CHAPTER II

THEORY

Grease is a solid to semisolid mixture of ingredients formulated to perform as a lubricant, seal, or protective coating. The characteristics of grease are determined by type and quantity of thickener, viscosity and quality of base oil, additive content and method of manufacture.

2.1 Grease composition and characteristics

As previously mentioned, grease consists of base oil, thickening agent, and performance enhancing additives.

2.1.1 Base oils

Base oils are the major components in grease formulations and exert considerable influence on behavior of the grease. For example, a light neutral oil might be chosen to formulate a grease lubricant which is appropriate for a high-speed, lightly-loaded bearing. On the other hand, slow moving and heavily loaded equipment requires a high-viscosity oil.

2.1.1.1 Mineral oils

Mineral stocks are produced by a number of processes depending on the crude oil refinery. For this reason, the choice of crude is important. Most favorite mineral oils are paraffinic oils, which give good yield of high viscosity index (HVI) stocks although they may contain a lot of wax. For certain applications, naphthenic oils are preferred because they yield high-quality, medium-VI (MVI) and low-VI (LVI) stocks with very little wax and naturally low pour points **[3]**.

The classes of the mineral oils include paraffinic, naphthenic and aromatic oils as shown in Figure 2.1. The properties of commercial mineral oil are summarized in Table 2.1 **[4]**. Aromatic oils are not recommended for using as lubricating oil, however, they contain in small amount in base oil.

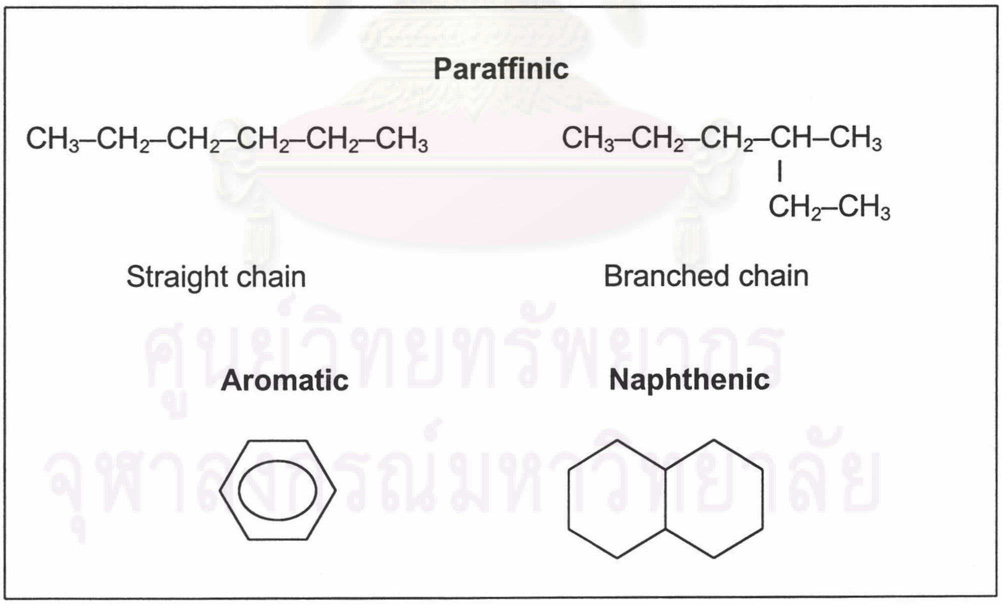


Figure 2.1 Structures of some compounds in mineral oils.

Table 2.1 Properties of commercial mineral oils

Properties	ASTM method	Paraffinic oil	Naphthenic oil		Aromatic oil
CAS#	-	64742-54-7	64741-96-4	64742-34-3	64742-03-6
Viscosity, cSt @40 °C	D 445	40	42	40	36
Viscosity, cSt @100 °C		6.2	5.0	5.0	4.0
Viscosity Index	D 2270	100	-15	0	-185
Flash Point, °C	D 92	229	180	174	16
Pour Point, °C	D 97	-15	-36	-30	-24
Molecular Weight	D 2503	440	320	330	246
Clay-Gel analysis	D 2007				
%Polars		0.2	2	3	8
%Aromatic		8.5	36	43	80
%Saturates		91.3	62	54	12

Poor low-temperature properties of base oil do not always define the behavior of the finished grease because certain thickeners themselves may function as pour-point depressants. Elastomer-seal compatibility may be influenced by the type of base oil present. Naphthenic oils may cause some seal materials to swelling while paraffinic oils exert a minimal effect.

2.1.1.2 Synthetic oils

Synthetic fluids are becoming increasingly more importance in greases designed for special extreme-temperature applications. These include polyalphaolefins, dibasic acid esters, polyol esters, polyglycols and halogenated ethers and hydrocarbons **[5]**.

Most of synthetic oils have viscosity in the range of lighter high-VI mineral oils. Their viscosity indexes and flash points are higher, and their pour points are lower. This makes them valuable blending components when compounding oils for extreme service at both high and low temperatures.

The main disadvantage of synthetic oils is that they are more expensive than mineral oils. This limits their use to special oils and greases. The esters have greater seal-swelling tendencies than hydrocarbons. Therefore, they cannot be used when contact elastomers.

Polyalphaolefins (PAOs)

PAOs are the most widely used in the U.S. and Europe. PAOs are hydrocarbons, and contain no sulfur, phosphorus or metals. Since PAOs are wax-free, they have low pour points (below –40 °C), viscosity in a range of 2 to 100 cSt and viscosity indexes above 140. PAOs have good thermal stability, but they require antioxidant additives to resist oxidation of double bond carbons in their molecules. They also have limited ability to dissolve some additives, and tend to shrink seals.

Diesters

Diesters are synthesized by a reaction of a dicarboxylic acid and an alcohol. Diesters have more various structures than PAOs. Like PAOs, they contain no sulfur, phosphorus, metals or wax. Pour points range from -50 to -65°C. Advantages of diesters include good thermal stability and excellent solvent.

Polyol esters

Like diesters, polyol esters are formed by a reaction of a carboxylic acid and a polyol. Polyol refers to a molecule with two alcohol functions in its structure such as trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritol (PE).

Polyol esters contain no sulfur, phosphorus or wax. Pour points range from -30 to -70 °C, and viscosity indexes from 120 to 160. The fluids have excellent thermal stability and resist hydrolysis better than diesters. With the proper additives, polyol esters are more oxidatively stable than diesters and PAOs. Seal-swelling behavior is similar to that of diesters.

Polyalkylene glycols (PAGs)

PAGs are polymers of alkylene oxides. Lubricant performance and properties of PAGs depend on the monomers, molecular weight and the nature of the terminal groups. Generally, PAGs have good high-temperature stability and high viscosity indexes, and can be used over a wide temperature range. Like other synthetics, PAGs require additives to resist oxidation.

Phosphate esters

Phosphate esters are synthesized from phosphorus oxychloride and alcohols or phenols. They are used as base oils and as antiwear additives in mineral and synthetic lubricants. Thermal stability is good, and pour point ranges from -25 to -5 °C. However, viscosity index is extremely low, ranging from 0 to -30, which limits their high temperature application.

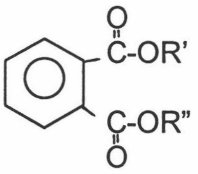
Chemical structures of ester oils used in the lubricant manufacturing are shown in Figure 2.2, and their properties are shown in Table 2.2 **[6]**.

Diesters (dioates)

$R'OOC(CH_2)_nCOOR''$ R', R" = linear, branched or mixed alkyl chain

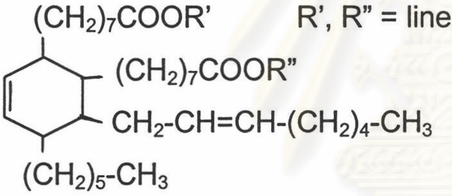
n = 4 = adipates
n = 7 = azelates
n = 8 = sebacates
n = 10 = dodecanedioates

Phthalate esters (1,2-benzene dicarboxylate)



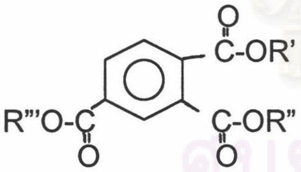
R', R" = linear, branched or mixed alkyl chain

C_{36} dimer acid esters



R', R" = linear, branched or mixed alkyl chain

Trimellitate esters (1,2,4-benzene tricarboxylate)



R', R", R''' = linear, branched or mixed alkyl chain

Polyols (hindered esters)

$C(CH_2OCOR)_4$	Pentaerythritol esters
$CH_3CH_2C(CH_2OCOR)_3$	Trimethylolpropane esters
$(CH_3)_2C(CH_2OCOR)_2$	Neopentylglycol esters

R = linear, branched or mixed alkyl chain

Figure 2.2 Chemical structures of ester oils.

Table 2.2 Properties of ester oils

Items	Diesters	Phthalates	Trimellitates	C36 dimer esters	Polyols
Viscosity@40 °C	6 to 46	29 to 94	47 to 366	13 to 20	14 to 35
Viscosity@100 °C	2 to 8	4 to 9	7 to 22	90 to 185	3 to 6
Viscosity index	90 to 170	40 to 90	60 to 120	120 to 150	120 to 130
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25	-50 to -15	-60 to -9
Flash point (°C)	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310
Thermal stability	good	very good	very good	very good	very good
%Biodegradability	75 to 100	46 to 88	0 to 69	18 to 78	90 to 100
Costs (PAO=1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0	1.2 to 2.8	2.0 to 2.5

2.1.2 Thickening agent

Thickener is the form of fiber, which interlocks and holds the oil phase by interfacial and dispersion forces. Many types and combinations of thickeners and base oils, giving final grease formulations with special properties, are shown in Table 2.3 **[7]**.

Table 2.3 Influence of thickener on grease characteristics

Thickener	Structure	Dropping Point (°F/°C)	Max Service Temperature (°F/°C)
Sodium soap	Fibrous	350/177	200-275/93-136
Calcium soap			
Simple	Smooth	290/143	250/121
Complex	Smooth, buttery	>450/>232	300/149
Lithium soap			
Simple	Smooth	390/199	325/163
Complex	Smooth, slightly stringy	>500/>260	350/177
Aluminum soap	Smooth gel	>500/>260	300/149
Clay	Smooth	>500/>260	350/177
Polyurea	Opaque, slightly mealy	>450/>232	350/177

2.1.2.1 Soap-based thickeners

Simple soaps are formed when a fatty acid or ester is combined with an alkali or alkaline earth metal with the application of heat, pressure or agitation. The mechanical stability and rheological properties of the finished grease depend on the fiber structure of the metal soap.

Complex soap greases were developed to withstand the higher operating temperatures of modern equipment. The thickener structure is formed by reacting a fatty-acid derivative and some other polar compounds, called a complexing agent. For example, co-reacting 12-hydroxystearic acid and azelaic acid with lithium hydroxide produce a more intricate lattice structure than that of a simple lithium soap. Complexing agents usually have a lower molecular weight than the fatty acid derivatives. Table 2.4 shows a comparison of the simple and complex soap greases characteristics **[8]**.

Table 2.4 Characteristics of metal-soap greases

Thickener	Grease characteristics
Aluminum	Smooth, like gel appearance, low dropping point, excellent water resistance, softening/hardening tendencies dependent on shear rate
Sodium	Rough, fibrous appearance, moderately high dropping point, poor water resistance, good adhesive (cohesive) properties
Calcium	Smooth, buttery appearance, low dropping points, good water resistance
Lithium	Smooth, buttery to slightly stringy appearance, high dropping point, resistant to softening and leakage, moderate water resistance
Calcium Complex	Smooth, buttery appearance, dropping points above 500 °F, good water resistance, inherent EP/load-carrying capability
Lithium Complex	Smooth, buttery appearance, dropping points above 500 °F, resistant to softening and leakage, moderate water resistance

2.1.2.2 Organic non-soap thickeners

Polyureas, the most widely used non-soap organic thickeners, are prepared by reacting isocyanates with amines. Polyurea greases are characterized by good water resistance and good thermal stability. They tend to be more costly than conventional soap-based greases because they require more sophisticated processing, and their raw materials are more expensive. The characteristics of organic non-soap grease are shown in Table 2.5 **[9]**.

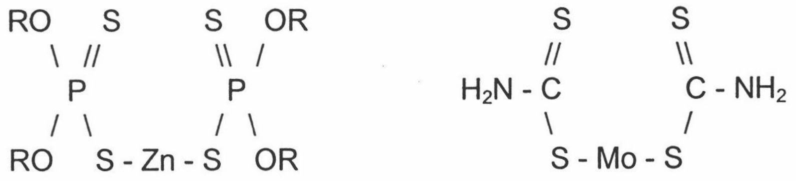
Table 2.5 Characteristic of non-soap thickened greases

Thickener type	Grease characteristics
Polyurea	Smooth, slight opaque appearance, dropping points above 450 °F, good water resistance, oxidation resistant, less resistant to softening and leakage
Organo-Clay	Smooth and buttery appearance, dropping point above 500 °F, resistant to leakage, good water resistance

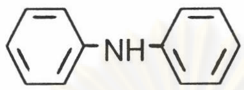
2.1.3 Additives

Additives can significantly alter the performance of lubricating greases. Factors influencing additive selection include product application, compatibility, environmental considerations (odor, disposal, biodegradability) and cost.

The additives used in this study are zinc dialkyldithiophosphate (ZDDP), molybdenum dithiocarbamate (MDTC) and diphenyl amine (DPA). The structures of these additives are shown in Figure 2.3.



zinc dialkyldithiophosphate (ZDDP) molybdenum dialkyldithiocarbamate (MDTC)



diphenyl amine (DPA)

Figure 2.3 Chemical structures of ZDDP, MDTC and DPA.

ZDDP, MDTC and DPA commonly serve hydraulic-fluid, gear-oil and turbine-oil applications, but they are also widely used in grease formulations. These additives are chemically active because they produce their effect through a chemical reaction either within the lubricant medium or on the metallic surface. Chemically active additives include oxidation inhibitors, rust and corrosion preventatives and extreme pressure/antiwear agents.

2.1.3.1 Oxidation Inhibitors

Like lubricating oils, greases under oxidizing conditions yield unstable materials called peroxides. Once formed, peroxides quickly decompose to form other materials which are even more susceptible to oxidation. The process is a chain reaction which is accelerated by increased temperatures and which is catalyzed by metals those present in soap-based thickening agents.

From Table 2.6, In the initiation stage, a hydrocarbon is thermally cleaved to form a free radical **[10]**. This is a highly reactive and unstable species that immediately combines with oxygen to form a less stable species. This, in turn, reacts with a second molecule of hydrocarbon to form a hydroperoxide and also to regenerate the initial radical. The hydroperoxide may decompose to form two radical species. Thus, oxidation reactions become exceedingly rapid in an initiation stage.

Table 2.6 Chain reactions involving oxidation process

Stage	Reaction
Initiation	$R - H + Metal \longrightarrow R^{\bullet} + H^{\bullet}$
Propagation	$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$ $ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$ $ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$
Termination	$ROO^{\bullet} + ROO^{\bullet} \longrightarrow ROO\text{-}OOR$ $R^{\bullet} + ROO^{\bullet} \longrightarrow ROO\text{-}R$ $R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R$

The final products of oxidation are gums, lacquers and acidic materials. In a grease composition, oxidation is manifested by any one or a combination of symptoms; increase in penetration, lowering of dropping point, increased uptake of oxygen, increased acid number. Oxidation inhibitors function by combining with the peroxides or radical species thereby terminating the free-radical chain reaction. Inhibitors are gradually destroyed in the process. Chemical compounds used to inhibit oxidation include hindered phenols, aromatic amines, heterocyclic nitrogen compounds, zinc dialkyldithiophosphates and dithiocarbamates.

Hydroperoxide decomposers

The ZDDP and MDTC convert hydroperoxides into non-radical products, thus preventing the chain propagation reaction. The ZDDP and MDTC perform as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxy radicals **[11]**. The ZDDP reacts with hydroperoxide to form disulfide (I) via the dithiophosphate radical (II).

$$(RO)_2PS_2]_2Zn + R_1OOH \xrightarrow[-R_1O^{\bullet}]{} [(RO)_2PS_2]_2ZnOH + \underset{(II)}{(RO)_2PS_2^{\bullet}} \qquad (1)$$

$$\underset{(II)}{2\,(RO)_2PS_2^{\bullet}} \longrightarrow \underset{(I)}{[(RO)_2PS_2]_2} \qquad (2)$$

The reaction results in a final rapid decomposition of the hydroperoxide provided the low concentration of the ZDDP. Under these conditions, the sulfur radical is unable to dimerize. Instead it reacts with hydroperoxide, leading to the acid catalyst.

$$(RO)_2PS_2^{\bullet} + ROOH \xrightarrow[-ROO^{\bullet}]{} (RO)_2PS_2H \qquad (3)$$

At temperature above 125 °C, the disulfide (I) could be a source of the acid catalyst followed by reactions (4) and (3).

$$[(RO)_2PS_2]_2 \longrightarrow 2\,(RO)_2PS_2^{\bullet} \qquad (4)$$

According to the reaction (3) regenerating the acid catalyst, $(RO_2)PS_2H$, which is a better inhibitor than the ZDDP. The function of MDTC is as same as ZDDP.

Radical scavengers

The most widely used types of radical scavengers are phenolic and aminic antioxidants. Diphenylamine (DPA) reacts with hydrocarbon free radical and peroxy radical to form more stable molcules, $(C_6H_6)_2N^{\bullet}$, thus stop the propagation reaction **[12]**.

$$(C_6H_6)_2NH + R^{\bullet} \longrightarrow (C_6H_6)_2N^{\bullet} + RH$$

$$(C_6H_6)_2NH + RO^{\bullet} \longrightarrow (C_6H_6)_2N^{\bullet} + ROH$$

$$(C_6H_6)_2NH + ROO^{\bullet} \longrightarrow (C_6H_6)_2N^{\bullet} + ROOH$$

2.1.3.2 Rust inhibitors

The corrosion of iron and steel bearing components, caused by the presence of oxygen and water, can lead to serious malfunctions **[13]**. Protection of metal surfaces from rusting is especially important in steel rolling-mill applications where large volumes of cooling water impinge on the bearings and where greases are expected to absorb much of that water without loss in performance.

Function: Thickeners are often impart natural rust-resisting properties, but rust inhibitors may be necessary if conditions warrant. These are usually highly polar oil-soluble compounds which function by adsorption on the metal surface to form a thin protective film, which excludes air and water.

Type: Typical rust inhibitors include fatty amines, fatty amides, carboxylic acids, sodium sulfonates, barium sulfonates and lead naphthenate.

2.1.3.3 Extreme pressure/antiwear agents

Greases are formulated with extreme-pressure (EP) agents to prevent seizure under conditions of high temperature, heavy loading or extended periods of operation **[14]**. Chemicals that serve as extreme-pressure agents usually contain sulfur, chlorine, phosphorus, metals or combinations of these elements.

Function: Extreme-pressure agents function under boundary conditions where metal surfaces are contact. As the surfaces move against one another, collision of surface asperities produces localized temperature rises which activate the EP agents. Distinct chemical compounds form and immediately plate out on the metal surface as a thin film. Sulfide, chloride and phosphide films shear more easily than the metal itself; consequently, less frictional heat is generated.

Type: Some of the materials which function as EP agents in greases include sulfurized olefins, lead naphthenate, sulfurized esters phosphate and thiophosphate esters, metal dithiocarbamates, metal dialkyldithiophosphates, chlorinated paraffins.

2.2 Lithium grease preparation

In this study, lithium base grease was prepared to use in bearing of spindle motor application. The advantages of lithium greases include:

(i) exceptional shear stability; suitable for use in high-speed plain and rolling bearings.

(ii) high dropping points and good thermal stability. Maximum service temperature approaches 140 °C.

(iii) good tolerance for water; resists washout in mill bearings.

(iv) rust and corrosion protection is equal to sodium greases.

(v) additives (rust inhibitors, oxidation inhibitors, EP agents) usually show greater response than in other soap media; therefore, lithium greases are more easily adapted to specific conditions and environments.

(vi) excellent sealant properties.

Lithium greases can be prepared from either preformed soap (method I) or soap prepared (method II). For economy and versatility, the method II is preferable and used by most manufacturers **[15]**. The method II is divided into two steps:

Step 1: lithium hydroxide + stearic acid → lithium stearate
Step 2: lithium stearate + base oil → grease
grease + additives → finished grease

Lithium stearate may be obtained by reacting stearic acid with lithium hydroxide. The saponification reaction is illustrated as the following

$$CH_3(CH_2)_{16}COOH + LiOH.H_2O \longrightarrow CH_3(CH_2)_{16}COOLi + 2H_2O$$

Lithium hydroxide is used as a solution in water and slowly poured into melted stearic acid. The saponification is carrying out by agitation and heat. Mayer **[16]** suggested that the reaction was rapid, and would have been completed when the mixture was heated at 80 to 90 °C.

The mixture of lithium soap and base oil should stir to a creamy consistency before heat was applied, otherwise it would be difficult to disperse later. The mixture was heated at 220 °C, then cooled down to room temperature and homogenized by roller.

2.3 Electron microscope study of lithium grease

The nature and characteristics of metallic soaps in lubricating greases have been very interested subjects due to their structural peculiarities. The scanning electron microscope (SEM) has now become one of the instruments for the study of the structure of metallic soap.

Various sample preparation techniques in the literature have been suggested for the study of soap fiber structure **[17]**. One limitation of using the electron microscope is the difficulty in preparing the grease sample. Soap particles in grease are extremely thin and slightly opacity to the electron beam. If the traces of oil present in the sample, the oil will hinder the investigation because the oil tends to scatter the beam, and disturbs in the soap structures.

The lithium soap was prepared from lithium hydroxide and fatty acids. The great difference in the lithium soap fibers of crystallite aggregates when used different fatty acids **[18]**. When oleic acid is used (Figure 2.4), long fibers are obtained. With stearic acid (Figure 2.5), small flat granular particles are formed. For the use of tallow (Figure 2.6), fibers of intermediate length without any twisting characteristics was obtained.

Figure 2.4 Fibers in lithium base grease made from oleic acid.

Figure 2.5 Fibers in lithium base grease made from stearic acid.

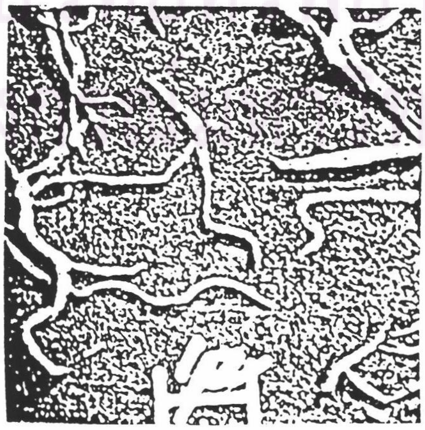


Figure 2.6 Fibers in lithium base grease made from beef tallow.

2.4 Grease rheology

Rheology is the study of how grease deforms or flows under stress. Factors influencing the rheology of grease include shear stress, shear rate, temperature and time **[19]**. Shear stress is the per unit load tending to cause relative movement between adjacent layers of a grease, and shear rate is the rate at which this movement occurs.

Definition of viscosity, shear stress and shear rate

$$F = \eta A\,(v/h)$$

Viscosity; $$\eta = \frac{F/A}{v/h} = \frac{\text{shear stress}}{\text{shear rate}}$$

Where; F = force (N)

η = viscosity

A = area (m^2)

v = velocity (m/s)

h = gap distance (m)

Fluid viscosity is defined as the ratio of shear rate to shear stress. Fluids that exhibit a constant viscosity (proportion of shear stress to shear rate is a constant) are called Newtonian fluids.

Grease and many plastic solids are non-Newtonian; that is exhibited a variable relationship between shear rate and shear stress. The non-Newtonian behavior of grease derives from the thickeners used in their formulation. Non-Newtonian fluids do not have a viscosity but exhibit an apparent viscosity that can vary widely with varying shear rates. Therefore, the apparent viscosity of a non-Newtonian fluid must be specified at a specific shear rate.

Viscosity profile is the plot of viscosity versus the applied shear rate, divided into 4 types (Figure 2.7).

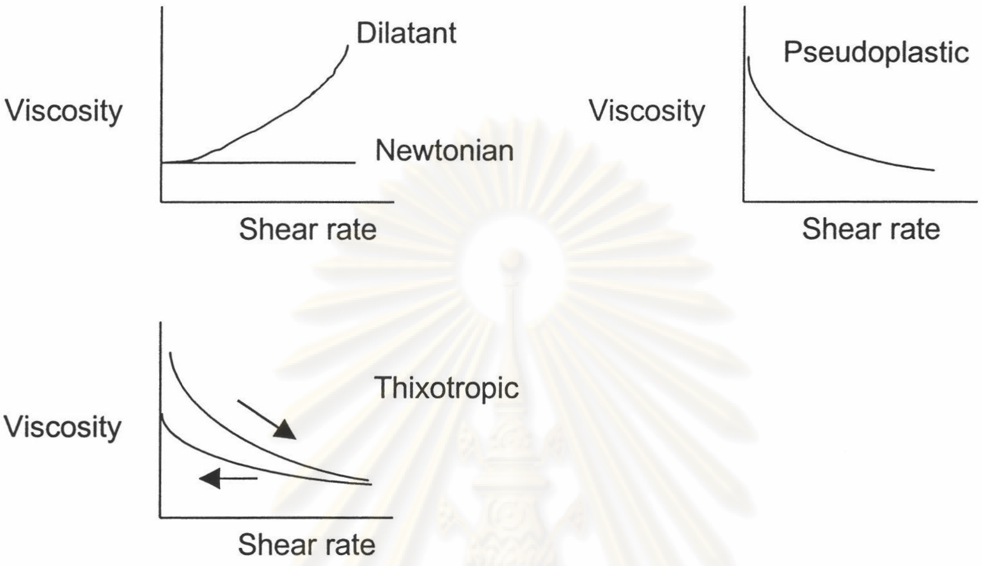


Figure 2.7 Viscosity profiles of non-Newtonian flow.

(i) dilatant flow; the apparent viscosity increases with increasing shear rate.

(ii) newtonian flow; the matter maintains the constant viscosity with shear rate increase. This is typical for oils, water or solvents.

(iii) pseudoplastic flow; the apparent viscosity decreases with increasing shear rate.

(iv) thixotropic flow; As shear rate is increased, viscosity decreased. As shear rate is decreased, viscosity rebuilds slowly due to the temporary loss of original structure. This is the representation for a lubricant system.

The non-Newtonian (thixotropic) behavior of grease derives from the thickeners, because of base oil behavior as Newtonian flow and additive containing in grease only few percent. When shear rate is increased, the thickener structure is temporary break down. This causes a decrease in the grease viscosity (apparent viscosity).

Under the sufficient time, the structure will rebuild to its unsheared state, leading to an increase in the viscosity being lower than the original state due to the loss of thickener original structure.

2.5 Basis of lubrication

The lubrication of surfaces is accomplished by separating them or protecting them from the effect of high wear or high friction. This is achieved by the information of the separating film between the surfaces. Depending on the type of separating film and its thickness, a number of lubricant regions can be identified by use of Stribeck-Hersey curve **[20]**. Figure 2.8 shows the coefficient of friction (μ) as a function of surface load (ρ), surface velocity (v), viscosity of lubricant (η) and film thickness of lubricant (h).

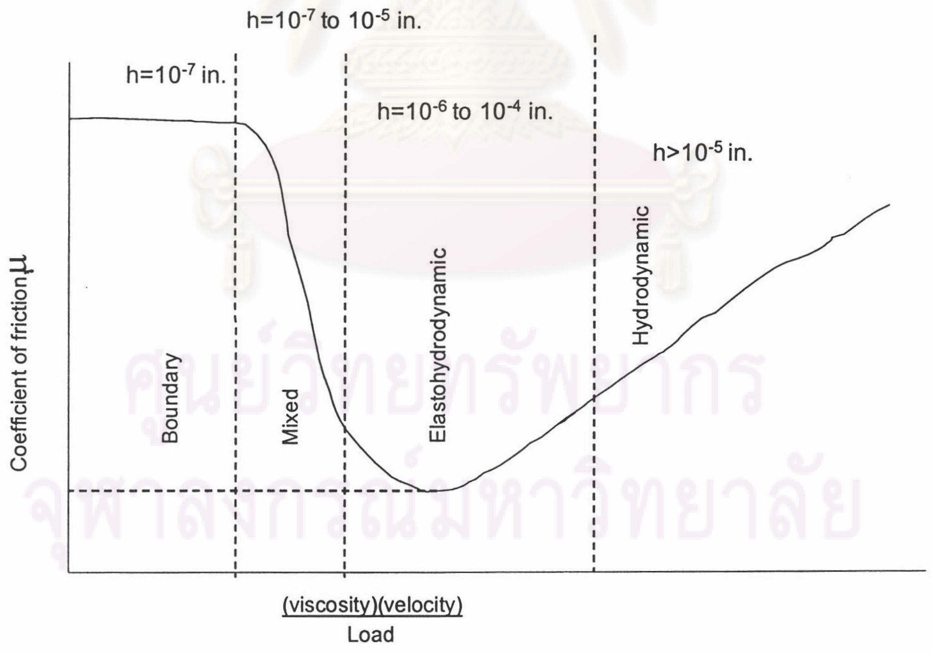


Figure 2.8 Coefficient of friction as the function of load, velocity and viscosity.

At the high value of $\eta v/\rho$, the surfaces are completely separated by a lubricating film. This is the hydrodynamic lubrication region, where the friction is determined by rheology of lubricant.

For non-conformal contacts, where load are high enough to cause the elastic deformation of surfaces and pressure-viscosity effects on the lubricant, this region is known as elastrohydrodynamic lubrication region (EHD). Since no surface interaction occurs in both hydrodynamic and EHD region, a little wear or no wear occurs.

As the EHD film becomes thinner, the mixed lubrication region is identified. The surface interaction begins to occur. The frictional forces are higher than EHD region. In this region, wear is low because the lubrication film effects still exist.

At the low values of $\eta v/\rho$ (boundary lubricating region), both the degree of metal-to-metal contact and the wear increases as the load increases. The lubricating film forms in boundary region tend surfaces to be damage.

2.6 Literature review

Lithium grease is used in bearings for electronic computers, due to low torque and excellent noiseless property. The amount of grease splashing from bearings must be controlled, to maintain the performances over a long period of operation time.

The consistency of lithium grease with antisplashing property was studied by Yokouchi *et al.* (1998) **[2]**. Grease was packed into bearing, and was preloaded to 1.5 kgf. The bearing was fitted to vessel having an air inlet and outlet, and was rotated by a motor at 3,600 rpm. A number of splashing particles having size of 0.3 μm or larger in every 0.01 cubic feet of air are counted by the particle counter.

Yokouchi *et al.* also reported that the penetration number of lithium grease higher than 250 increased the splashing amount to cause the recording media of electronic computers to be contaminated. On the other hand, the penetration number lower than 190 results in too firm grease, and fairly deteriorates the noiseless property and the torque performance.

The work on the oxidation stability of base oil has been reported **[21-23]**. Hiroshi *et al.* (1997) **[21]** studied the oxidation stability of polyol esters in the presence of 1% *N*-phenyl-naphthylamine by corrosion and oxidation stability test (COST). The total acid number (TAN), viscosity at 40 °C and sludge amount of oils were determined after oxidation. The results showed that pentaerithritol ester (PE) and trimethylolpropane ester (TMP) having acid carbon numbers of 4 and 5 gave better oxidation stability than did esters having longer acid carbon number.

Konishi *et al.* (1997) **[22]** studied the effect of chemical structure of polyol ester. The value of the wear and friction coefficient for the commercial polyol esters was measured by a four-ball wear test machine. Insignificant difference of the results was obtained for neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). Carboxylic acids with long chain and branching affected the wear and friction coefficient of polyol ester base fluids.

Kramer *et al.* (2000) **[23]** investigated the oxidation stability of mineral oil. They found that base oil containing saturated hydrocarbons more than 90% and sulfur less than 0.03% had better oxidation and thermal stability than that containing aromatic and nitrogen heterocyclic compounds.

Several papers have been reported on antioxidant additives used in grease **[24 - 26]**. Igarashi *et al.* (1994) **[24]** reported a method for determination of the oxidation stability of the antioxidants by pressurized differential scanning calorimetry (PDSC) using oxygen pressure 1.96 MPa and temperature 218 ^{o}C. They defined the oxidation stability as the induction time where the exothermic onset peak due to the oxidation observed. The results showed that the aminic and phophorous-containing additives improved the oxidation life, whereas nitrogen- and sulfur-containing additives and triazole gave no change in oxidation stability.

Rakesh *et al.* (1999) **[25]** reported the use of antiwear, extreme pressure and antioxidant additives in lubricant oil. Eight alkylamino phosphorodithioates with varying alkyl chain lengths from C5 to C18 were synthesized, and compared to zinc dialkyldithiophosphate (ZDDP). It was found that antiwear and antioxidation properties of these eight compounds and ZDDP are similar. However, their antifriction and extreme pressure properties were less than ZDDP.

Enthoven *et al.* (2000) **[26]** published that the addition of 2% of the following additives in TMP base oil provided the lowest friction coefficient: amine phosphate, phosphorodithioate, dithiocarbamate and tricresyl phosphate.

The fibrous structure of soaps and the mechanism of soap micelles in grease have been discussed **[27-28]**. Moore (1992) **[27]** studied fiber structure of lithium soap by scanning electron microscopy (SEM). It was found that the thickener contained 50 to 80% of fiber more than 0.5 μm in width and over 10 μm in length, making the grease mechanically stable. The remaining fibers were less than 0.1 μm in width and 4 μm in length, making grease non-bleeding.

Kumar *et al.* (1995) **[28]** suggested that the mechanism of lithium soap micelles in grease is divided into three stages; partial melting, shearing and then recrystallization. The grease ingredients (base oil and lithium soap) are melt when the temperature increased to 220 °C, and allowed the oil to penetrate the soap structure. After that the shearing forces of milling assisted soap micelles disperse in base oil, then the soap was crystallized to form the crystal lattice or fibers.