

**SYNTHETIC GREASE FROM GLYCEROL, FATTY ACIDS
AND USED COOKING OIL**



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Title of special Project Synthetic grease from glycerol, fatty acids and used cooking oil

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Abstract

The aim of this research is to prepare base oil and thickener for grease formulation. Base oil was synthesized from the esterification between glycerol and oleic acid in 1 to 1 mol ratio at 100°C for 3 days followed by the esterification with adipic acid in 1 to 1 mol ratio at 140°C for 3 days, while thickener was synthesized as solid ester from the esterification reaction between glycerol and palmitic acid in 1 to 1 mol ratio at 100°C for 5 days followed by the esterification with adipic acid in 1 to 1 mol ratio at 140°C for 7 days, and as soap from the saponification of used cooking oil. The products were characterized by ¹H-NMR and FT-IR spectroscopy, DSC and TGA. Three sample of grease were formulated by using the oil/thickener ratio of 90:10, 80:20 and 70:30. The grease with 90 to 10 ratio was not thick enough. The other grease samples were subjected to the tests of dropping point. It was found that the dropping point of grease with 80:20 and 70:30 ratios were 94°C and 77°C. Then the grease sample with 80:20 ratio which had higher dropping point was tested by water wash out characteristic to find the percentage of weight loss at 38°C. It was found that 92% weight was lost by water. By comparing the prepared grease samples with the industrial grease, it can be concluded that the product from this work are not suitable for use.

Keyword: Synthetic base oil, Polyester, Thickener, Grease

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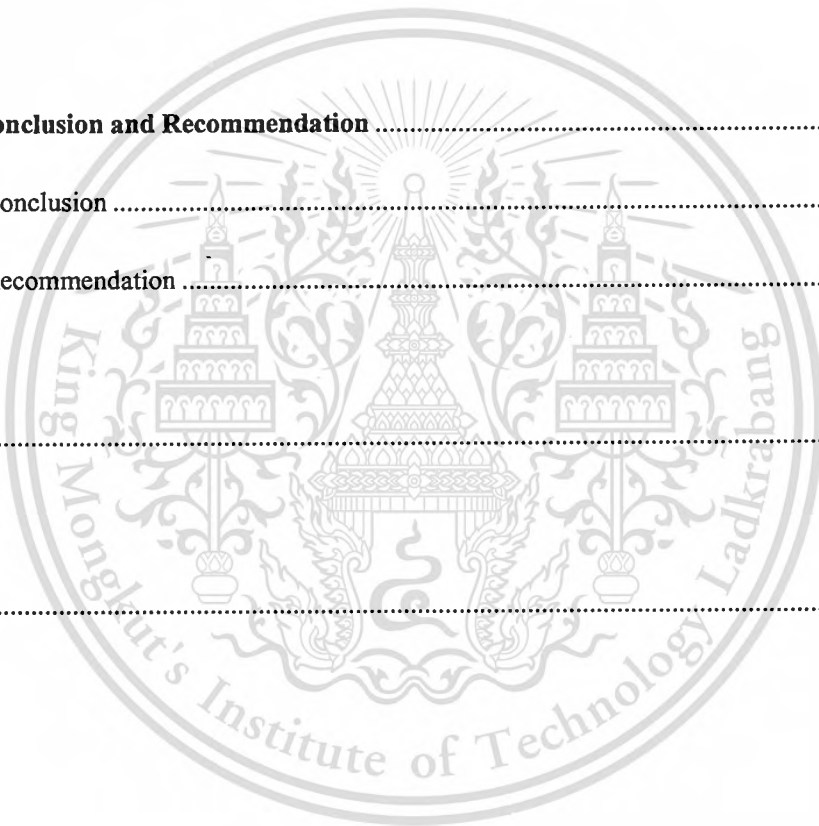
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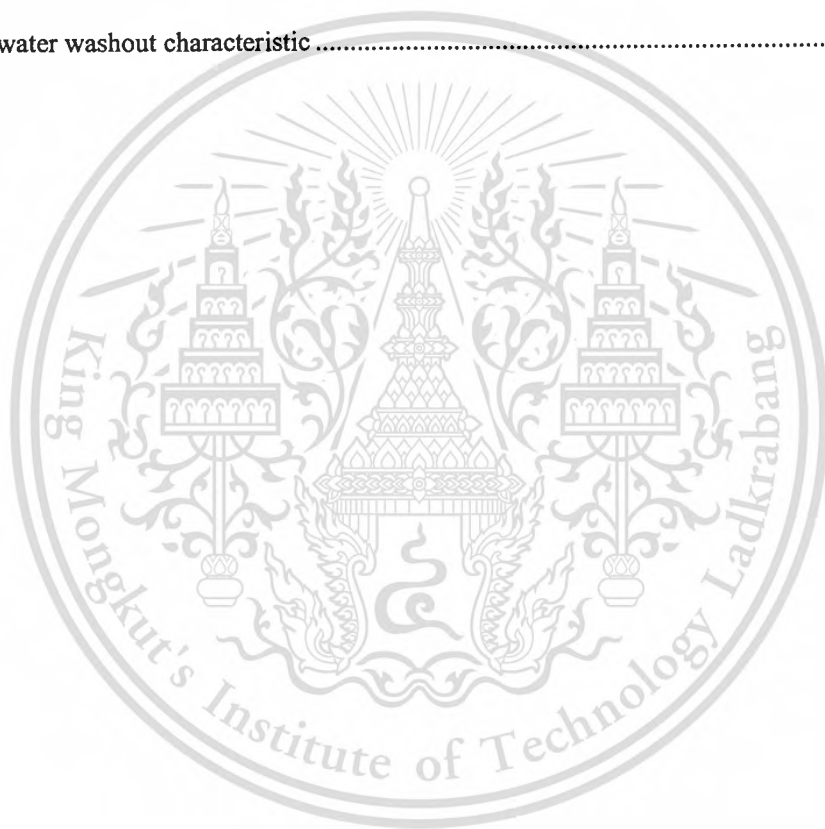


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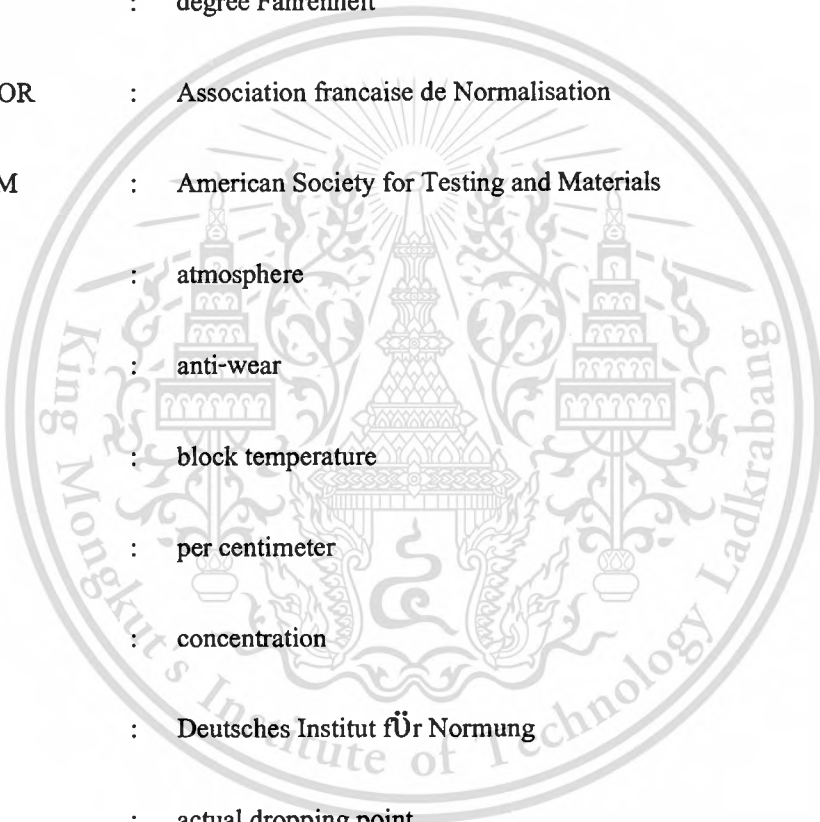
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ABBREVIATIONS



%w/w	:	percentage by weight per weight
°C	:	degree Celcius
°F	:	degree Fahrenheit
AFNOR	:	Association francaise de Normalisation
ASTM	:	American Society for Testing and Materials
atm	:	atmosphere
AW	:	anti-wear
BT	:	block temperature
cm⁻¹	:	per centimeter
conc.	:	concentration
DIN	:	Deutsches Institut für Normung
DP	:	actual dropping point
DSC	:	Differential Scanning Calorimeter
EP	:	extreme-pressure
FT-IR	:	Fourier Transform Infrared Spectroscopy
g.	:	gram

ABBREVIATIONS (Continued)

GOST	:	Gosudarstvennyy Standart
h	:	hour
ISO	:	International Organization for Standardization
K	:	Kelvin
L/day	:	liter per day
M	:	molar
MACs	:	multiply alkylated cyclopentanes
min.	:	minute
ml	:	milliliter
mm	:	millimeter
mm ² /s	:	square millimeter per second
mol	:	mole
NLGI	:	National Lubricating Grease Institute
NMR	:	Nuclear Magnetic Resonances
NPG	:	neopentyl glycol
ODP	:	observed dropping point

ABBREVIATIONS (Continued)

PAOs	:	poly-alpha olefins
PET	:	polyethylene terephthalate
PFPEs	:	perfluoropolyethers
PPEs	:	polyphenylethers
ppm	:	part per million
PTFE	:	polytetrafluoroethylene
RCW	:	rolling contact wear
rpm	:	round per minute
SBO	:	soybean oil
TGA	:	Thermal Gravimetric Analysis
TMP	:	trimethylol propane
VI	:	Viscosity Index
δ	:	chemical shift
μm	:	micrometer

Chapter 1

Introduction

1.1 Background [1-8]

Historically, it has been found from the earliest times that animal and vegetable oils were used as lubricants in general transportation or machinery to reduce friction and wear. However, while still useful, they are now not adequate for our industrialized society, either in volume or in desirable properties. Lubricants are classified into lubricating oils and greases. Greases in general contain base oils and thickeners.

The most favorable lubricating base oil are mineral base oils from petroleum because of the high quality, good stability and low price comparing with animal and vegetable oils. However, the reservoirs of petroleum oil are limited and may be exhausted by the end of the next century. Recently, Animal and vegetable oils have regained more interest because of its environmental benefits and the fact that it is made from renewable resources. Vegetable oils, in general, are non-toxic and actually have some excellent properties, such as high viscosity index, high flash point, low evaporative loss and high biodegradability. Synthetic esters are now used in many applications, including the uses as automotive engine oils, marine engine oils, compressor oils, hydraulic fluids, gear oils and in grease formulation.

Transesterification of alkyl esters plays an important industrial role with numerous applications, such as the production of biodiesel from vegetable oil and animal fat such as palm oil, the production of polyester or PET in the polymer industry. Homogeneous acid such as sulfuric acid, sulfonic acid, phosphoric acid and hydrochloric acid are mostly used as catalysts in transesterification of animal fats and vegetable oils because they are cheap, easy to use and plenty. Homogeneous base catalysts are better than homogeneous acid catalysts because they give the higher reaction rates and the lower process temperatures. Table 1.1 and Figure 1.1 show that the trend of biodiesel production in the USA has been increasing since 2007 to 2009. Glycerol is

by-product from biodiesel production. Therefore, high production of biodiesel will also lead to high yield of crude glycerol. There is also a possibility for glycerol to be used as a starting material in the synthesis of carboxylic acid ester for use as base oil or thickener in grease formulation.

Table 1.1: The production of biodiesel in USA during 2007 and 2009[1]

		Volume (L)	average (L/day)	Volume (L)	average (L/day)	Volume (L)	average (L/day)
Month	No. of days	2007	2007	2008	2008	2009	2009
Jan	31			29.47	0.95	43.20	1.39
Feb	28			36.58	1.31	43.81	1.56
Mar	31			44.58	1.44	45.02	1.45
Apr	30			40.10	1.34	47.52	1.58
May	31			39.02	1.26	52.27	1.69
Jun	30	3.64	0.12	41.05	1.37	50.30	1.68
Jul	31	5.18	0.17	35.25	1.14	50.71	1.64
Aug	31	7.97	0.26	37.42	1.21		
Sep	30	12.34	0.41	36.32	1.21		
Oct	31	10.84	0.35	33.54	1.08		
Nov	30	11.97	0.40	34.39	1.15		
Dec	31	15.85	0.51	39.80	1.28		
Total	365	67.77	2.22	447.52	14.73	332.83	10.99

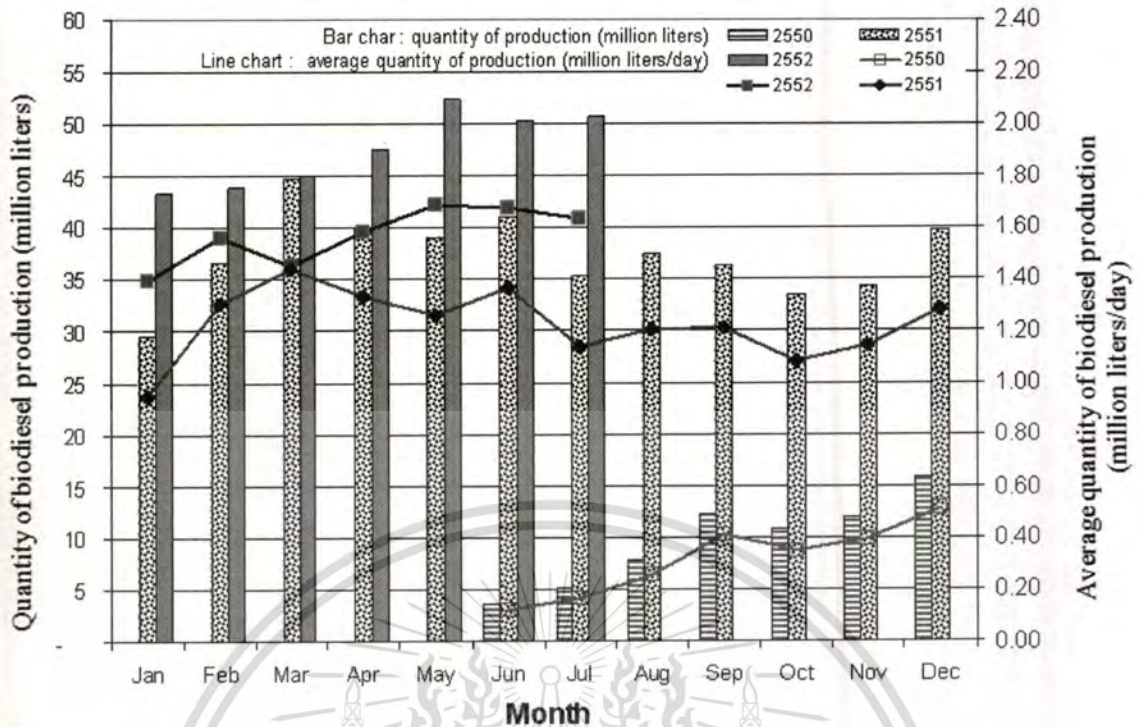


Figure 1.1: The trend of biodiesel production in USA during 2007 and 2009[1]

In addition, since Thailand has a huge palm oil reserve, so palm oil will be a good candidate as the starting material for use in the transesterification reaction with glycerol to produce carboxylic acid esters. Figure 1.2 shows the production of palm oil in Thailand which has been increasing.

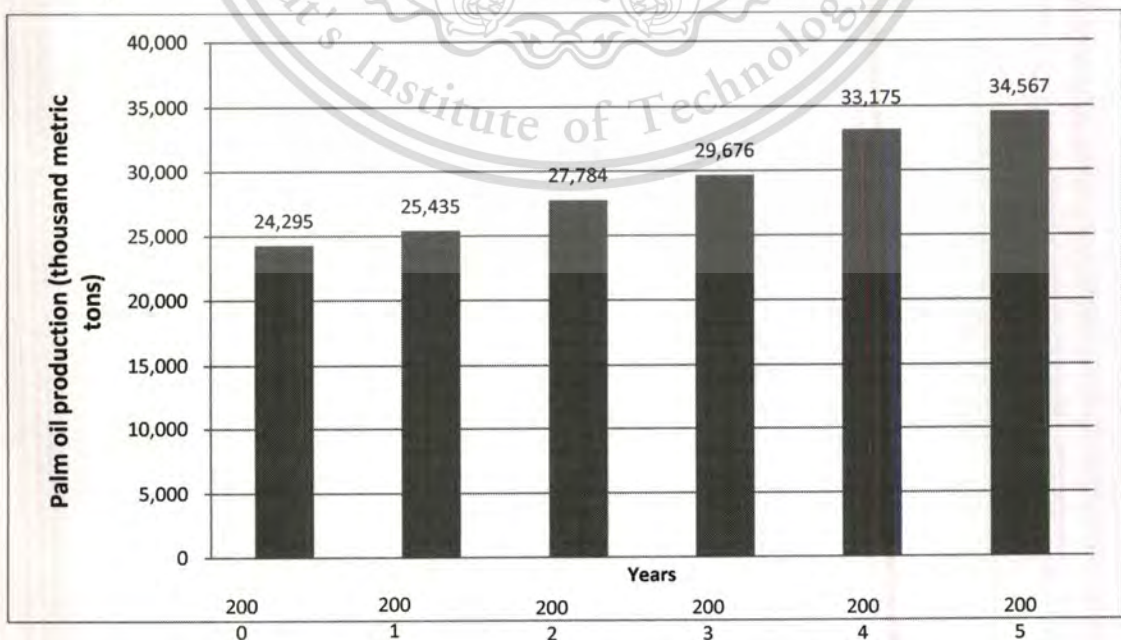


Figure 1.2: Production of palm oil in Thailand between 2000 and 2005[2]

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A.Adhvaryu, C. Sung and S.Z.Erhan have demonstrated a grease producing experiment. The aim of their experiment was the preparation of lithium soap-based soy greases using different fatty acids and the determination of crystallite. Lithium soaps were from palmitic, stearic, oleic, and linoleic acids. Then they were synthesized and mixed with soybean oil (SBO) and additives to obtain different grease compositions. The result of the experiment was that the Li stearate-based soy grease has more compact fiber structure than Li palmitate. The linoleic acid (C18, =) with two sites of C-C unsaturation in the chain exhibits a much thinner and more compact fiber network than oleic acid (C18, =).

According to M. A. Delgado, M. C. Sanchez, C. Valencia, J. M. Franco and C. Gallegos, lithium lubricating greases were prepared by inducing the saponification reaction between 12-hydroxystearic acid and hydrated lithium hydroxide within a naphthenic lubricating oil medium, applying a controlled-temperature programme. The result showed that the differences of the rheological properties of lubricating grease during processing have been mainly related to both the soap concentration in the reacting mixture and the waxy soap transition at high temperatures and the further cooling steps. The sample obtained during the saponification step, a highly concentrated dispersion where the soap crystallites were not still formed, showed high values

Table 1.2: The chemical composition of palm oil [3]

Chemical	% Composition in palm oil
Laurate	0.1
Myristate	0.1
Palmitate	44
Stearate	5
Oleate	39
Linoleate	10
Linolenate	0.3

Table 1.2 shows the chemical composition of palm oil which contains a lot of palmitate and oleate. Therefore, in this work, palmitic acid or oleic acid, two main fatty acid components in palm oil and glycerol will be used as starting materials for transesterification into monoesters, followed by the reaction of monoesters with adipic acid to oligomers. After that, greases will be prepared by using the synthesized oligomer as base oil or thickener. The thickener will also be prepared as sodium soap of used cooking oil. The suitable formulation of grease will be determined. The physical and chemical properties, such as melting point and dropping point will also be tested.

1.2 Objectives

1. To synthesize esters from glycerol, fatty acids and adipic acid to be used as base oil and thickener.
2. To prepare grease formulas from the synthesized ester and soap from used cooking oil.
3. To test properties of grease according to ASTM method

1.3 Scope of study

1. Saponification of used cooking oil and NaOH solution in the ratio of 1:3 in order to produce sodium soap.
2. Esterification reaction between glycerol, palmitic acid/oleic acid and adipic acid in the ratio of 1:1:1 in order to synthesize base oil or thickener, and their characterization using NMR technique.
3. Grease preparation from oil and soap by varying the ratio between oil and thickener/soap from 70:30, 80:20 and 90:10.
4. Test properties
 - Melting point of ester products by Differential scanning calorimeter (DSC)

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- Thermal properties of ester products by Thermal gravimetric analysis (TGA)
- Dropping point of grease by ASTM D 2265
- Water washout of grease by ASTM D 1264

1.4 Expected Results

Grease could be prepared by mixing soap from used cooking oil with ester oil from glycerol.



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Chapter 2

Theory and literature reviews

2.1 Lubricating Greases [9]

Lubricants are used to reduce the friction when two objects in contact are moved relative to each other. It also reduced the demand for muscle power. In the ancient transportation sector, animal fats were used in conjunction with inorganic fillers to reduce the frictional forces between the bearing surface and shaft on chariot wheels.

Lubricating greases can be defined as solid to semi-fluid products of the dispersion of a thickening agent in a liquid lubricant. The thickening agent is usually a metal soap and the transition of lubrication greases are fluid. There are 2 sides of thickening agent; the first one is liquid side which oil containing less than 5% w/w thickening agents. They are already having structural viscosity but not get a yield point yet. Therefore they have been named non-fluid oils. The second one is solid side which suspensions greater than 40% w/w solid lubricants in oils are usually called pastes. When greases contain both thickening agent typical of greases, they are also called grease pastes. Nevertheless, greases in general contain from 65 to 95% w/w base oils, from 5 to 35% w/w thickeners and from 0 to 10% w/w additives.

Greases have been named in way they have used, e.g. steel mill greases for after the kind of application, wheel bearing greases for after their prevalent application temperature, low temperature greases for after their range of application, and multi-purpose greases. The meaning of the latter name has changed with the years and the other names do not say much about the quality of the performance of the grease.

The consistency of a solid to semi-fluid body is a very complex subject, but the penetration of one body into another one can be measured easily and with simple devices. Greases are named according to the consistency classes defined by the US National Lubricating Grease

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Institute (NLGI) in 1983 and in accordance with the cone-penetration method developed in 1925 as show in Table 2.1.

Nowadays the performance of lubricating greases is described by norms such as ISO 6743-9 or DIN 51825 defining mainly consistency, upper and lower operating temperature, water resistance, and load-carrying capacity, and for automotive greases by ASTM D4950, which has been followed by the consideration of reference greases and the introduction of the NLGI Certification Mark.

Table 2.1: Classification of greases by NLGI numbers [9]

NLGI number	Appearance	ASTM worked penetration (1/10 mm)	Application
000		445-475	Gear greases
00	Semi-fluid	400-430	
0		355-385	
1	Soft	310-340	
2	Creamy	265-295	Greases for bearings
3		220-250	
4		175-205	
5		130-160	
6	Soap-like	85-115	Block greases

2.2 The Composition of Synthetic Grease [9]

Grease consists of two fundamental components: a base fluid representing the principle ingredient in the formulation and a thickening agent that is used to immobilize the fluid. The concentration of the thickener determines the consistency of the finished product; however, it is

the nature of the oil that determines whether the grease will be classified as a synthetic. The lubricating oils commonly used to formulate synthetic lubricating greases are listed in Table 2.2

Table 2.2: Lubricating oils commonly used in synthetic greases [9]

Fluids	Characteristic
Diesters	Suitable for making grease serviceable to -73°C (-99°F)
Polyol esters	Higher viscosity than the diesters with better oxidative stability and less volatility
Pentacrythritol esters	Primarily used to formulate synthetic greases requiring excellent lubricating properties from -40°C to over 177°C
Polyglycols	These oils which tend to produce less carbonaceous residue upon degradation, find use in formulating greases for arcing electrical equipment.
Poly(α -olefins) (PAOs)	A relatively new class of synthetic hydrocarbon fluid available in a range of viscosities, these oils exhibit improved compatibility with ester-vulnerable thermoplastics and elastic
Polybutenes	A subset of synthetic hydrocarbons with better viscosity-temperature characteristics than the PAOs and good properties as tackifier or damping fluid, but with a tendency to degrade under high shear.
Silicones	Outstanding thermo-oxidative stability, chemically inert, low and high temperature usefulness, and unmatched viscometric properties as a function of temperature. The viscosity index of one phenylsilicone is over 600.
Halocarbons	Chemically inert toward oxygen and possessing excellent innate boundary and extreme pressure lubricating properties, as well as extremely low temperature performance for the lighter viscosity grades.

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Table 2.2: Lubricating oils commonly used in synthetic greases (Continue)[9]

Fluids	Characteristic
Polyphenylethers (PPEs)	Two grades of these fluids are available, a five-ring and a six-ring molecule. The fluids possess exceptional radiation resistance, have outstanding thermo-oxidative stability and high surface energy, and have been used extensively for lubricating noble metal electrical contacts.
Phosphate ester	Can be used to manufacture relatively in expensive greases that are able to resist ignition.
Perfluoropolyethers (PFPEs)	Synthetic greases formulated from “branched” and “linear” versions of these fluids are inert toward oxygen and all but the most aggressive chemicals. Greases made from these oils have unsurpassed thermo-oxidative stability. The PFPEs with a straight polymer chain morphology (“linear PFPEs”) also have excellent viscosity index and low temperature performance.
Multiply alkylated cyclopentanes (MACs)	The newest commercially available synthetic fluid, demonstrating exceptionally low volatility under hard vacuum and elevated temperature.

Synthetic greases are prepared from both organic and inorganic thickeners. Organic thickeners are prepared from the reaction of a suitable alkali metal with either high molecular weight carboxylic acids or fats. The alkali metal are usually reacted with stearic acid, myristic acid, 12-hydroxystearic acid, or hydrogenated castor oil, a triglyceride that liberates 12-hydroxystearic acid during saponification.

Inorganic thickeners, such as chemically modified clay, amorphous silica, and polytetrafluoroethylene, can also be used to form grease, but without the need for a chemical reaction for grease formation to occur. The efficiency of a particular thickener to convert synthetic oil into greases depends on the ultimate surface area of the thickener, its ability to bond

with hydrogen. The thickener must have an affinity for the base fluid that is intermediate between the forces that lead to greater solubility and the forces tending to induce phase separation. This mesosolubility is a prerequisite for all successful grease formation.

2.3 Thickeners [9]

Thickeners are substances which, when added to an aqueous mixture it can increase its viscosity without substantially modifying its other properties. They provide body, increase stability, and improve suspension of added ingredient. Thickeners are not only transformed liquid lubricants into consistent lubricants. They also change the properties of the liquid lubricants. When all their properties are taken into consideration none of the commercially important thickeners stands out from any other as show in Table 2.2. They are comparably competitive and suited for their tasks. The differences mainly lie in the more special demands made on them.

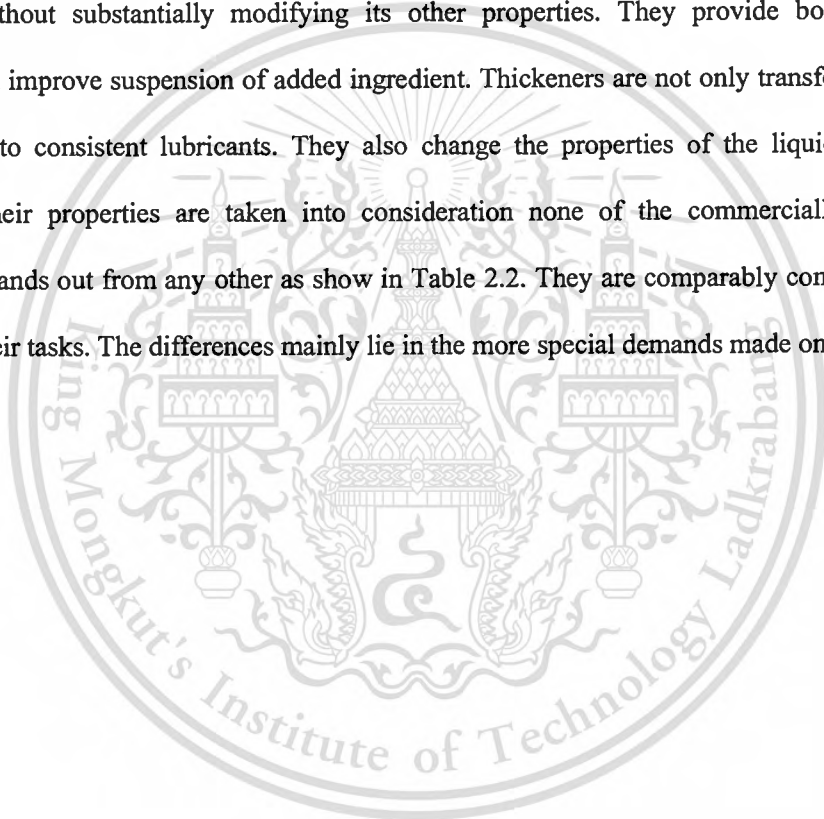


Table 2.3: Competitiveness of thickeners [9]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Sum
Lithium hydroxystearate	2.5	1.0	2.0	1.5	2.0	2.0	2.5	1.5	2.5	2.0	1.0	3.0	2.0
Calcium hydroxystearate	3.0	1.0	3.0	1.0	1.5	1.0	2.5	1.0	2.0	2.0	1.0	3.0	1.8
Lithium complexes	1.5	2.0	1.5	2.0	1.5	2.0	2.0	2.5	1.5	2.0	2.0	2.5	1.9
Aluminum complexes	2.0	2.0	2.0	2.5	1.5	2.0	2.0	2.5	2.0	2.0	2.0	2.5	2.1
Calcium complexes	2.0	3.0	2.0	2.0	1.0	1.5	1.5	3.0	1.5	2.0	2.0	2.0	2.0
Inorganic thickeners	1.5	1.0	1.0	3.0	3.0	1.0	3.0	1.0	3.0	3.0	2.5	3.0	2.2
Polyureas	1.0	1.5	1.5	2.5	2.0	1.5	2.5	2.0	3.0	3.0	1.0	2.0	2.0
Terephthalamates	1.5	1.5	1.5	1.0	2.5	1.5	2.0	1.0	2.5	2.0	1.0	2.0	1.7
Calcium-sulfonate complexes	2.0	3.0	2.0	2.0	1.0	2.0	1.5	3.0	1.0	1.0	2.0	1.5	1.8
Carbamte-like thickeners	2.0	1.5	2.0	2.0	2.0	2.0	2.5	1.5	2.0	2.0	1.0	2.0	1.9

I = high temperature,

II = low temperature,

III = aging,

IV = compatibility,

V = oil loss,

VI = toxicity

X = shear,

XI = friction,

XII = wear

1.0 = excellent,

2.0 = average,

3.0 = poor

Table 2.4: Thickeners commonly used in synthetic greases [9]

Gellants	Characteristic
Paraffin Wax	Low cost; low melting point
Alkali soap	Temperature to 200°C, pumpability, most common thickener
Organoclay	Temperature to 250°C, high loads, incompatible with some polar additives
Alkali complex soap	Temperature to 250°C, pumpability, water resistance
Polyurea	Temperature to 250°C, pumpability, stability, excellent in high load bearing
PTFE	Temperature to 300°C, low coefficient of friction, inert, moderate load only
Silica	Nonmelting, water resistance, low oil separation/good oil retention
Metal oxide	Nonmelting, thermal conductivity, inert

Table 2.5: Alkali metals used to prepare alkali soap thickener greases [9]

Alkali	Formula
Lithium hydroxide monohydrate	$\text{LiOH}\cdot\text{H}_2\text{O}$
Calcium hydroxide	$\text{Ca}(\text{OH})_2$
Sodium hydroxide	NaOH
Aluminum hydroxide	$\text{Al}(\text{OH})_3$

2.3.1 Simple Soaps

In general, a maximum thickening effect is achieved with carboxylic acids having 18 carbon atoms. Soaps are usually prepared from vegetable-derived 12-hydroxystearic acid or from animal- or vegetable-derived stearic acid, or from their esters, usually their glycerides, and from the hydroxides of elements of the alkali and alkaline earth metals. Soaps, by gelling their base oils give grease most of their unique properties. They are not only present as crystallites and dissolved molecules, but above all in a separate phase represented by agglomerates called fibrils or fibers.

All components are present, and have the properties of grease, even in the smallest lubrication gap.

2.3.2 Soap Anions

The carbon chain length of a carboxylic acid affects the solubility and surface properties of soap. Longer and shorter carbon chains reduce its thickening capacity. Increasing the chain length increases the solubility in the base oil, shortening the chain length reduces it. A branched alkyl chain lowers the melting point of soap and reduces its thickening effect. Carboxylic acids containing carbon double bonds, so called unsaturated acids, are more soluble in mineral oils and also reduce the thickening effect and lower the dropping point. Their use is limited because of their lower oxidation stability. Hydroxyl groups increase the melting point and the thickening effect of soap because of its increased polarity.

2.3.3 Soap Cations

The soap cations also are responsible for essential properties of soap greases. The cations govern the thickener yield, the dropping point, according to DIN ISO 2176 the temperature at which a grease gets liquid under normal conditions, the water resistance, and, to some extent, the load-carrying capacity of a greases.

2.3.4 Lithium Soaps

Nowadays Lithium soap-based greases are usually prepared by reacting lithium hydroxide as a powder or dissolved in water with 12-hydroxystearic acid or its glyceride in mineral oils or synthetic oils. Whether the free acid or its glyceride is preferred depends on the relationship between cost and performance. The production temperature is between 160 and

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250°C, depending on the base oil and the type of reactor in use. The dropping point of mineral oil-based NLGI 2 grease is usually between 185 and 195°C. For such a multi-purpose grease ca 6% w/w of soap is required with a naphthenic oil, ca 9% w/w with a paraffinic oil, and ca 12% w/w with a polyalphaolefin, and a kinematic viscosity of ca $100 \text{ mm}^2 \text{ s}^{-1}$ at 40°C (the thickening effect depends not only on the carbon distribution in a base oil, but also on its viscosity).

The fiber size in lithium 12-hydroxystearate greases is usually between 0.2×2 and $0.2 \times 20 \mu\text{m}$. Good multi-purpose properties, e.g. a high dropping point, good water resistance, good shear stability – which has been related to hydrogen-bonding of the hydroxyl groups – and good response to additives are the reasons why lithium 12-hydroxystearate-based greases have now been the most popular for more than half a century. They have found a wide range of applications from extreme-pressure (EP) greases based on oils with kinematic viscosities of ca 200 to $1000 \text{ mm}^2 \text{ s}^{-1}$ at 40°C for heavy loads, through multi-purpose greases based on mineral oils with kinematic viscosities from 60 to $120 \text{ mm}^2 \text{ s}^{-1}$ at 40°C for all kinds of bearings, greases made with diesters or polyalphaolefin oils and kinematic viscosities of 15 to $30 \text{ mm}^2 \text{ s}^{-1}$ for high-speeds, to those with oil-insoluble polyalkyleneglycols for gears. The lower application temperature limit for a lithium soap thickened grease, as for all other greases, depends mainly on the physical properties of its base oil, of course. The upper limit is depending on the base oil, it lies between 120 and 150°C. It is readily apparent that between the dropping point and the upper application temperature limit there can be a gap of between 60 and 100°C. Oil separation has been discussed as a criterion for both lower and upper application temperature limits.

2.3.5 Calcium Soaps

Calcium soaps prepared from 12-hydroxystearic acid, called anhydrous calcium soaps. Similar to the corresponding lithium soaps they indeed contain up to 0.1% w/w water, but that water is not present as a crystallization component, as in stearic acid based soaps, although technical 12-hydroxystearates contain up to 15% w/w stearic acid. Calcium greases of this type

are produced in the same way as lithium soap-based greases, but at temperatures between 120 and 160°C. The size of their fibers lies between those for lithium soaps and hydrated calcium soaps. The greases can be used up to 120°C. Their dropping point is between 130 and 150°C, depending on their base oil. They usually have a very good corrosion resistance and good oxidation stability; when prepared from suitable base oils they are possibly the best low-temperature greases.

Calcium soaps mainly based on stearic, palmitic, or oleic acid still are called hydrated calcium soaps. For these greases the cost of raw materials, and the performance levels, are lowest. They are prepared by neutralization of slurry of calcium hydroxide in water with fatty acids or fats in mineral oil. Fats are cleaved in the first reaction step into fatty acids and glycerol. This is usually performed in a pressure vessel. Stable greases can only be obtained in the presence of some water, usually ca 10% w/w of the soap. The water content is usually adjusted in a second step in a stirring, or cooling vessel. When the water is removed, the grease structure collapses. The dropping point of this type of grease is therefore only 90 to 110°C and the upper application temperature limit is only ca 80°C

The greases have very good water resistance and good adhesive properties. Because their manufacture is rather demanding in relation to the performance obtained, their importance is declining rapidly.

2.3.6 Sodium Soaps

Compared with lithium and calcium 12-hydroxystearate greases the importance of greases based on sodium soaps is nowadays low, although in the form of semi-fluid products they still are of some interest for the lubrication of gears. Sodium greases made from fatty acids or fats have dropping points of ca 165 to 175°C. Their upper temperature limit is ca 120°C. Products are available with short and long fiber structures; the latter reaching up to 1 x 100 µm and are responsible to some extent for the rather high load carrying capability in gears. Although the greases have extraordinary good corrosion-preventive properties if only small amounts of water

are present, their main disadvantage is the solubility of the sodium soaps in larger amounts of water; this leads first to gel formation, which dramatically increases the apparent viscosity, and later to breakdown of the whole structure.

2.3.7 Other Soaps

Aluminum soap-based greases are usually produced with pre-manufactured aluminum soaps, usually aluminum stearate. They have dropping points of up to 120°C, their upper temperature limit is 80 to 90°C above 90°C they tend to gel. Typical of this soap is a particle size of less than 0.1 x 0.1 μm, which is to some extent responsible for the low shear stability and the pronounced thixotropic behavior of the products. Aluminum greases are usually very transparent and smooth. They have good water resistance and adhesive properties, but have been widely replaced by lithium greases, partly because, for consistent products, aluminum greases must not be stirred during the finishing process but poured into pans and left for several hours to cool.

Barium soap-based greases have high water resistance and shear stability, and lead soap-based greases have advantageous load-carrying capacity and wear protection properties. Both have, nevertheless, been completely replaced, mainly for toxicological reasons.

Lithium-calcium greases have become quite popular as specialized multi-purpose greases. Greases mainly based on sodium-aluminum stearate, have been used as substitutes for lithium greases, for example in the former GDR. Cation mixed soap greases are usually manufactured by a one-step process, because the stability of mixtures of finished products are not always satisfactory.

2.4 Base Oil [9]

Base oil is the main component of lubricant blends. In general only oils with kinematic viscosities from 15 to 1500 mm²s⁻¹ at 40°C are used. The oils with the lowest viscosities and the

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best low-temperature properties have the lowest operational temperatures at the highest speeds. The oils with the highest viscosities have the best performance at the lowest speeds and the highest loads, the lowest evaporation loss, the strongest adhesion and the best water or solvent resistance.

2.4.1 Mineral Oils

Oils with low viscosity indexes (VIs) usually require less thickener than those with high VIs and the same kinematic viscosity. The latter can be used over a wider temperature range. In principle the thickening effect (yield) depends on the difference between the solubility parameters of the base oil and thickener. Because oil separation depends on the concentration of thickener, at a given temperature oil separation is most pronounced for greases based on low VI oils, e.g. aromatic oils or alkyl-benzenes. Oil separation goes through a minimum with increasing kinematic viscosity for a given kind of base oil. This can easily be understood when only the dependence of particle interactions on the size of the involved particles is considered. Some of the specific properties of greases also depend on the ratio of the temperature and pressure coefficients of the viscosity of their base oils. If all this is taken into account, the effect of even a small change in base oil composition on the performance of grease should not be underestimated.

2.4.2 Synthetic Base Oils

Synthetic oils are used in greases only when the performance required cannot be achieved with mineral oils. Even today greases of this kind represent less than 5% of overall grease consumption.

2.4.2.1 Synthetic Hydrocarbons

Poly(α -olefins) is the ideal base oils for wide temperature-range greases. They are usually used in the same viscosity range as their mineral oil equivalents, but whereas the upper kinematic viscosity border of the former is ca $50 \text{ mm}^2 \text{ s}^{-1}$ at 100°C , Poly(α -olefins) and similar products are available to ca $2000 \text{ mm}^2 \text{ s}^{-1}$ at 100°C . In contrast with mineral oils they are preferably shrinking rather than swelling polymeric sealing materials. Therefore, esters with softener properties must be added. Greases made from Poly(α -olefins) with standard viscosities are usually meant for lifetime lubrication, those made from mixtures with mineral oils are often called semi-synthetic and are used in specialized greases to increase lifetime.

Polybutenes and comparable polymers are usually used to increase the viscosity of standard base oils; occasionally they are used as a base oil component, or even the only base oil.

2.4.2.2 Other Synthetic Base Oils

High molecular-weight esters made from diols or polyols and dicarboxylic acids with viscosities greater than $2000 \text{ mm}^2 \text{ s}^{-1}$ at 40°C are used as base oils in greases that must be solvent resistant.

Silicone oils can be regarded as polyethers of alkylated silicic acids. In contrast with other greases silicone greases are better distinguished according to the properties of their base oils. The kinematic viscosities of silicone oils for greases range from ca 75 to ca $10000 \text{ mm}^2 \text{ s}^{-1}$ at 40°C . Dimethylsilicone oils are physiologically inert; when thickened with highly dispersed silicic acid they are mainly used as sealants or in applications where specific electrical and thermal conductivity is important.

Apart from being suitable for temperatures up to 270°C perfluorinated ethers thickened with PTFE powders are the only greases that can work in the presence of aggressive chemicals such as oxygen or chlorine. This is also their main advantages over the corresponding greases based on partially fluorinate silicone oils.

2.4.2.3 Immiscible Base Oil Mixtures

Greases are the only lubricants that with their thickeners have brackets at their disposal to force immiscible liquid component into one lubricant. Friction of hydrocarbon or ester-based greases can be reduced in this way and lifetime can be prolonged with polyethers and with polyester. Similar results have been reported for greases made from Poly(*α*-olefins) and perfluorinated ethers.

2.5 Additives [9,10]

Most of the additives used in liquid lubricants can be used in greases, although in general at clearly higher concentrations as shown in Table 2.6. Interactions of thickeners and additives must therefore always be considered.

Table 2.6: Usual grease additive levels (%) [10]

Additives	% wt. in grease
Antioxidants	0.10 – 1.00
Corrosion inhibitors	0.50 – 3.00
EP/AW additives	0.50 – 5.00
Metal deactivators	0.05 – 0.10
Solid lubricants (black)	1.50 – 3.00
Tackifiers	0.10 – 1.00

EP (extreme pressure) is the additive for lubricants with a role to decrease wear of the parts of the gears exposed to very high pressures. EP typically contains organic sulfur, phosphorus or chlorine compound including sulfur-phosphorus and sulfur-phosphorus-boron compound, which chemically react with the metal surface under high pressure condition. AW is the anti-wear additives to prevent metal to metal contact between parts of gears. AW typically contains zinc and phosphorus compound.

A typical lithium 12-hydroxystearate-based multi-purpose grease contains at least 0.2% w/w of an antioxidant or a mixture of antioxidants, between 0.5 and 1.0% w/w of one or several corrosion inhibitors, ca 0.05% w/w of a metal deactivator and (in its EP-version up to 2.5% w/w EP/AW additives) depending on the type chosen.

2.6 Manufacture of Greases [9]

The properties of greases, especially metal soap-based greases, depend not only on their composition but also, and to nearly the same extent, on the way in which the thickeners are prepared and dispersed.

2.6.1 Metal Soap-Based Greases

2.6.1.1 Batch Production with Preformed Metal Soaps

It is possible, as one stage of grease manufacture, for a metal soap prepared in an independent first step, or a commercially available soap, to be dissolved or dispersed and heated and cooled again under defined conditions in suitable base oil. But because of the higher costs of the thickener this method can be recommended only for highly sophisticated synthetic greases with precise chemistry or for functional base fluids that

would react with the water or, even worse, with the steam generated during the neutralization process.

2.6.1.2 Batch Production with Metal Soaps Prepared In-situ

In general fatty acids or their glycerides or even their methyl esters are reacted with aqueous solutions or suspensions of the described metal hydroxides in part of the base oil. Each batch of a grease is produced by following a ten-point schedule as shown in Table 2.7

When base oils such as silicone oils used for the in-situ production of soap greases, the thickeners are sometimes formed and dispersed in the presence of solvents which are subsequently removed by extraction or evaporation.

The batch production of metal soap greases can be automated. This has been achieved with the aid of value engineering and computer control.

Table 2.7: Batch production of soap based greases – ten-point schedule. [9]

Schedule	Instructions
1	Dissolution or dispersion of the fatty acids in one third to two thirds of the base oil at temperatures up to 90°C;
2	Addition of the metal hydroxides as a solution or suspension in water,
3	Heating to temperatures between 115 to 150°C or under pressure at 180 to 250°C depending on the type of reactor,
4	Dehydration of the soap by heating to 80 to 200°C or by pressure release;
5	Crystallization during cooling to 150 to 130°C combined with addition of more base oil;
6	Addition of additives at temperatures below 80°C;
7	(pre)filtration and homogenization with one of several possible devices;
8	Adjustment of the specified consistency or flow pressure;

Table 2.7: Batch production of soap based greases – ten-point schedule (cont.) [9]

Schedule	Instructions
9	(end)filtration and deaeration; and
10	Packing into containers

2.6.1.3 Continuous Production

The advantages of such a unit are its compact size (a few hundred liters only), its minimal energy consumption, and the uniformity of the product; the disadvantages are the difficulty of producing different ranges of products and the capacity of such units – far bigger than the need for common greases nowadays. Continuous production of highly sophisticated greases has not been possible for many years, but recently the continuous manufacture of lithium complex greases has been reported.

Comparison of the different processes used to make metal soap-based greases shows that no single process is optimum for every kind of grease and investigation of four processing systems for lithium greases, including high concentrate saponification, indicates that manufacturing greases by conventional methods is not necessarily a disadvantage.

2.7 Grease Performance[9]

The performance of grease is, again, probably best judged in terms of the thickener. From a more theoretical view there are twelve main phenomena which must be considered. Of these twelve, all but two – tackiness and toxicity – are related either to pressure or to temperature. The action or effect of pressure or temperature results in twenty-four requirements (Table 2.8). It is out of question for a real grease to satisfy all these requirements, because there are eleven necessary performance contradictions and thirty-three more or less marked restrictions. The

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suitability of grease for both high- and low-temperature applications is, for example, difficult to achieve, although the lower and upper temperature limits of grease exceed those of its base oil, by analogy with Raoult's law. This means that the thickener acts as an impurity that, on the one hand, hinders crystallization and thus lowers the pour-point of the oil yet, on the other hand, reduces its vapor pressure. The effect can be increased by use of the kinds of polymer employed as pour-point depressants and viscosity index improvers in lubricating oils. The temperature-dependence of the apparent viscosity of grease – at constant shear rates – is less pronounced than that of its base oil.

Table 2.8: Twenty-four properties of greases [9]

Twelve phenomena	Twenty-four properties
High temperature	Maximum thermal stability Minimum evaporation loss Maximum viscosity
Low temperature	No (regular) crystallization Minimum viscosity
Aging	Maximum oxidation resistance Resistance to changes in structure

Table 2.8: Twenty-four properties of greases (cont.) [9]

Twelve phenomena	Twenty-four properties
Compatibility	No reaction with non-ferrous metals Maximum corrosion inhibition Maximum polymer compatibility Immiscibility with foreign liquids Deflection of foreign solid matter
Oil loss	Optimum oil loss ^{a)}
Toxicity	No toxicity Biodegradability
Tackiness	Optimum tackiness ^{a)}
Flowability	Optimum relaxation ^{a)} Maximum pumpability
Shear	Maximum mechanical stability, or Optimum relaxation time ^{a)}
Load	Optimum elasticity ^{a)} Maximum lubricating film thickness Maximum emergency running properties
Friction	Minimum, or optimum friction ^{a)}
Wear	Minimum wear

^{a)} According to application.

Sometimes, usually when a unit is lubricated with a new grease, the performance of the second grease can be affected by the first. Cleaning of the unit is, therefore, always the best solution. The danger resulting from mixing two greases is nevertheless often overestimated and some of the charts describing incompatibilities in the grease literature are seen contradictory.

Possible incompatibility is best checked experimentally with the so-called Shell-roller test. A

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change in the structure usually leads to softening of the mixture and to a decrease of the dropping point. Mention is to make of two incompatibilities only – that between lithium and sodium soap-based greases and that between inorganic thickened greases and other greases with many additives. Both occur in practical grease lubrication and are caused by the thickeners. Loss in performance otherwise is simply because of the lower efficiency of the first grease. If the greases contain very different and reactive additives this can also result in incompatibility

2.8 Applications of Greases [9]

Increased knowledge of base oils and thickener systems enables the selection and naming of greases on the basis of these chemical and physical insights. The selection of a grease is always a compromise between the demands of a customer and the circumstances the grease must face during its operational life – temperature, speed, load including centrifugal forces and vibrations, re-lubrication intervals based on a knowledge of the lubrication points, for applications which can be roller bearings, plain bearings, chassis, joints, 5th wheels, door locks, switches and seals of different design.

2.9 Test Methods for Grease [9-11]

Many test methods are used today; all are meant to judge the single or combined and more or less complex properties of greases. The last summary containing detailed descriptions of ASTM and DIN methods was written by Schultze in 1962; another emphasizing on Russian GOST and former East German TGL methods was published in 1984. The most important ASTM and DIN methods are described in Table 2.9 and 2.10. Complete collections are published regularly; the same is true for the French AFNOR, the English IP, the Japanese JIS, and some other national collections. The development of international standards (EN and ISO) is slowly proceeding.

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Because of the large number of publications about the different test methods, their improvement, and their comparison, few surveys concerned with EP, wear and with standard tests or performance tests using real components are cited. There are also at least two new test methods that might be helpful in the future, the tipping rod method for determination of the yield point of semi-fluid greases and the Vogel-Marawe test device for determination of oil separation under pressure and which enables the observation of hardening tendencies simultaneously.

Table 2.9: Important ASTM test methods for lubricating greases. [9]

Test Method	Properties
ASTM D 1092-93	Apparent viscosity
ASTM D 1263-94	Leakage tendencies of automotive wheel bearing greases
ASTM D 1264-96	Water washout characteristics
ASTM D 1478-91	Low-temperature torque of ball bearing greases
ASTM D 1742-88	Oil separation during storage (air pressure method)
ASTM D 1743-94	Corrosion preventive properties
ASTM D 1831-88	Roll stability
ASTM D 2509-93	Load carrying capacity, Timken method
ASTM D 3337-94	Life and torque in small bearings
ASTM D 3527-95	Life performance of automotive wheel bearing greases
ASTM D 4049-86	Resistance to water spray
ASTM D 2265-06	Dropping point of lubricating grease over wide temperature range

Table 2.10: Important DIN (ASTM) test methods for lubricating greases [9]

Test Method	Descriptions
DIN 51350-4 (ASTM D 2596-97)	Testing in the Shell four-ball tester, determination of the welding load of consistent lubricants
DIN 51350-5 (ASTM D 2266-91)	Testing in the Shell four-ball tester, determination of the wear parameters of consistent lubricants
DIN 51801 (ASTM D 566-97), replaced by DIN ISO 2176	Determination of dropping point of greases
DIN 51802	Testing of rolling bearing greases with regard to their corrosion-inhibiting properties, SKF-Emcor method
DIN 51804-1 (ASTM D 217-97), replaced by DIN ISO 2137	Determination of cone penetration of greases with hollow cone and solid cone
DIN 51804-2 (ASTM D 1403-97, replaced by DIN ISO 2137)	Determination of cone penetration of greases with one-quarter cone
DIN 51805	Determination of yield pressure of lubricating greases, Kesternich-method
DIN 51807-1	Test for the behavior of greases in the presence of water, static test
DIN 51808 (ASTM D 942-90)	Determination of oxidation stability of greases, oxygen method
DIN 51810	Determination of flow behavior of greases in the rotary viscometer
DIN 51811 (ASTM D 4048-86)	Testing of corrosive effects of greases on copper, copper strip test
DIN 51817	Determination of oil separation from greases under static conditions
DIN 51821-2	Test using the FAG roller bearing grease testing apparatus FE 9

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2.10 Literature reviews [11-14]

According to S. Gryglewicz, W. Piechocki, G. Gryglewicz whose experiment topic is preparation of polyol esters based on vegetable and animal fats. The possibility of using some natural fats: rapeseed oil, olive oil and lard, as starting material for the preparation of neopentyl glycol (NGL) and trimethylol propane (TMP) esters is reported. The synthesis of final products were performed by alcoholysis of fatty acid methyl esters, obtained from natural fats studied, with the appropriate polyhydric alcohol using calcium methoxide as a catalyst. The basic physicochemical properties of the NPG and TMP esters synthesized were the following: viscosity at 40 °C in the range of 13.5-37.6 cSt, pour point between -10.5 and -17.5 °C and very high viscosity indices, higher than 200. Generally, the esters of neopentyl alcohol were characterized by higher stability in thermo-oxidative conditions in comparison of native triglycerides. Due to the low content of polyunsaturated acids, the olive oil based esters showed the highest thermo-oxidative resistance. Also, methyl esters of fatty acids of lard would constitute a good raw material for the synthesis of lubricating oils, provided that their saturated acids content was lowered. This permits synthesis of NPG and TMP esters with a lower pour point (below -10 °C) than natural lard (+33 °C). Generally, the synthesized esters show moderate thermal oxidative stability, the characteristic feature of most synthetic oil produced from natural triglycerides. In similar thermal-oxidative conditions, the viscosity and acid number of hydrocarbon oils increased only slightly. Oils synthesized from natural products are generally approved of as environmentally friendly functional fluids and therefore they can be used widely.

Monoglyceride synthesis by glycerolysis of methyl oleate on solid acid-base catalyst which is wrote by Critián A. Ferretti, Agostina Soldano, Carlos R.Apesteuña, J. Isabel Di Cosimo. The synthesis of monoglycerides by glycerolysis of methyl oleate, an unsaturated fatty acid nethyl ester, was studied on acid-base solid catalysts as an alternative to the current commercial technology that uses liquid base catalysts. Initially, the reactor conditions such as catalyst particle size and stirring rate required for operating the four-phase semi-continuous

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reactor under a kinetically controlled-regime were determined. Then the optimization of the reaction parameters for achieving high monoglyceride yields was performed using MgO. MgO compared favorably with the corresponding homogeneously catalyzed process. In fact, when using high reaction temperatures (493-523K), glycerol/methyl oleate molar ratios between 2 and 6, and catalyst/reactant ratios of about 30g/mol, glycerolysis of methyl oleate yields up to 77% monoglycerides in 2 h, a much higher value than those usually obtained via the liquid base-catalyzed homogeneous process (40-60%). The acid-base site requirements for the glycerolysis reaction were investigated using single oxides with different electronegativities. A good correlation was found between the catalytic activity and the base site density. In addition, results show that glycerolysis of methyl oleate requires strong base sites such as those of MgO.

According to Relationship among microstructure, rheology and processing of a lithium lubricating grease by M.A. Delgado, M.C. Sánchez, C. Valencia, J.M. Franco and C. Gallegos. Their work was to evaluate the evolution of the microstructure and rheology of lubricating grease during its manufacturing process. With this aim, lithium lubricating greases were prepared by inducing the saponification reaction between 12-hydroxystearic acid and hydrated lithium hydroxide within a naphthenic lubricating oil medium, applying a controlled-temperature programme. The manufacturing process was followed through the mixing rheometry technique by measuring the evolution of torque with processing time. Samples of incipient and finished grease were taken from the stirred tank at different processing times. Rheological (linear visco-elasticity and viscous flow) and mechanical stability tests, as well as morphological studies, were carried out on each sample. The changes found in the microstructure and rheology of a lubricating grease during its processing have been related to the soap concentration in the reacting mixture, the waxy soap transition at high temperatures and the further cooling steps. From the experimental results obtained, we may conclude that a suitable lithium lubricating grease is a highly structured system, based on the development of a three-dimensional network due to the presence of metallic soap crystallites.

Influence of grease composition on rolling contact wear: experimental study which is researched by V. Mota, L.A. Ferreira. They present an experimental study on the influence of grease composition on rolling contact wear (RCW). Experimental tests for three greases and correspondent base oils were carried out on a twin-disc machine under pure rolling conditions. The following parameters were varied: base-oil viscosity, percentage of soap concentration and the presence of additives. The second aim of these tests is to analyse the use of artificial dents as a technique to evaluate RCW: prior to the tests, artificial dents were printed on one of the contacting surfaces. These dents were used to calculate the wear volume that is removed from the surfaces, based on the assumption that when the material is removed, the diameter of these dents diminishes. For each stop, images obtained using video-microscopy were analysed and the diameter of the dents, at a given number of cycles, was calculated. It was found that tests with different lubricants resulted in different damaged areas around the dents. Based on this, a comparison of this area growth throughout the fatigue cycles was used as a way to compare the influence of grease composition on RCW.

Lubricants based on renewable resources - an environmentally compatible alternative to mineral oil products by Andreas Willing which is about the development of lubricants like, e.g. engine and hydraulic oils was traditionally based on mineral oil as a base fluid. This fact is related to the good technical properties and the reasonable price of mineral oils. In addition, environmental problems associated with the production and use of chemicals and the limited capacity of nature to tolerate pollution became obvious, and the critical discussion included besides acid rain, smog, heavy metals, and pesticides also mineral oil. A disadvantage of mineral oil is its poor biodegradability and thus its potential for long-term pollution of the environment. From the early development of lubricants for special applications (e.g. turbojet engine oils) it was known, those fatty acid polyol esters have comparable or even better technical properties than mineral oil. Subsequently, innumerable synthetic esters have been synthesized by systematic variation of the fatty acid and the alcohol components. Whereas the alcohol moiety of the synthetic esters is usually of petrochemical origin, the fatty acids are almost exclusively based on

renewable resources. The physico-chemical properties of oleochemical esters can cover the complete spectrum of technical requirements for the development of high-performance industrial oils and lubricants (e.g. excellent lubricating properties, good heat stability, high viscosity index, low volatility and superior shear stability). This article will focus on the ecological properties of oleochemical (synthetic) esters. The environmental relevance of oleochemicals in comparison to petrochemicals is discussed, and then the principles of an ecological assessment are described. The ecotoxicological properties and the biodegradability of oleochemical esters are presented. Finally, the ecological properties of the oleochemical esters are discussed with regard to existing environmental classification and labeling systems.



Chapter 3

Experiment details

3.1 Chemicals and materials

1. Glycerol: Carlo Erba Reagent, Code no.:453755
2. Oleic acid: Aldrich, LOT: 10529CH-039
3. Adipic acid 99% : ACROS organic, LOT: A0229157
4. Conc. H₂SO₄: Baker Analyzed, LOT: G10W62
5. Palmitic acid: Riedel-de Haën, LOT: 71710
6. Sodium Hydroxide: Lab-scan analytical sciences, Code no.: K2001
7. Used cooking oil from Betago company

3.2 Equipments and instruments

1. Magnetic bar
2. Heater with thermostat: IKA, Model: C-MAG HS7
3. Beaker: 250 ml and 100 ml
4. Round-bottom flask: 250 ml and 100 ml
5. Oil bath
6. Pipe thread tape
7. Distillation apparatus
8. Aluminum foil
9. Graduated cylinder
10. Nuclear Magnetic Resonance (NMR): Bruker, Model: Avance DPX 300
11. Differential scanning calorimeter (DSC): Perkinelmer, Model: Pytis diamond DSC

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12. Fourier transform infrared spectroscopy (FT-IR): Perkin Elmer Ltd, Model: FT-IR Spectrum GX
13. Blender: PHILIPS, Model: HR2001 5 stars blade and 350w motor
14. Dropping point apparatus: Petrotest, Model: Jumotron
15. Water washout apparatus: Stanhope seta, Model: 19610-4
16. Thermal gravimetric analysis (TGA): Perkin Elmer, Model: Pyris1 TGA

3.3 Polyester synthesis

1. Add 9.2 g. (0.1 mol) of glycerol with 31.38 g. (0.1 mol) of oleic acid in a 250 ml round-bottom flask. And then, add 3 drops (0.114g.) of conc. H_2SO_4 (approximately 1% by mol of glycerol).
2. Put a magnetic bar in the flask, cover the flask thoroughly with aluminum foil.
3. Place the flask in an oil bath and then connect other glasswares into a distillation apparatus. Cover the distillation head with foil instead of a thermometer and tighten with pipe thread tape.
4. Pierce one small hole through foil in order to make the pressure inside the distillation apparatus to approximately 1 atm.
5. Connect the adapter at the end of the condenser and tighten all the joints with pipe thread tape.
6. Place a cylinder beneath the adapter, also tighten with pipe thread tape.
7. Heat the oil bath up to $105^{\circ}C$ using hot plate stirrer. Then, keep heating and stirring for 3 days or until no more water is produced.
8. Increase the temperature to $140^{\circ}C$ while slowly adds 14.614g. (0.1mol) of adipic acid. Then, keep heating and stirring the reaction mixture for about 2 days or until no water is produced.

9. Finally, cool down the reaction to room temperature and store the product in a plastic bottle. Keep it for use in part 3.5
10. Repeat step 1-9 again by changing oleic acid to 25.646 g (0.1mol) of palmitic acid with 9.217 g (0.1 mol) of glycerol and 14.509 g (0.1 mol) of adipic acid.

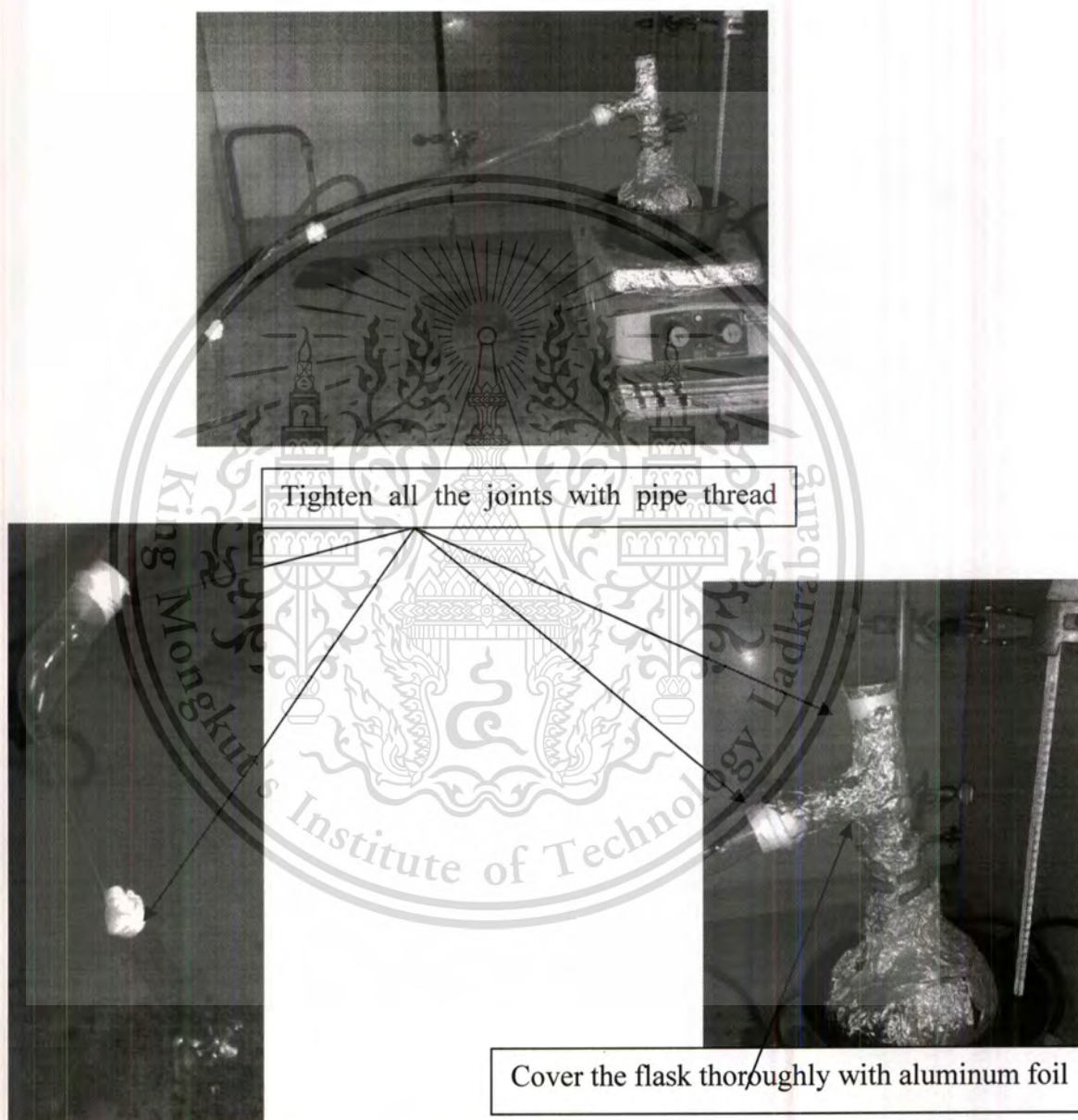


Figure 3.1: The apparatus of oil synthesis

3.4 Soap preparation

1. First mix 4.901g of sodium hydroxide with 10 ml of water in a 50 ml beaker.
2. Then, stir it until sodium hydroxide completely dissolves into 12.25 M NaOH
3. After that, place 20ml of waste cooking oil in a 100 ml beaker.
4. Finally, add 12.25 molar of NaOH solution from above dropwise while heating and stirring at 70 °C until it becomes solid.

3.5 Grease preparation

1. Add 70 g. of synthetic base oil from part 3.3 to 30 g. of the soap mixture from part 3.4
2. Blend the mixture using blender for 30 minutes until it becomes smooth cream.
3. Repeat step 1-2 again by changing the amount of base oil to 80 and 90 g, and soap to 20 and 10 g, respectively.

3.6 Dropping Point Testing by ASTM D 2265 [15]



Figure 3.2: Dropping point apparatus

1. Insert empty test tubes in every test tube well and a thermometer having a range from -5 to 400°C in the thermometer well of the oven
2. Turn on the oven and select the lowest aluminum block oven temperature setting from the four listed below that will result in an observed dropping point at or below the corresponding maximum observed dropping point shown for that oven temperature setting.
3. Select and use test tubes and accessories to minimize wobble of the thermometer. All components must be at room temperature prior to the test. Place the components through on the thermometer. Adjust the bushing and the bushing support ring so that is about 25 mm from tip of the thermometer. Place the cup support in tube. Insert the thermometer depth gage and the thermometer assembly in the tube. Position the thermometer so that the tip bottoms in the gage. Adjust the bushing and thermometer clamp so that the bushing shoulders on the top edge of the tube.
4. Select a clean cup, and fill it with grease either by pushing the cup into the sample presented or by using a small spatula. Overfill the cup, and use the spatula to force some of the grease out of the bottom hole of the cup to help remove any trapped air. Add more samples, and strike off the excess grease level with the top of the cup. Gently press the cup, held in a vertical position with the smaller opening at the bottom, down over the metal rod until the latter protrudes about 25 mm. Press the rod against the cup in such a manner that the rod makes contact at both the upper and lower peripheries of the cup. Maintain this contact, rotating the cup on the rod along the index finger to give it a spiral-like motion down the rod to remove a conical section of the grease which adheres along the rod. As the cup approaches the end of the rod, carefully slip the rod out of the cup, without marring the inside surface of the grease, so that a smooth film of reproducible thickness remains inside the cup. If surface has been touched by the rod or any air bubbles are noted, repack the cup.

5. Remove the thermometer assembly and depth gage from the tube. Place the grease cup on the cup support in the test tube and carefully reinsert the thermometer assembly. Make no further adjustment as the thermometer bulb is now positioned to provide adequate clearance between the tip of the bulb and grease sample in the cup.
6. After making certain that the oven temperature has stabilized, remove an empty tube from the oven and gently insert the tube assembly in its place. Exercise care to ensure that the cup remains upright in the cup support. If the cup is tilted, the thermometer bulb can come in contact with the film of grease and result in an erroneous value.
7. When the first drop of material falls free of the cup orifice and reaches the bottom of the test tube, record both the temperature of the cup and of the oven to the nearest degree. Certain grease, for example, some simple soap compositions, or those containing some types of polymers can form a drop with a tailing thread which can hold until the drop reaches the bottom of the test tube is recorded as the observed dropping point.

3.7 Water washout characteristics by ASTM D 1264 [16]



Figure 3.3: Water washout apparatus

1. Pack the tared bearing with 4.00 ± 0.05 g of test grease. Insert the bearing and tared shields into the housing, and assemble the unit in the test apparatus.

2. Add a minimum of 750 mL of preheated distilled water to the reservoir, but keep the water level below the bearing housing. Without starting the bearing, start the water circulating pump while diverting the water spray from the housing by means of a piece of tubing attached to the capillary discharge tube or with a deflecting metal shield until equilibrium temperature is attained. When the test is to be made at the higher temperature of $79 \pm 1.7^\circ\text{C}$, it will be necessary to heat the water to the specified temperature by a previously selected source of heat.
 - If the rig has one motor driving both pump and test bearing, remove the belt from the test bearing spindle pulley during water warm-up time.
3. When the water reaches the specified temperature, adjust the by-pass valve to give a water-flow rate, through the rubber tubing and into a glass graduate, of 5 ± 0.5 mL/s. Remove the rubber tubing from the capillary discharge tube, and adjust the water jet so that it impinges on the end plate 6 mm above the outer opening of the bearing housing. Start the bearing.
4. With the bearing operating at a speed of 600 ± 30 rpm, continue the operation for 60 ± 1 min.
5. Shut off the motor and heating source, if used. Remove the test bearing and shields place them on a tared watch glass, with the shields being separated from the bearing and placed with their inner faces upward to expose the wet grease to the air.
6. Dry the bearing and shields for 15 ± 0.25 h at $77 \pm 6^\circ\text{C}$, and then weigh to determine the grease loss. The grease remaining on the shields, and any leakage occurring during the drying period, should not be considered as grease lost. Duplicated tests shall be run.

Chapter 4

Results and discussion

4.1 Polyester synthesis

Grease generally contains base oil and thickener. The purpose of this research is to formulate grease from glycerol. The preparation of base oil and thickener were attempted from the esterification reaction of glycerol with oleic acid and adipic acid (to produce base oil), and with palmitic acid and adipic acid (to produce thickener) as explained in Chapter 3 part 3.3.

4.1.1 Reaction with oleic acid

To produce base oil from oleic acid, the preparation was carried out in 2 steps. Firstly, the esterification of glycerol with oleic acid was performed to acquire a liquid product. $^1\text{H-NMR}$ spectrum of this product is illustrated in Figure 4.1

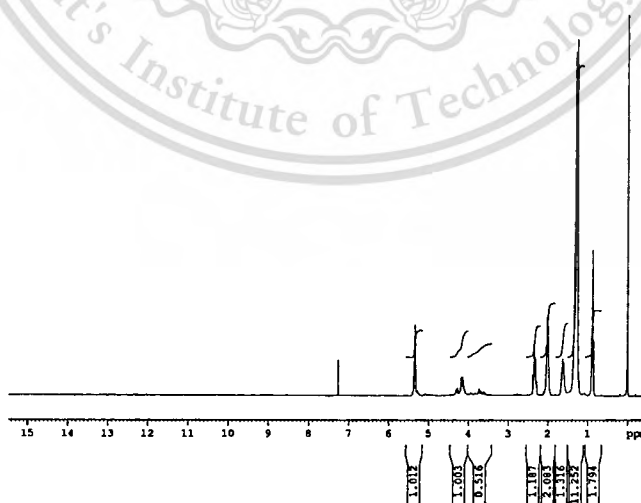


Figure 4.1: The $^1\text{H-NMR}$ spectrum of product from the reaction of glycerol with oleic acid

Table 4.1: The signals from $^1\text{H-NMR}$ spectrum of product from the reaction of glycerol with oleic acid

δ (ppm)	Signals
0.8-1.0	(CH_3 -)
1.2-1.5	($-\text{CH}_2$ -)
1.5-1.7	($-\text{OOC-CH}_2\text{-CH}_2$ -)
1.9-2.2	($-\text{CH}=\text{CH-CH}_2$ -), ($-\text{CH-OH}$), ($-\text{CH}_2\text{-OH}$)
2.3-2.5	($-\text{OOC-CH}_2$ -)
3.6-3.8	($-\text{CH-OH}$), ($-\text{CH}_2\text{-OH}$),
4.0-4.5	($-\text{COO-CH}_2$ -), ($-\text{COO-CH}$ -)
5.3-5.5	($-\text{CH}=\text{CH}$ -)

The signals of the product the first step are listed in Table 4.1 which shows that the peak of ($-\text{COO-CH}_2$ -) and ($-\text{COO-CH}$ -) groups appears at δ 4.0-4.5 ppm and the integration of signal from ($-\text{CH-OH}$) and ($-\text{CH}_2\text{-OH}$) groups of glycerol at δ 3.6-3.8 ppm are reduced. This proves that the reaction between glycerol and oleic acid occurred. Moreover, the condensing water from the esterification was also detected.

However, the integration of ($-\text{COO-CH}_2$ -) and ($-\text{COO-CH}$ -) signal should be less than those from ($-\text{CH-OH}$) and ($-\text{CH}_2\text{-OH}$) since the mole ratio of glycerol to oleic acid used was 1 : 1, but the opposite result is shown by the NMR. In addition, the water which condensed from the reaction should be 1.8 ml when the glycerol/acid ratio is 0.1 mol: 0.1 mol. Therefore the water should be condensed 0.1 mol also. On the other hand, 2.4 ml of water was produced. This is probably due to the immiscibility of glycerol in oleic acid, so the reaction occurred only at the interface. More of hydroxyl group was disappeared than expected because some hydroxyl group of glycerol reacted with each other. Hence, the etherification reaction also occurred in the process. (Figure 4.14 and 4.15) Moreover, the dehydrogenation of hydroxyl groups of glycerol to form acetal and acrolein could occur.

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As notice, acrolein and acetal have double bonds which could react with the reaction mixture. To form several by products which, as a consequence, made the color of finish-product became dark brown.

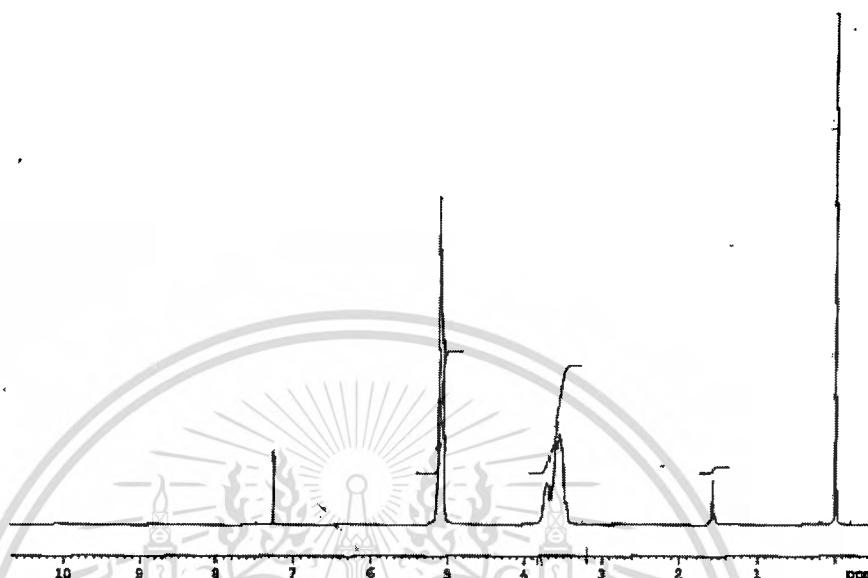


Figure 4.2: The $^1\text{H-NMR}$ spectrum of glycerol

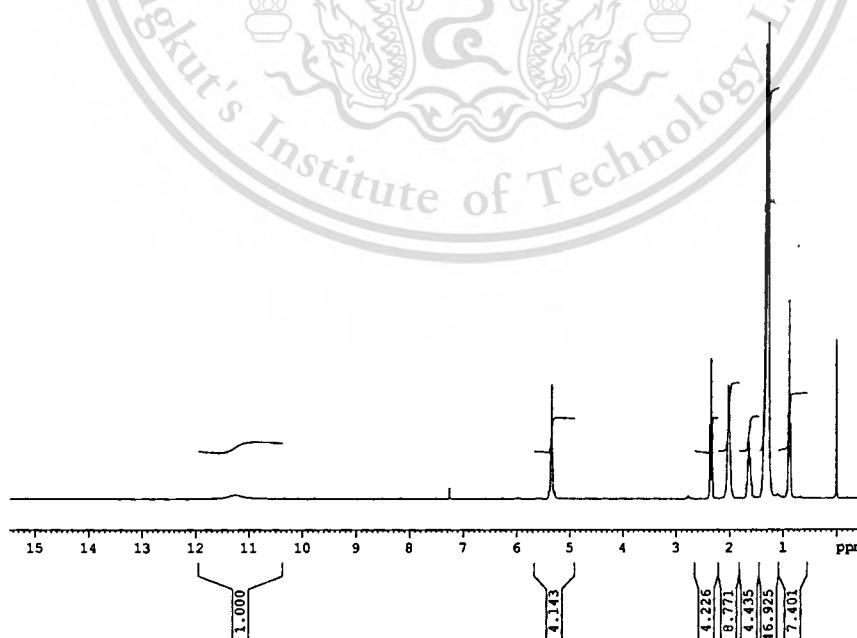


Figure 4.3: The $^1\text{H-NMR}$ spectrum of oleic acid

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Finally, the product from the esterification of glycerol with oleic acid in the first step was next reacted with adipic acid to produce a finished liquid product via another esterification. ^1H -NMR spectrum of this product is illustrated in Figure 4.4.

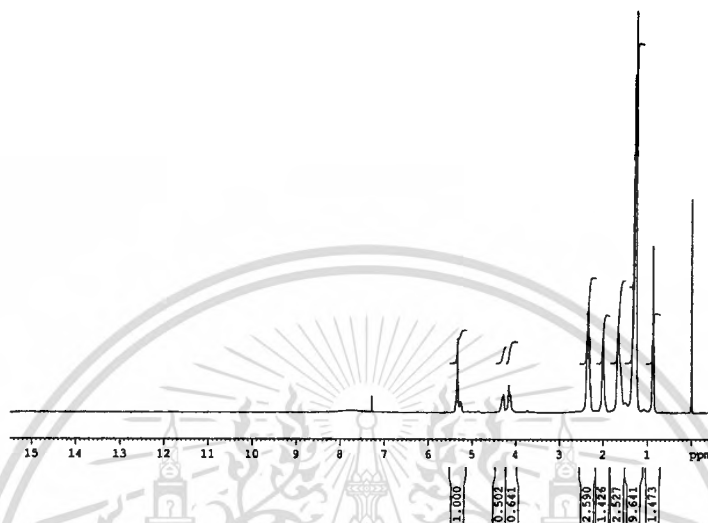


Figure 4.4: The ^1H -NMR spectrum of product from the reaction of glycerol with oleic acid and adipic acid

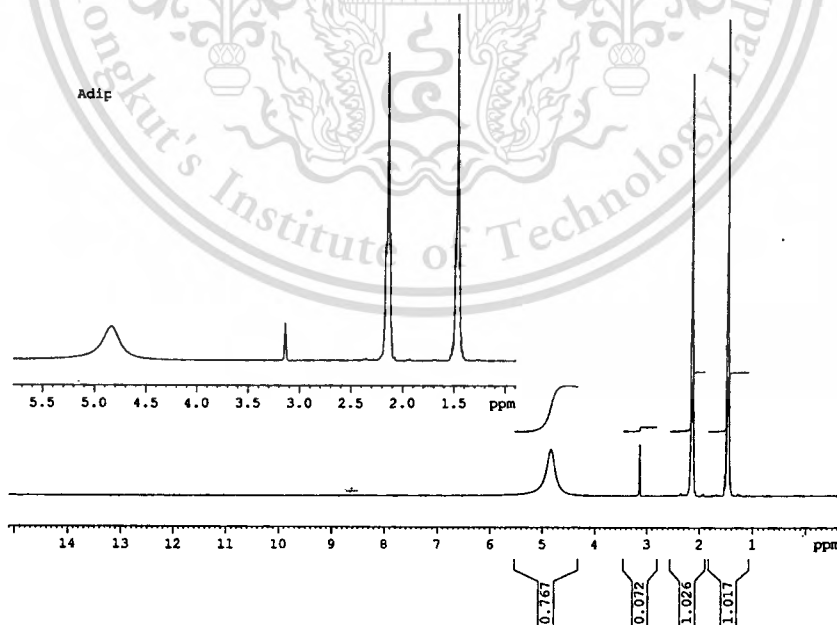


Figure 4.5: The ^1H -NMR spectrum of adipic acid

Table 4.2: The signals from $^1\text{H-NMR}$ spectrum of product from glycerol with oleic acid and adipic acid

δ (ppm)	Signals
0.8-1.0	(CH_3-)
1.2-1.5	($-\text{CH}_2-$)
1.5-1.7	($-\text{OOC-CH}_2-\text{CH}_2-$)
1.9-2.2	($-\text{CH}=\text{CH}-\text{CH}_2$)
2.3-2.5	($-\text{OOC-CH}_2-$)
3.8-3.9	($-\text{CH-OH}$), ($-\text{CH}_2-\text{OH}$),
4.0-4.5	($-\text{COO-CH}_2-$), ($-\text{COO-CH-}$)
5.3-5.5	($-\text{C}=\text{CH-}$)

The signals of the finished product after the reaction with adipic acid are listed in Table 4.2 which shows that the signal intensity of ($-\text{CH-OH}$) and ($-\text{CH}_2-\text{OH}$) groups at δ 3.8-3.9 ppm are insignificantly low as well as the appearances of signals of ($-\text{CH}_2-\text{OOC-}$) and ($-\text{COO-CH}_2-$) groups at δ 4.0-4.5 ppm. In addition, the signals of ($-\text{OOC-CH}_2-\text{CH}_2-$) group at around δ 1.5-1.7 ppm and of ($-\text{OOC-CH}_2-$) group at around δ 2.3-2.5 ppm of finished product both have higher intensity than those of the product before the addition of adipic acid (Figure 4.1). This results show that adipic acid was presumably reacted into the finished product.

However, the signals of ($-\text{OOC-CH}_2-\text{CH}_2-$) group of finished product and of adipic acid are very close which both appear at around δ 1.5-1.7 ppm. Similarly, the signals of (HOOC-CH_2-) group of finished product and of adipic acid both also appear at around δ 2.3-2.5 ppm. Moreover, since the water which condensed from the reaction should be 3.6 ml when the alcohol/acid ratio is 1:1 mol, but 1.6 ml of water was produced. So, these two signals could be from free non-reacted adipic acid remained in the product.

Thermal gravimetric analysis illustrated in Figure 4.6 shows weight loss at 218.2°C and 363.8°C. This is presumably because the vaporization of finished product started at 218°C. After

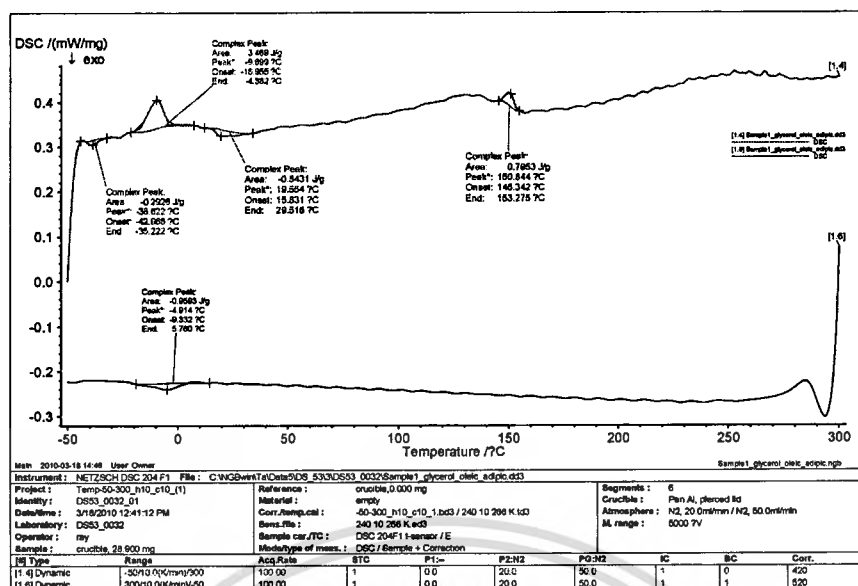


Figure 4.7: DSC of synthetic base oil from oleic acid

4.1.2 Reaction with palmitic acid

To produce thickener from palmitic acid, the preparation was carried out in 2 steps. Firstly, the esterification of glycerol with palmitic acid was performed to acquire a solid product. $^1\text{H-NMR}$ spectrum of this product is illustrated in Figure 4.8

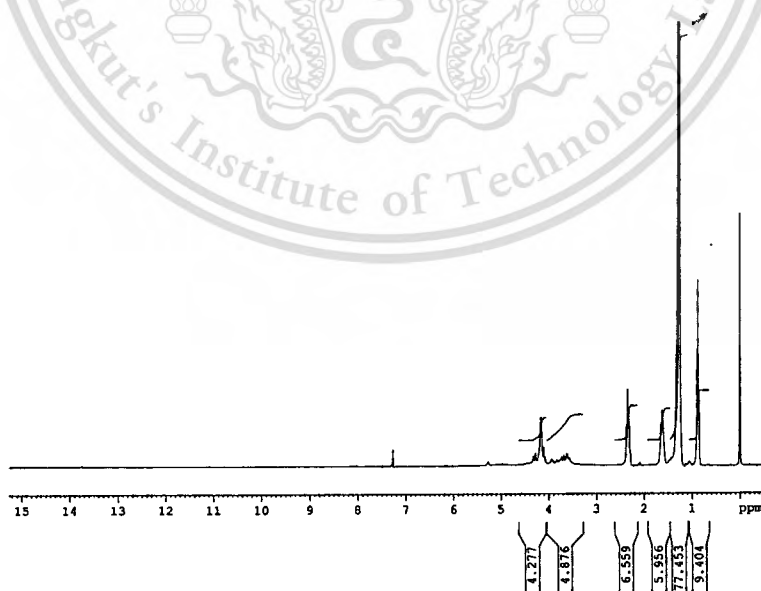


Figure 4.8: The $^1\text{H-NMR}$ spectrum of product from the reaction of glycerol with palmitic acid

Table 4.3: The signals from $^1\text{H-NMR}$ spectrum of product from the reaction of glycerol with palmitic acid

δ (ppm)	Signals
0.8-1.0	(CH_3-)
1.2-1.4	($-\text{CH}_2-$)
1.5-1.7	($-\text{OOC-CH}_2-\text{CH}_2-$), ($-\text{CH}_2-\text{OH}$), ($-\text{CH-OH}$)
2.2-2.4	($-\text{OOC-CH}_2-$)
3.5-4.0	($-\text{CH}_2-\text{OH}$), ($-\text{CH}_2-\text{OH}$), ($-\text{CH-OH}$)
4.0-4.4	($-\text{COO-CH}_2-$), ($-\text{COO-CH-}$)

The signals of the product are listed in Table 4.3 which shows that the peak of ($-\text{OOC-CH}_2-\text{CH}_2-$) and ($-\text{OOC-CH}_2-$) groups appear at δ 1.5-1.7 and 2.2-2.4 ppm, respectively, and the peak of ($-\text{CH}_2-\text{COOH}$) group which normally appears at δ 11.0-12.0 ppm is absent. This proves that the reaction between glycerol and palmitic acid occurred. Moreover, the condensing water from the esterification was also detected.

Since the mole ratio of glycerol to palmitic acid used was 1:1, the water which condensed from the reaction should be 1.8 ml when the glycerol/acid ratio is 0.1 mol:0.1 mol. However, 1.7 ml of water was observed.

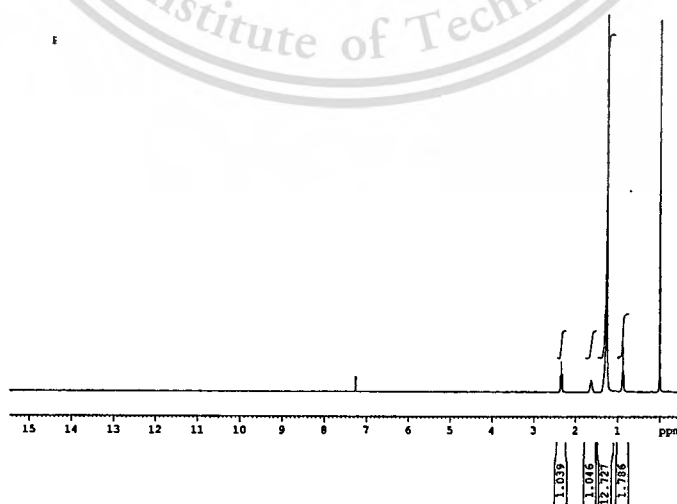


Figure 4.9: The $^1\text{H-NMR}$ spectrum of palmitic acid

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Next, the product from the esterification of glycerol with palmitic acid in the first step was reacted with adipic acid to produce a finished solid product via another esterification. ^1H -NMR spectrum of this product is illustrated in Figure 4.10.

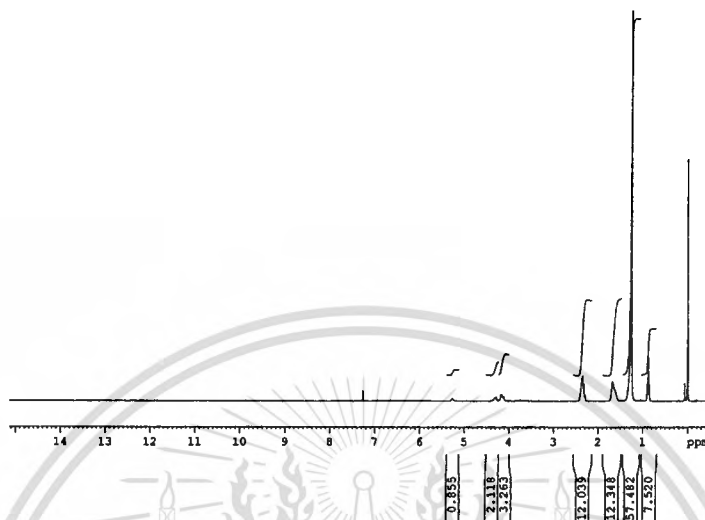


Figure 4.10: The ^1H -NMR spectrum of product from the reaction of glycerol with palmitic acid and adipic acid

Table 4.4: The signals from ^1H -NMR spectrum of product from the reaction of glycerol with palmitic acid and adipic acid

δ (ppm)	Signals
0.8-1.0	(CH_3 -)
1.2-1.4	($-\text{CH}_2$ -)
1.5-1.9	($-\text{OOC}-\text{CH}_2-\text{CH}_2-$), ($-\text{CH}_2-\text{OH}$), ($-\text{CH}-\text{OH}$)
2.2-2.5	($-\text{OOC}-\text{CH}_2-$)
3.6-3.8	($-\text{CH}_2-\text{OH}$), ($-\text{CH}_2-\text{OH}$), ($-\text{CH}-\text{OH}$)
4.1-4.5	($-\text{COO}-\text{CH}_2-$), ($-\text{COO}-\text{CH}-$)

The signals of the finished product after the reaction with adipic acid are listed in Table 4.4 which shows that the signal intensity of ($-\text{CH}-\text{OH}$), ($-\text{CH}_2-\text{OH}$) and ($-\text{CH}_2-\text{OH}$) groups at δ 3.6-3.8 ppm are insignificant. It also shows the appearances of ($-\text{CH}_2-\text{OOC}-$) groups at δ 4.1-4.5

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ppm. In addition, the signals of (-OOC-CH₂-CH₂-) group at around δ 1.5-1.9 ppm and of (-OOC-CH₂-) group at around δ 2.2-2.5 ppm of finished product both have higher intensity than those of the product before the addition of adipic acid (Figure 4.8). This results show that adipic acid was presumably reacted into the finished product.

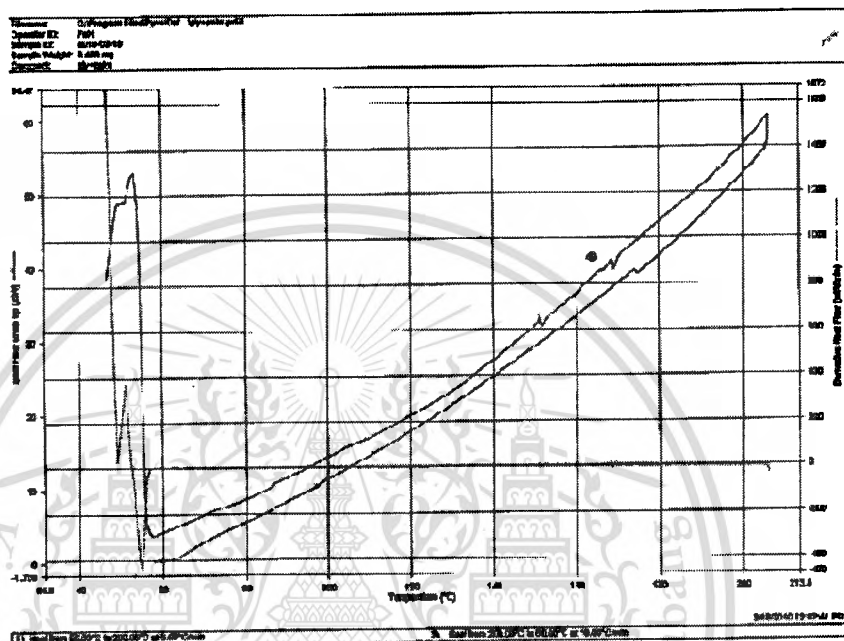
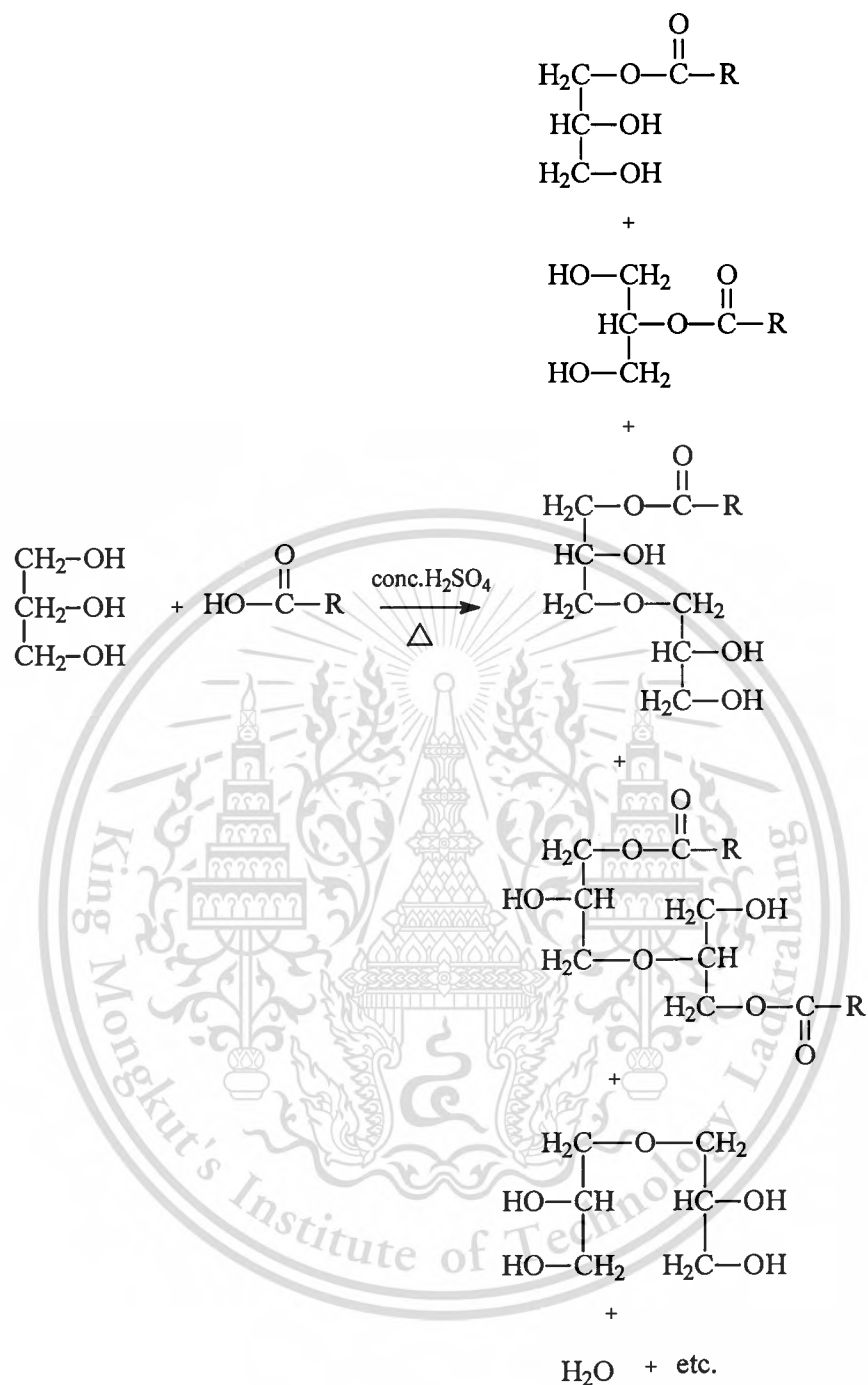


Figure 4.11: The DSC of finished product from palmitic acid

Figure 4.11 shows that the melting point of product is approximately 53 °C, therefore it is not suitable to produce the thickener.

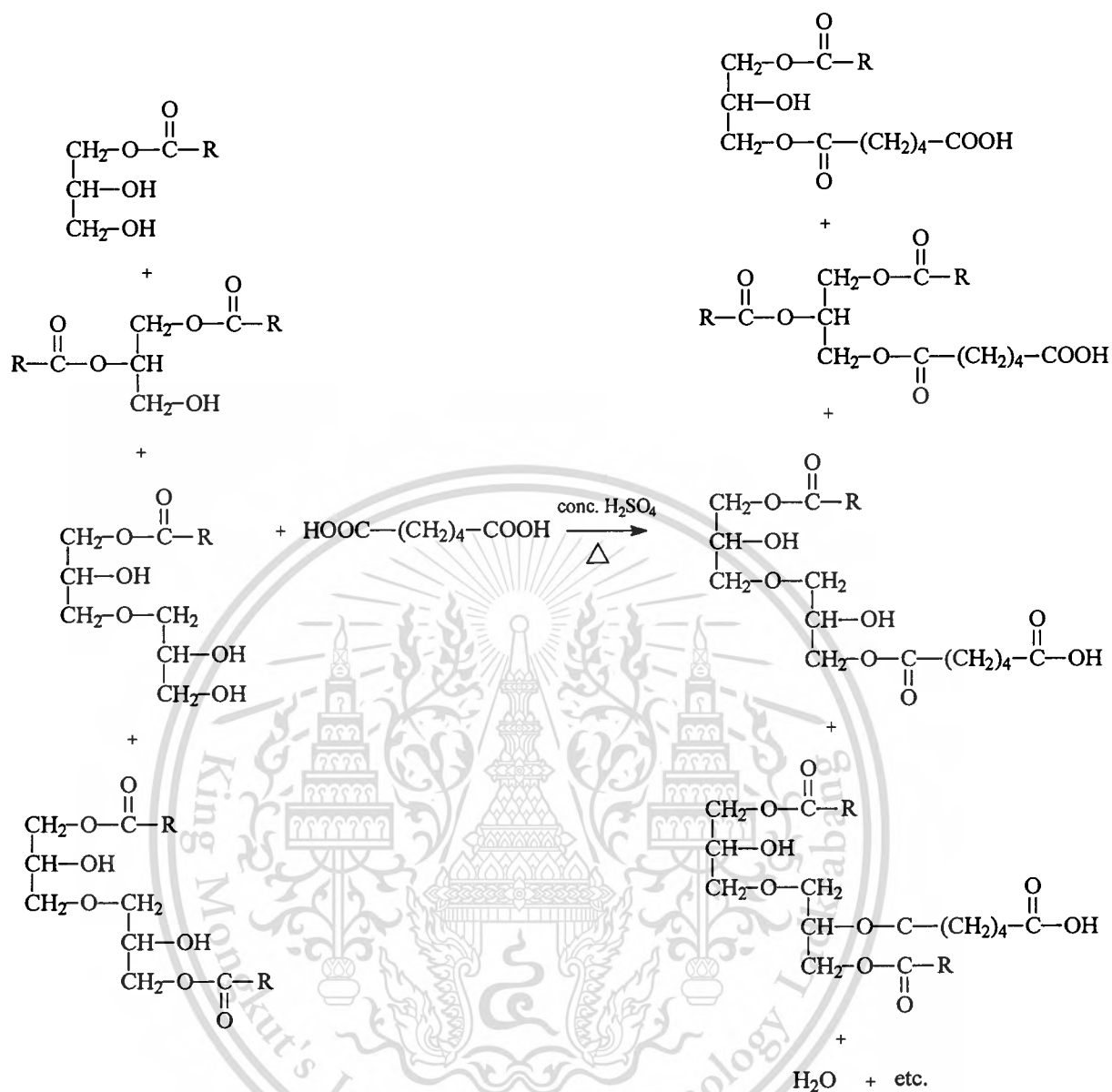
From the above explanations, some of the possible reactions between glycerol and oleic acid or palmitic acid from step 1 could be illustrated in Figure 4.12. Some of the possible reactions from step 2 are also illustrated in Figure 4.13 and 4.14. Dehydrogenation reactions of glycerol are shown in figure 4.15 and 4.16.



where R is $-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$

or $-(\text{CH}_2)_{13}-\text{CH}_3$

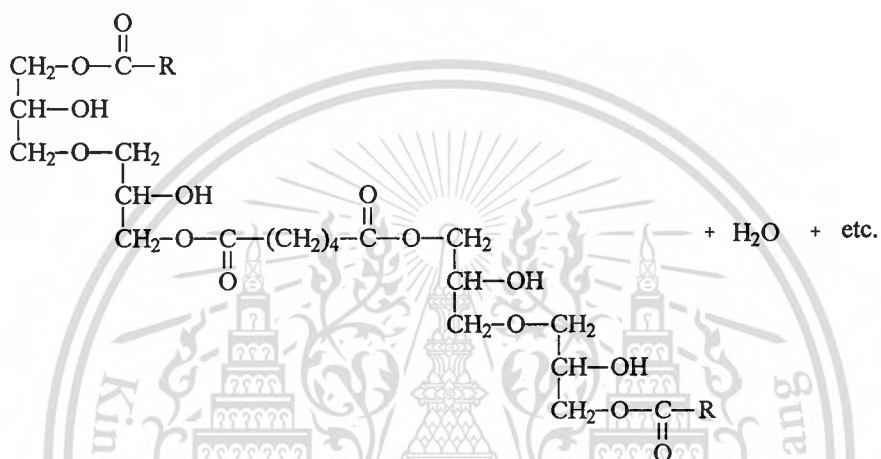
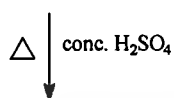
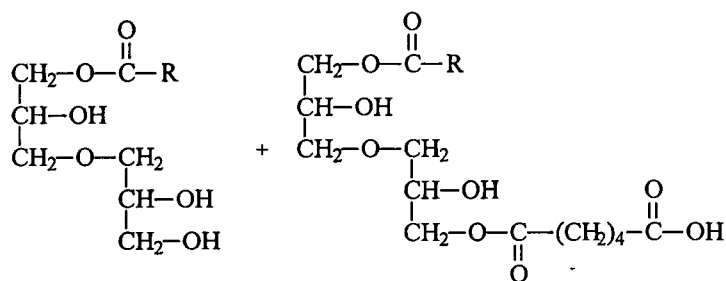
Figure 4.12: Some of the possible reactions between glycerol and oleic acid/palmitic acid



where R is $\text{-(CH}_2\text{)}_7\text{-CH=CH-(CH}_2\text{)}_7\text{-CH}_3$

or $\text{-(CH}_2\text{)}_{13}\text{-CH}_3$

Figure 4.13: The possible finished products after the reaction with adipic acid



where R is $\text{---(CH}_2\text{)}_7\text{-CH=CH---(CH}_2\text{)}_7\text{-CH}_3$
 or $\text{---(CH}_2\text{)}_{13}\text{-CH}_3$

Figure 4.14: More of the possible finished products after the reaction with adipic acid

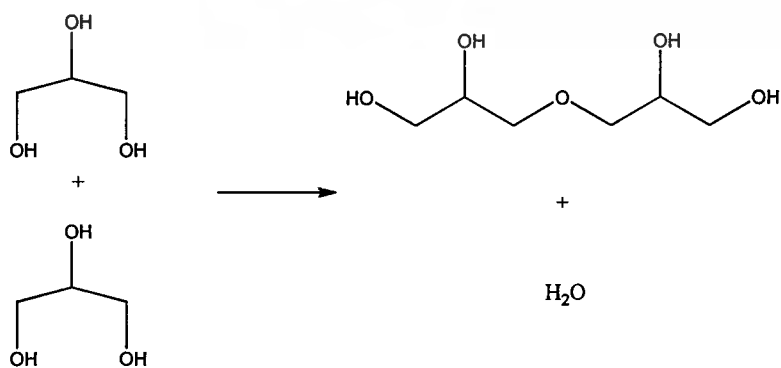


Figure 4.15: Etherification between hydroxyl groups of glycerol

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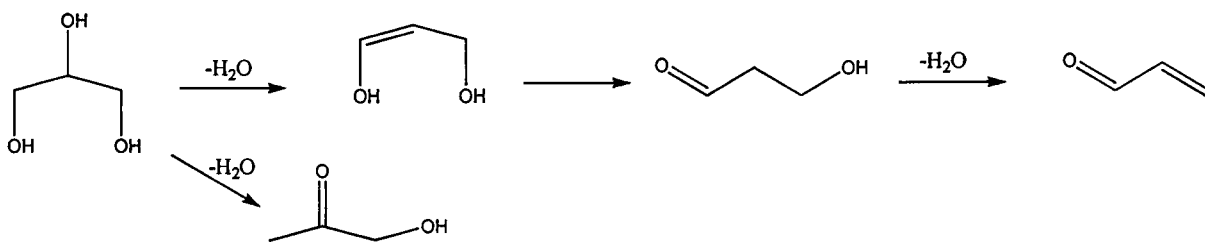


Figure 4.16: Dehydrogenation of glycerol to acrolein and acetal

4.2 Soap synthesis from used cooking oil

Sodium soap was produced from used cooking oil by following the procedure described in Chapter 3 part 3.4. Typically, the oxidation reaction certainly occurs when cooking oil is used. However, by comparing the $^1\text{H-NMR}$ spectrum of used palm oil (Figure 4.17) with that of virgin palm oil (Figure 4.18), they are not much different. As the result, it was used in this research to prepare sodium soap, a thickener, to blend with the synthesized base oil into grease. The functional groups of sodium soap were characterized by FT-IR spectrometer (Figure 4.20).

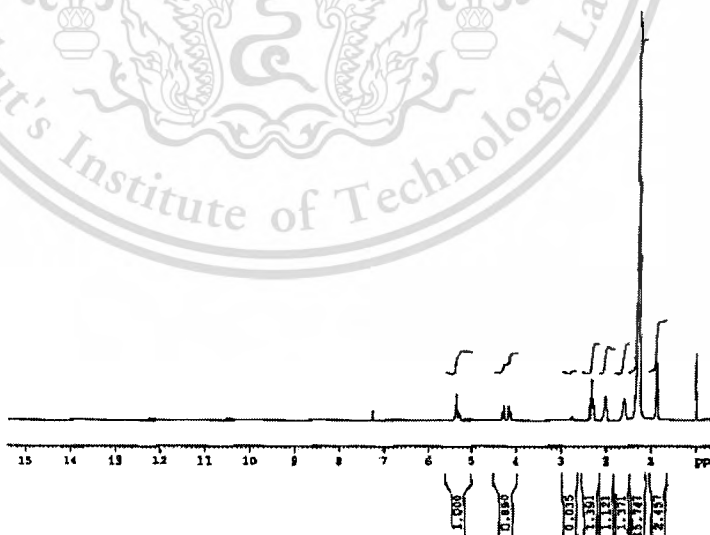


Figure 4.17: $^1\text{H-NMR}$ of used palm oil

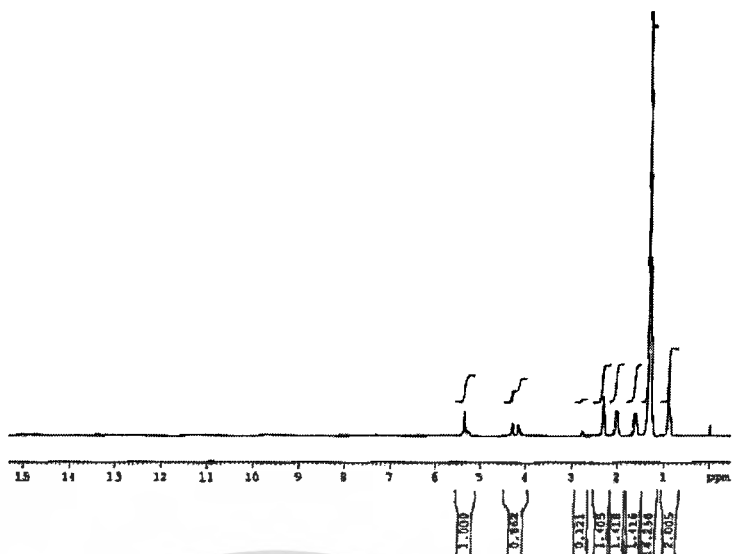


Figure 4.18: $^1\text{H-NMR}$ of virgin palm oil

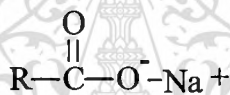


Figure 4.19: The structure of sodium soap

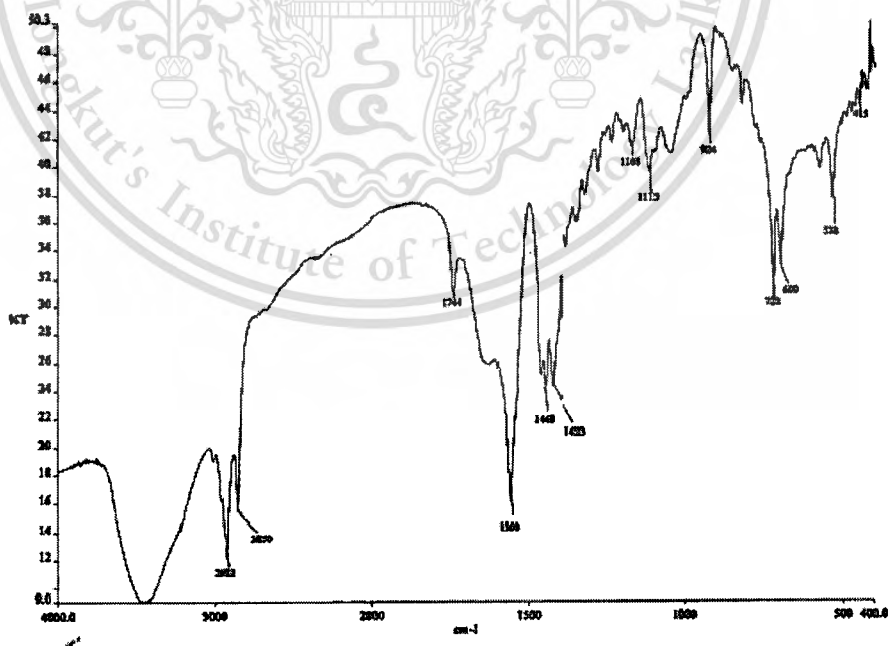


Figure 4.20: FT-IR spectrum of sodium soap from used palm oil

The signals at 1744 cm^{-1} and at between $1113\text{-}1168\text{ cm}^{-1}$ belong to C=O and C-O stretching of the products, respectively. The signal at 2922 cm^{-1} belongs to C-H stretching. The signals at around 3500 cm^{-1} belong to O-H stretching.

4.3 Testing of grease

Greases in this work were formulated into 3 oil to thickener ratio; 90:10, 80:20 and 70:30. The 90 to 10 ratio was too thin and soft; therefore it was not used in testing.

4.3.1 Dropping point

Dropping point of grease was tested by ASTM D 2265. The observed dropping point of 80:20 oil to soap ratio from the experiment was 80°C , whereas the block temperature of the instrument was set at 121°C . The actual dropping point, as calculated by the following formula, was 94°C .

$$DP = ODP + \left[\frac{(BT - ODP)}{3} \right]$$

Where: DP is the actual dropping point ($^{\circ}\text{C}$)

ODP is the observed dropping point ($^{\circ}\text{C}$)

BT is the block temperature ($^{\circ}\text{C}$)

The observed dropping point of 70:30 oil to soap ratio from the experiment was 50°C . The actual dropping point, as calculated by the formula, was 77°C .

When comparing 2 synthesised greases with the industrial one, the dropping point of them was 77°C , 94°C and 117°C , respectively reference from ASTM standard. This indicates that the greases from this work are not good enough. The lower dropping point is probably caused by the low molecular weight of the base oil which softens the grease more rapidly at high

temperature. Furthermore, adipic acid left in base oil could also interfere with the interaction between oil and soap. Finally, since the soap was made from used cooking oil, the soap molecules are supposed to be partly smaller.

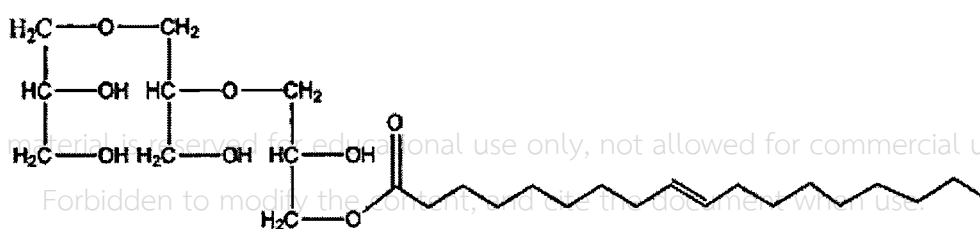
4.3.2 Water washout characteristic

Water washout characteristic was tested by ASTM D 1264. The dropping point of grease with composition ratio of base oil and soap at 70:30 was too low. Therefore, the experiment was carried out with water temperature of 38 °C using only the one with 80:20 oil to soap ratio. Table 4.5 shows the result from weight loss after water washout process.

Table 4.5: the result of water washout characteristic

No.	Lists	Weight before test (g.)	Weight after test (g.)
1	Ball bearing	113.8793	114.4355
2	Bearing housing	40.5894	40.6883
3	Shield and tray	109.0138	109.1195
4	Core	179.1500	179.1652
5	Total	442.6325	443.4085
6	Grease	4.0058	0.776

It was found that the percentage of total weight loss is 80.62%. The test result implies that the major components in grease can be soluble in warm water. This is because the 2-phase nature of the reaction between glycerol and fatty acids which leads to an increasing condensation between glycerol molecules. There are a lot of polar parts such as the one shown below which can be washed by water.



Chapter 5

Conclusion and Recommendation

5.1 Conclusion

The solid ester which was produced in this work from the esterification of glycerol with palmitic acid and adipic acid is not good enough for use as thickener in grease formulation because their melting point is too low.

On the other hand, the liquid ester which was produced in this work from the esterification of glycerol with oleic acid and adipic acid has the possibility to be used as base oil in grease formulation. However, the 2-phase nature of the reaction between glycerol and fatty acids led to an increasing condensation between glycerol molecules and the' dehydrogenation of glycerol results from dehydrogenation of glycerol to form acrolein and acetal As a consequence, the synthesis gave base oil with low molecular weight, and thus lowers the dropping point. In addition, it also produced the base oil with big polar segments which led to high weight loss after water washout process. The best grease formulation from this work is the one with the ratio of 80 %wt of oil to 20 %wt of soap.

5.2 Recommendation

The reason why the test results were poor was presumably because of the low molecular weight and high polarity of base oil. In order to increase its molecular weight and reduce its polarity, the following suggestions could be attempted.

1. The increase in miscibility between 2 phases of glycerol and fatty acid in order to reduce the self condensation between OH groups of glycerol, and thus raise the esterification between OH groups of glycerol and COOH groups of acid. This could be done by the addition of surfactants.
2. The extraction of polyester synthesis must be done before blending with soap.



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Appendices



Designation: D 2255 – 06

An American National Standard

Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range¹

This standard is issued under the fixed designation D 2255; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript (e) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the determination of the dropping point of lubricating grease.

1.2 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:²

D 217 Test Methods for Cone Penetration of Lubricating Grease

D 566 Test Method for Dropping Point of Lubricating Grease

D 3244 Practice for Utilization of Test Data to Determine Conformance with Specifications

E 1 Specification for ASTM Liquid-in-Glass Thermometers

3. Terminology

3.1 Definitions:

3.1.1 *dropping point, n*—a numerical value assigned to a grease composition representing the corrected temperature at which the first drop of material falls from the test cup and reaches the bottom of the test tube.

3.1.1.1 *Discussion*—In the normal and proper operation of this test method, the observed dropping point is corrected by adding to it a value representing one third of the difference between the oven block temperature and the observed dropping point temperature. This corrected value is recorded as the dropping point of the grease.

3.1.2 *lubricating grease, n*—a semi-fluid to solid product of a thickener in a liquid lubricant.

3.1.2.1 *Discussion*—The dispersion of the thickener forms a two phase system and immobilizes the liquid lubricant by surface tension and other physical forces. Other ingredients are commonly included to impart special properties. D 217

3.1.3 *observed dropping point, n*—the value noted on the thermometer monitoring the internal temperature of the grease test cup when the first drop of material falls from the test cup and reaches the bottom of the test tube.

3.1.4 *thickener, n—in lubricating grease*, a substance composed of finely-divided particles dispersed in a liquid to form the product's structure.

3.1.4.1 *Discussion*—Thickeners can be fibers (such as various metallic soaps) or plates or spheres (such as certain non-soap thickeners), which are insoluble or, at most, only very slightly soluble in the liquid lubricant. The general requirements are that the solid particles be extremely small, uniformly dispersed, and capable of forming a relatively stable, gel-like structure with the liquid lubricant. D 217

4. Summary of Test Method

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

4.2 As the temperature increases, 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 is recorded to the nearest degree as the observed dropping point. At the same time, the temperature of the aluminum block oven is also recorded to the nearest degree.

4.3 One third 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 grease.

5. Significance and Use

5.1 The dropping point is useful to assist in identifying the grease as to type and for establishing and maintaining bench marks for quality control. The results are to be considered to

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.G0 on Lubricating Grease.

Current edition approved May 1, 2006. Published May 2006. Originally approved in 1904. Last previous edition approved in 2000 as D 2255-00.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

DROPPING POINT APPARATUS

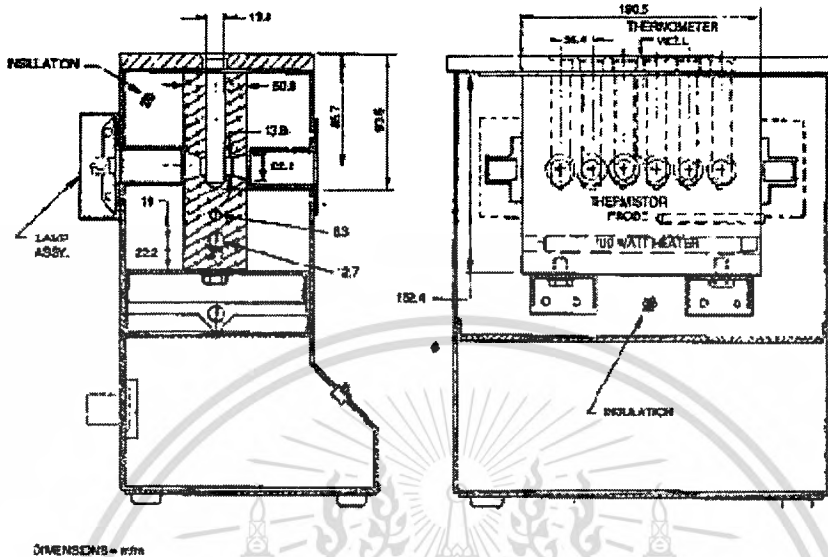


FIG. 2 Aluminum Block Oven

8.2 Use only cups that are clean and free of any residue. When the interior plating of the cup shows indications of wear, discard.

8.3 When new cups are to be used, check their dimensions by using the cup plug gage (E-7 of Fig. 1). To check the bottom opening of the cup a 2.78 mm rod should fit easily while a 2.82 mm rod should not.⁴ If the hole is undersize, ream to the correct size. If too large, discard. Cups of the proper dimensions need not be rechecked before each test run.

8.4 Test tubes shall be clean and free of residues and conform to the dimensions shown in B, Fig. 1. Inspect for chips or cracks and replace when necessary.

8.5 Sample thermometer bulb shall be clean and free of residues. Inspect bushings for cleanliness and be certain the thermometer clamp, E-1, Fig. 1, is sufficiently tight to hold the thermometer in position.

8.6 The glass sleeve used to support the cup shall be free of any cracks or chips, residue or stain, and conform to the dimensions shown in C, Fig. 1. Replace when necessary.

9. Procedure

9.1 Insert empty test tubes in every test tube well and a thermometer having a range from -5 to 400°C in the thermometer well of the oven.

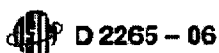
9.2 Turn on the oven and select the lowest aluminum block oven temperature setting from the four listed below that will result in an observed dropping point at or below the corresponding maximum observed dropping point shown for that oven temperature setting.

Oven Temperature, °C	Maximum Observed Dropping Point, °C
121 ± 3	148
232 ± 3	221
288 ± 3	277
318 ± 3	304

9.3 Select and use test tubes and accessories E-1, E-2, and E-3 to minimize wobble of the thermometer. All components must be at room temperature prior to the test. Place the components E-1 through E-4 on the thermometer in the order shown by the thermometer assembly (F) Fig. 1. Adjust the bushing E-3 and the bushing supporting ring E-4 so that E-4 is about 25 mm from the tip of the thermometer. Place the cup support C in tube B. Insert the thermometer depth gage E-5 and the thermometer assembly in the tube. Position the thermometer so that the tip bottoms in the gage. Adjust the bushing E-2 and the thermometer clamp E-1 so that the bushing shoulders on the top edge of the tube.

9.4 Select a clean cup, and fill it with grease either by pushing the cup into the sample presented or by using a small spatula. Overfill the cup, and use the spatula to force some of the grease out of the bottom hole of the cup to help remove any trapped air. Add more sample, and strike off the excess grease level with the top of the cup. Gently press the cup, held in a vertical position with the smaller opening at the bottom, down over the metal rod E-6, Fig. 1, until the latter protrudes about 25 mm. Press the rod against the cup in such a manner that the rod makes contact at both the upper and lower peripheries of the cup. Maintain this contact, rotating the cup on the rod along the index finger to give it a spiral-like motion down the rod to remove a conical section of the grease which adheres along the rod. As the cup approaches the end of the rod, carefully slip the

⁴ These are commonly available as a 3/64-in. drill and a No. 34 drill, respectively.



D 2265 – 06

13. Keywords

13.1 dropping point; greases; lubricating grease

APPENDIX

(Nonmandatory Information)

X1. PRECISION VALUES

X1.1 The precision values shown in 12.1.1 and 12.1.2 were developed from the round robin of 1991 using seven greases: a lithium complex synthetic base, two lithium complex oil bases, two lithium 12-hydroxy stearates, an aluminum complex, and a polyurea.

X1.2 The original values for the deleted 343°C block temperature are noted below for informational purposes.

Repeatability 6°C

Reproducibility 24°C

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Designation: D 1264 – 00

An American National Standard

Standard Test Method for Determining the Water Washout Characteristics of Lubricating Greases¹

This standard is issued under the fixed designation D 1264; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This test method has been adopted for use by government agencies to replace Method 92.2 of Federal Test Method Standard No. 79 lb.

1. Scope

1.1 This test method covers the evaluation of the resistance of a lubricating grease to washout by water from a bearing, when tested at 38 and 79°C (100 and 175°F) under the prescribed laboratory conditions. It is not to be considered the equivalent of service evaluation tests. This test method may not be suitable for some greases containing highly volatile components.

1.2 The values state in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.3 and 7.1.

2. Referenced Documents

2.1 ASTM Standards:

D 235 Specification for Mineral Spirits (Petroleum Spirits) Hydrocarbon Dry Cleaning Solvent²

3. Summary of Test Method

3.1 The grease is packed in a ball bearing, the bearing is then inserted in a housing with specified clearances, and rotated at 600 ± 30 rpm. Water, controlled at the specified test temperature, impinges on the bearing housing at a rate of 5 ± 0.5 mL/s. The amount of grease washed out in 60 ± 1 min is a measure of the resistance of the grease to water washout.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.G on Lubricating Greases.

Current edition approved Dec. 10, 2000. Published January 2001. Originally published as D 1264 – 53 T. Last previous edition D 1264 – 96.

² *Annual Book of ASTM Standards*, Vol. 06.04.

4. Significance and Use

4.1 This test method estimates the resistance of greases to water washout from ball bearings under conditions of the test. No correlation with field service has been established.

5. Apparatus³

5.1 *Ball Bearing*, ASTM test bearing size 6204.⁴

5.2 *Bearing Housing and Shield* with dimensions as shown in Fig. 1.

5.3 *Reservoir, Bearing-Housing Mount, Circulating Pump, and Drive Motor*, similar or equivalent to those shown in Fig. 1. Table 1 provides the metric equivalents.

5.4 *Heating Source*, to maintain the water temperature at $79 \pm 1.7^\circ\text{C}$ ($175 \pm 3^\circ\text{F}$).

NOTE 1—Suitable temperature control may be obtained by the use of immersion heaters, steam coils, or infrared heat lamps, in conjunction with transformers or thermostats.

5.5 *Thermometer or Thermocouple*, to determine the temperature of the water reservoir.

6. Materials and Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society.

³ This apparatus is available from the Precision Scientific Co., 3737 Cortland St., Chicago, IL, Labline Inc., 3012-82 W. Grant Ave., Chicago, IL, 60622 as Catalog No. 4165, and Starhope-Seti Limited, Park Close, Englefield Green, Egham, Surrey, England, TW20 0XD, as Catalog No. 1961.

⁴ The ball bearing has been standardized by Subcommittee D02.01 on Lubricating Grease of Committee D02 and is available from ASTM Headquarters at a nominal cost by specifying A9D3336. Copies of correspondence and test data regarding the selection of the test bearing can be obtained from the Information Center at ASTM Headquarters by requesting Research Report RR: D02-1272.

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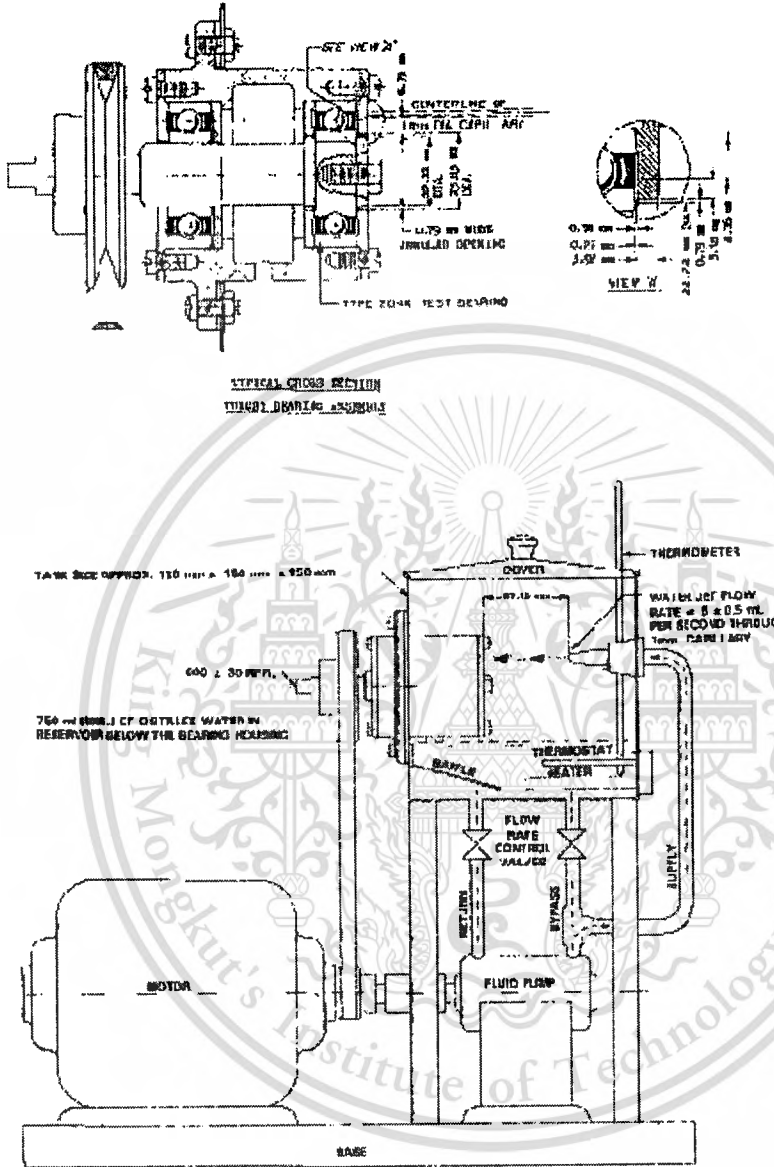


FIG. 1 Water Washout Characteristics of Lubricating Grease Apparatus

TABLE 1 Metric Equivalents for Fig. 1

in.	mm	in.	mm	°F	°C
0.010	0.25	0.875	22.22	100 ± 5	37.8 ± 3
0.015	0.38	0.938	23.81	175 ± 3	79.4 ± 2
0.031	0.79	1 1/4	31.75		
1/4	3.18	1	25.4		
3/8	3.87				
1/2	4.78				
1	8.35				

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where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2. Distilled Water

6.3 *Cleaning Solvent* capable of sufficiently cleaning the test bearing for use in the test. Either Stoddard solvent (Warning—Combustible. Vapor harmful.) in accordance with the requirements of Specification D 235, or American Chemical Society reagent grade *n*-heptane⁵ (Warning—Flammable. Harmful if inhaled.) has been found suitable for use.

7. Preparation of Apparatus

7.1 Clean the reservoir and water passages by flushing with distilled water. Wipe off any oil scum which has been deposited on the surfaces of the reservoir. Clean the test bearing with cleaning solvent (see 6.3).

8. Procedure

8.1 Pack the tared bearing with 4.00 ± 0.05 g of test grease. Insert the bearing and tared shields into the housing, and assemble the unit in the test apparatus.

8.2 Add a minimum of 750 mL of preheated distilled water to the reservoir, but keep the water level below the bearing housing. Without starting the bearing, start the water circulating pump while diverting the water spray from the housing by means of a piece of tubing attached to the capillary discharge tube or with a deflecting metal shield until equilibrium temperature is attained. When the test is to be made at the higher temperature of $79 \pm 1.7^\circ\text{C}$ ($170 \pm 3^\circ\text{F}$), it will be necessary to heat the water to the specified temperature by a previously selected source of heat.

8.2.1 If the rig has one motor driving both pump and test bearing, remove the belt from the test bearing spindle pulley during water warm up time.

8.3 When the water reaches the specified temperature, adjust the by-pass valve to give a water-flow rate, through the rubber tubing and into a glass graduate, of 5 ± 0.5 mL/s (Note 2). Remove the rubber tubing from the capillary discharge tube, and adjust the water jet so that it impinges on the end plate 6 mm ($1/4$ in.) above the outer opening of the bearing housing. Start the bearing.

NOTE 2—Sufficient experience should be obtained with a particular tester to make sure that the water-flow rate can be maintained within the specified limits for a 60 ± 1 min test run.

8.4 With the bearing operating at a speed of 600 ± 30 rpm, continue the operation for 60 ± 1 min.

8.5 Shut off the motor and heating source, if used. Remove the test bearing and shields and place them on a tared watch glass, with the shields being separated from the bearing and placed with their inner faces upward to expose the wet grease to the air.

8.6 Dry the bearing and shields for 15 ± 0.25 h at $77 \pm 6^\circ\text{C}$ ($170 \pm 10^\circ\text{F}$), and then weigh to determine the grease loss (Note 3). The grease remaining on the shields, and any leakage occurring during the drying period, should not be considered as grease lost. Duplicate tests shall be run.

NOTE 3—Some weight loss may be experienced for greases containing highly volatile oils because of evaporation during drying.

NOTE 4—Some greases may contain components which make it difficult to completely dry the sample at $77 \pm 6^\circ\text{C}$ ($170 \pm 10^\circ\text{F}$). For those greases, the drying temperature may be increased to $93 \pm 3^\circ\text{C}$ ($200 \pm 5^\circ\text{F}$) to facilitate removal of water during the time specified.

9. Report

9.1 Report the average of duplicate tests as the percentage weight of grease washed out at the test temperature, and indicate the temperature at which the bearing assembly and grease were dried.

10. Precision and Bias

10.1 The precision of this test method was obtained using the ASTM Committee D02 on Petroleum Products and Lubricants Precision Program (D2PP).⁶

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

	Repeatability
38°C	$r = 0.8 (X + 2)$
70°C	$r = 0.8 (X + 4.6)$

where:

X is the average of two results in %.

10.2.1 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty.

	Reproducibility
38°C	$R = 1.4 (X + 2)$
70°C	$R = 1.1 (X + 4.6)$

where:

X is the average of two results in %.

10.3 *Bias*—The procedure in this test method has no bias because the value of grease washout can be defined only in terms of a test method.

11. Keywords

11.1 grease; washout; water

⁶ Available from ASTM Headquarters at a nominal cost. Request PCN 13-52X00-12.

⁵ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U. S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

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