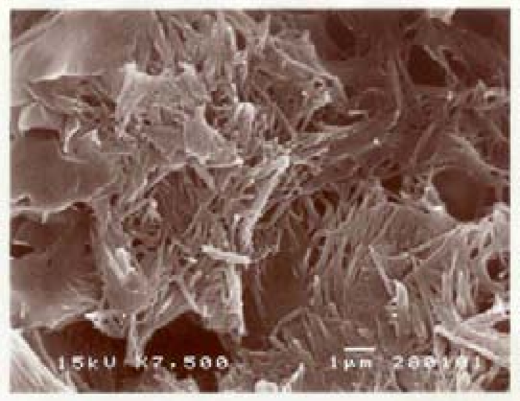


C-5 : Stearic acid calcium soap

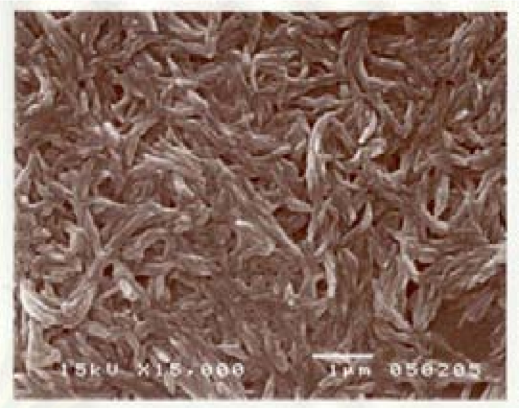


C-6 : Stearic acid calcium grease

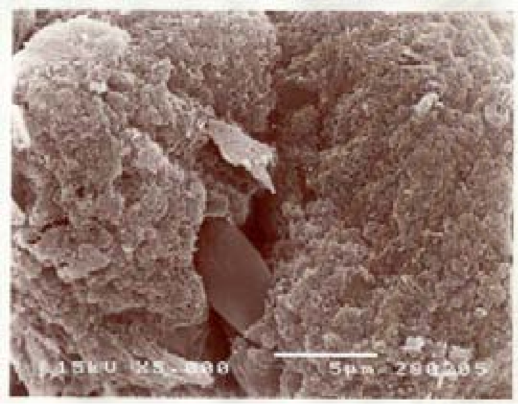
Figure C-1 - C-6 Scanning electron micrographs of the thickeners and greases of calcium soap.



C-7 : Palm oil lithium soap

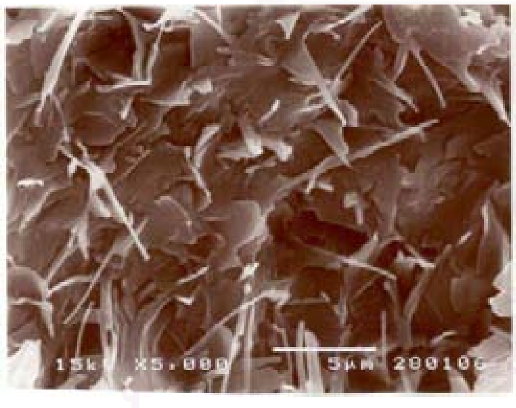


C-8 : Palm oil lithium grease

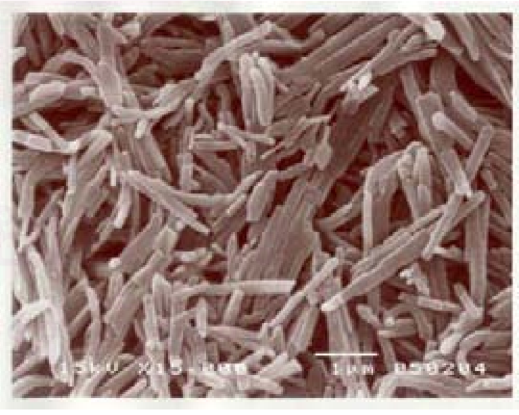


C-9 : 12-Hydroxystearic acid lithium soap

C-10 : 12-Hydroxystearic lithium grease



C-11 : Stearic acid lithium soap



C-12 : Stearic acid lithium grease

Figure C-7 - C-14 Scanning electron micrographs of the thickeners and greases of Li soap.

VITA

Miss Suwitanan Boonsri was born on March 19, 1978 in Prachuapkhirikhun, Thailand. She received her Bachelor Degree of Science in Chemistry from Chulalongkorn University in 1999. She continued her Master study in program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed her degree in 2002.