CHAPTER II

THEORY

2.1 Definition

Lubricating grease is a solid to semi-fluid product of the dispersion of thickening agent in a liquid lubricant. Grease lubrication and oil lubrication serve the same purpose which is to minimize friction and wear between moving surfaces. Greases are most often used instead of liquid lubricants when the lubricant will be required to stay in place. As such, satisfactory performance of the grease requires it to provide a reduced friction and wear on contact surfaces, act as a seal to prevent ingress of contaminants, withstand a certain amount of contamination without suffering performance deterioration, prevent rust and corrosion.

2.2 General Characteristics

2.2.1 Consistency

The degree of hardness of grease (may be vary considerably with temperature).

2.2.2 Shear Stability

The ability of the grease to resist changes in consistency during mechanical working.

2.2.3 Oil Separation

The percentage of oil which separates from the grease under static (storage) condition.

2.2.4 High Temperature Stability

The ability of the grease to retain consistency at elevated temperatures.

2.2.5 Oxidation Stability

The ability of the grease to resist chemical reaction with oxygen thus is minimizing deterioration.

2.2.6 Low Temperature Mobility

The ability of the grease to flow and provide adequate lubrication at low temperatures.

2.2.7 Water Resistance

The ability of the grease to withstand deterioration in the presence of water.

2.2.8 Corrosion Resistance

The ability of the grease to protect metal surfaces against chemical attack, including water.

2.2.9 Anti-Wear

The ability of the grease to prevent metal to metal wears.

2.2.10 Extreme Pressure

The ability of the grease to prevent metal to metal welding or scoring under heavily loaded conditions.

These characteristics are controlled by the physical and chemical properties of the grease- both the fluid lubricant and the thickener [1].

2.3 Grease Component

Lubricating grease consists of three components such as base oil (65-95%), thickene (5-35%) and additives (0-10%). The base oil is the major component in grease. The thickeners chosen may be simple metal soaps, complex soaps, or non-soap. Additive can account for 0 to 10 percent or more of the final grease formulation, depending on what performance criteria and targets need to be met [2].

2.3.1 Base oil

The type of oil or oil blend in grease depends on the desired performance and/or proposed application. Oils commonly used in the grease industry are naphthenic, paraffinic, synthetic and vegetable oils. Oils that have single bond between the carbon atoms are referred to saturate and oils that have double bonds between the carbon atoms are referred to unsaturated. Unsaturated oils are less thermally stable and tend to be more easily oxidized. Saturated oils are desirable for grease manufacturing. The followings are provided as generalities [3].

2.3.1.1 Type of Base Oils

Naphthenic Oil

- Have lower pour points than paraffinic oils.
- Perform well in greases designed for low temperatures.
- Incorporate well into the grease structure and mix well with most additives.
- Generally promote good thickening.
- Have higher evaporation rates than paraffinic oils.
- Are less thermally stable than paraffinic oils.
- May have lower Viscosity Index (VI) than paraffinic oils.

Paraffinic Oils

- Have higher pour point.
- Produce lower grease yields.
- Have lower evaporation rates.
- Have better thermal stability.
- Have higher Viscosity Index (VI).

Synthetics

- Have excellent thermal stability.
- Have lower Pour Point.
- Have excellent low temperature flow characteristics.
- Are generally more expensive than mineral oils.
- Usually have a very high Viscosity Index (VI).
- Have low evaporation rates.
- Can exhibit good biodegradability.

Vegetable Oils

- Are relatively expensive.
- Many produce lower yields than mineral oils.
- Generally exhibit good biodegradability.

2.3.1.2 Characteristic of Base Oil

The oil component in grease must meet certain requirements regarding:

- Solubility
- Viscosity / Viscosity index
- Evaporation loss
- Oxidation loss
- Purity
- Environmental and health aspects

Solubility

The most important property of oil in the manufacture of grease is solubility. It is important that the thickening soap is properly dissolved in the oil. Various parameters can be used to classify the solvating power of different base oils. The viscosity gravity constant (VGC), aniline point and aromatic content can all be used.

The complex solubility structure of the soap must be balanced against the solubility of the oil. Excessive solubility may disrupt the structure of the soap while too low of the solubility may result in too much bleeding. Paraffinic oils can have to problem with bleeding, due to their lower solvating power than that of naphthenic oil.

Viscosity

The viscosity of the oil in grease is about the same as when the oil alone is used in an application. For low temperature application, low viscosity oil are needed. However in most cases, grease has to perform over a wider range (go to 250 cSt. at 40°C) of conditions than oil. The choice of base oil viscosity therefore has to be compromise. High viscosity oil gives good bleeding properties and better load capacity of the oil film. Low viscosity oil gives better heat transfers and low temperature properties.

Viscosity index

The viscosity index is an indication of the effect of change in temperature on change in viscosity. The lower the viscosity indexes, the greater the change in viscosity over a specific temperature range. In most cases, it is desirable to have as little viscosity change as possible over the operating temperature range that the grease is required to function. When a higher viscosity index is needed, naphthenic oils are still often used in as mixture with paraffinic oils.

Evaporation loss

The temperature for manufacturing grease is quite high. Greases are also often used at high operating temperatures such as bearings or gearboxes. Therefore, low evaporation loss is desirable [4].

Flash Point

For grease chemistry, this is more of a measurement of oil volatility than it is an indication of fire hazard. This gives an indication of realistic usable upper temperature limitations that can be placed on the grease.

Pour Point

Pour point indicates the temperature below which it is not possible to pour the oil from a container. It therefore becomes an indication of the lower temperature limit at which the grease can be pumped [1].

Aniline Point

Aromatic hydrocarbons exhibit low aniline points, paraffinic hydrocarbons exhibit high aniline points, and naphthenic exhibit intermediate aniline points. In general, better yields can be obtained from oils with lower aniline points (higher degree of solvency).

2.3.2 Grease Thickener

Thickener systems most often used to form grease are soaps such as those formed by the saponification of fatty material with an alkali metal. The byproduct most commonly formed in this reaction are water, methanol, and glycerin depending on which fatty acid were used.

Grease is classified by the type thickener used because the thickener, which has the greatest influence on the final properties of grease such as soap thickened, complex soap thickened, or non-soap thickened [3].

2.3.2.1 Simple soap

$$RCO_2H + MOH \longrightarrow RCO_2M + HOH$$

Fatty acid metal alkali metallic soap water

Soap thickener is the product of the reaction between a metal or alkali metal hydroxide with fatty acid. Soap base greases account for about 90% of the greases made. The metal / alkali metal are usually lithium, calcium, sodium or aluminum. Calcium soaps were the first used. They have rather low dropping points (~ 100°c) while sodium soaps exhibits higher dropping points (~ 160°c). Lithium soap that have even higher dropping points (~ 180°c). Lithium 12-hydroxy stearate is the most used soap for lubricating greases today.

The physical properties of carboxilic acid reflect a considerable degree of association through hydrogen bonding, especially as the -O-H bonds are strongly polarized. They also have the possibility of forming hydrogen bonds to the negative oxygen of the carbonyl dipole rather than just to the oxygen of another hydroxyl group, as a result, they exist mostly as cyclic dimers.

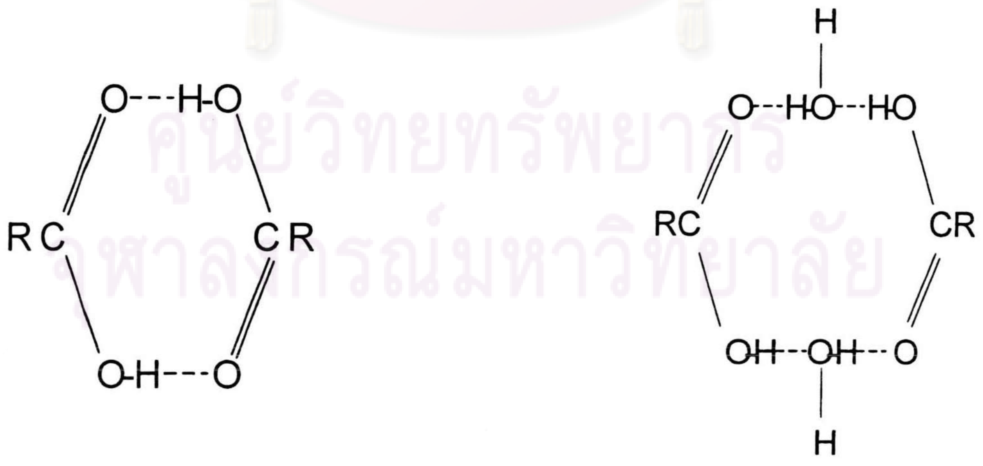


Figure 2.1 -O-H Bonding

A common carboxylic acid used in soap manufacturing is 12-hydroxysteric acid, $(CH_3\,(CH_2)_5\,CHOH\,(CH_2)_{10}\,CO_2H)$. In this acid, the hydrogen on 12th carbon in the chain is replaced by a hydroxyl group. This provides another location for hydrogen bonding to occur [1].

Aluminum Soaps

Aluminum soaps are made by reacting aluminum hydroxide with a fatty acid, such as stearic acid. These finished greases are characterized by having a smooth, gel-like appearance, a low dropping point, good water resistance and thixotropic behavior (softening or hardening dependent on shearing rate). Aluminum greases were used on slow-speed bearings under wet conditions; however, usage of this type of grease has greatly decreased in favor of the higher dropping point complex analogs.

Sodium Soaps

Sodium soaps are made by reacting sodium hydroxide with tallows derived triglyceride or fatty acid. Greases containing sodium soaps have a fibrous structure, dropping points above 177°C, natural rust resistance, poor water resistance and poor low temperature properties. Sodium greases are not widely used in the U.S. but are still widely used in the Latin American market as general-purpose industrial greases, as automotive lubricants and in certain plain, slow speed bearings and in gearboxes where water contact is low. These greases should never be used in applications with any appreciable exposure to water [3].

Calcium Soaps

Calcium soaps are made by reacting calcium hydroxide (lime) with either 12-hydroxystearic acid (derived from, castor oil) or a tallow-derived triglyceride. The greases made using the castor oil derivative is usually referred to as anhydrous calcium grease; whereas, the grease made from the tallow derivative is referred to as water-stabilized calcium grease. Water-stabilized calcium grease contains up to about 2 wt. % water which aids in the formation of the soap fibers. Both types of calcium greases are characterized by having a smooth, buttery appearance and good water resistance. The major difference between the two types is the dropping points. Anhydrous calcium greases have dropping points of about 265-285°F, water-stabilized calcium greases have dropping points of about 200-220°F. Calcium greases are used in plain and rolling bearings, in gearboxes and in general industrial applications where good water resistance is needed.

Lithium Soaps

Lithium soaps are made by reacting lithium hydroxide with a castor oil derivative fatty acid, such as 12-hydroxystearic acid. The finished grease is characterized by having a smooth, slightly texture, dropping points about 390°F, good resistance to softening or mechanical stability, low leakage and moderate water resistance. Lithium greases represent approximately 50% of the U.S. market and are used in roller bearings, as automotive chassis and wheel bearing lubricants and as general-purpose industrial greases.

2.3.2.2 Complex greases

Complex greases are formed from at least two very different acid and one metal / alkali metal or acids of two different metals. The properties of complex grease are very different from conventional grease and usually superior in some important respects, particularly in high temperature properties, i.e. higher dropping point [3].

Complex soaps

Fatty Acid + Alkali + Dibasic Acid = Soap + By product(s)
(complexing agent)

Aluminum Complex Soaps

Aluminum complex soaps are made by reacting an organoaluminum compound, such as aluminum isoprepoxide, with a fatty acid, such as stearic acid, and a cyclic acid, such as benzoic acid. Aluminum complex greases have a smooth, slightly gel-like appearance, excellent resistance to softening, good water resistance, and a dropping point above 450°F. Aluminum complex greases are widely used in the steel industry because of their good water resistance properties and good pumpability.

Calcium Complex Soaps

Calcium complex soaps are made by reacting calcium hydroxide with a fatty acid, such as 12-hydroxystearic acid, and acetic acid. Calcium complex greases have a smooth, buttery appearance, good water resistance, inherent EP or load carrying capabilities and dropping points above 450°F. These greases are generally used in industrial applications especially steel mills where both high temperature and water resistance properties are required [3].

Lithium Complex Soaps

Lithium complex soaps are made by reacting lithium hydroxide with a fatty acid, such as 12-hydroxystearic acid, and a dicarboxylic acid, such as azelaic acid. Lithium complex greases have properties similar to those of regular lithium grease except for its improved high temperature properties. Such greases are finding wide application as automotive and general-purpose industrial greases. In the U.S., automotive applications are being driven by the recently adopted D4950 specification, which covers the relubrication of chassis systems and wheel bearings of passenger cars, trucks and other vehicles.

2.3.2.3 Non-Soap greases

Finely divided solids act as thickeners and can also be used. Typical materials are treated clay, silica, Carbon black, a number of pigments / dyes and several different polyamines.

Polyurea

Polyurea thickeners are made by reacting a diisocyanate with a diamine and a monoamine. In addition to the polyurea thickeners, diurea and urea/urethane derivatives can also be used. Diurea thickeners are made by reacting the diisocyanate with a monoamine. The urea/urethane thickeners are made by reacting the diisocyanate with an amine and an alcohol. All of these types of greases are generally smooth (but somewhat opaque), exhibit dropping points above 450°F, and have very good resistance to oxidation. They are widely used to lubricate ball and roller bearings, such as those used in electric, and to lubricate automotive constant velocity joints [3].

Organo-Clay

The organo-clay thickeners used to make greases are referred to as organophilic bentonites, such as montmorillonite and hectorite. To make a grease, the clay is mixed with a lubricating oil after which a polar dispersant, such as water or acetone, is added. As the clay platelets separate, the oil coats each platelet forming a stable gel structure. The finished grease has a smooth, buttery appearance and good heat resistance since the clay is non-melting Clay greases are often used is high temperature applications where frequent relubrication can be done such as on furnace door bearings, kiln car bearings and bearings on shafts extending through furnace.

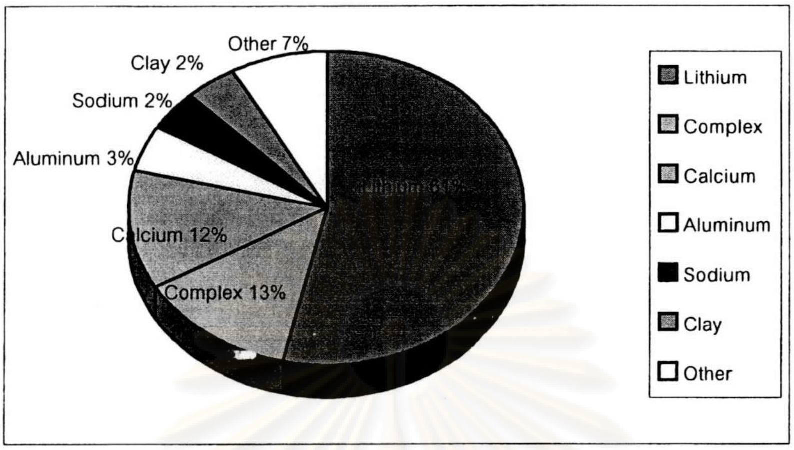


Figure 2.2 Type of greases

2.3.3 Additive

Additives are used to modify and improve certain properties of the grease. The principal types of additives used are antioxidants, rust inhibitors, extreme pressure/antiwar agents, polymers and solid fillers. Polymer is used to improve the water resistance of grease and to allow the grease to adhere better to metal surface. Solid fillers include materials such as graphite and molybdenum disulfide. Other additives are tackiness additive, anti-bleed additives *etc* [3].

2.4 Grease Properties

2.4.1 Consistency

Consistency is the degree of hardness of grease and may vary considerably with temperature [5]. Greases are classified according to their consistency (hardness) in to NLGI grade determined by measuring the penetration (distance in min/10) of a standard cone at 25 °C. The measurement is usually made after "working" the grease for to strokes in a standard grease worker [4].

Table 2.1 The NLGI grades

NLGI grade number	Penetration range (worked 60 str.)	Grade description
000	445-475	Semi-fluid
00	400-430	Semi-fluid
0	355-385	Very soft
1	310-340	Very soft
2	265-295	Soft
3	220-250	Almost solid
4	175-205	Hard
5	130-160	Very hard
6	85-115	Soap-like

2.4.2 Dropping point

The dropping point is the temperature at which the grease passes from a semi-solid to liquid state. Working temperature for greases is below the dropping point.

2.4.3 Bleeding

When oil separate from grease, bleeding is said to occur. The stability of grease can be determined by measuring the bleeding tendency ASTM D1742 determined the amount of oil likely to bleed out of grease under pressure. IP 121 or DIN 51817 is used for determination of oil bleed at static condition (shelf life). The bleeding increase as the temperature raise[4].

2.5 Temperature limits

Table 2.2 Shows the recommended working temperature limits for different types of grease [4].

Type of grease	Recommended Working Temperature	
	Min, (°C)	Max, (°C)
Lithium soap	-30	+110
Lithium complex	-20	+140
Sodium soap	-30	+80
Sodium complex	-20	+140
*Calcium soap	-10	+60
Calcium complex	-20	+130
Barium Complex	-20	+130
Aluminum complex	-30	+110

2.6 Manufacture of Grease

There are three basic steps used to manufacture grease.

1. Saponification

   These steps include the reactions of fatty materials with alkali metals to form soap.

2. Dehydration

   These steps are the removal water and the conditioning of soaps.

3. Finishing

   These steps are the incorporation and dispersion of the oil and additives to form finished grease.

Each of these steps must be done under specific condition, which include temperature, concentration, and mixing order to obtain finished grease with the desired performance properties. There are three commercial processes, which include the kettle process, the contractor process and the continuous process [3].

2.7 Grease Structure

A dispersion in lubricating fluid of soap crystallites arranged in aggregates called fibers, which are oriented in a secondary structure to help the immobilization of the fluid [6].

With the advent of the electron microscope in 1938, greases were found to contain fiber structure, providing a new approach to study grease structure. Calcium soap fibers are shown have a rope-like appearance [7] (Figure 2.3).

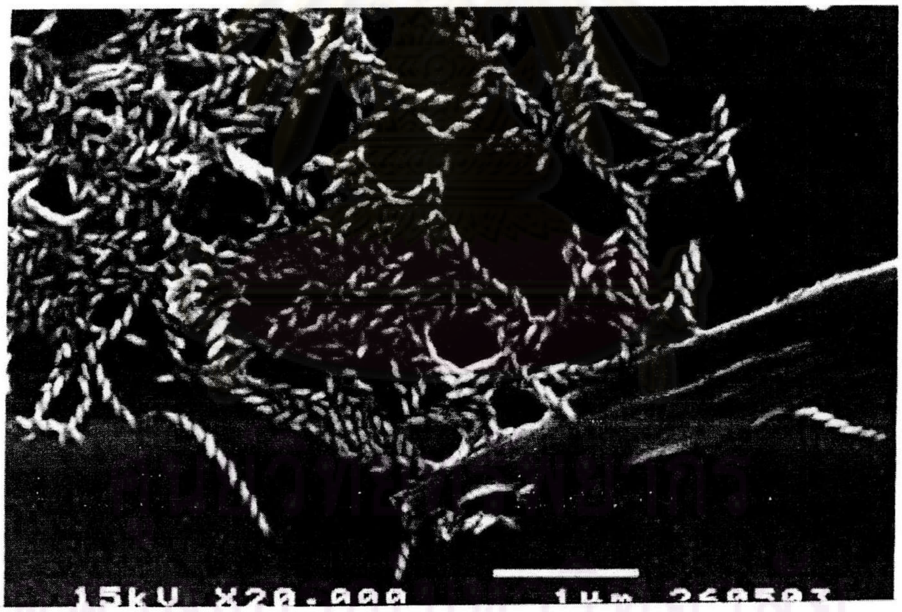


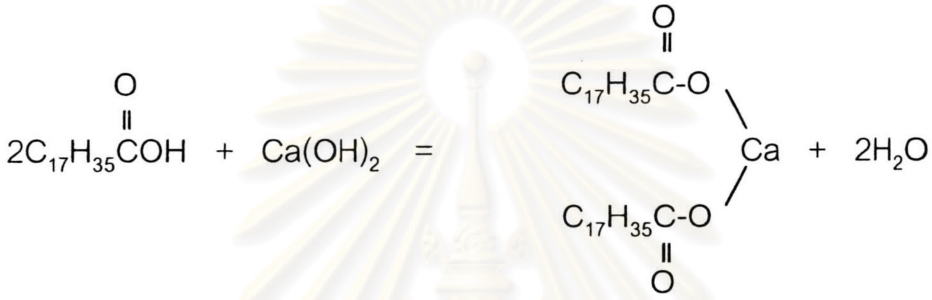
Figure 2.3 The fibers of calcium grease

2.8 Hydrated Calcium Grease

2.8.1 Chemical Reaction

The component acids present in tallow react with calcium hydroxide to form soaps. The following example is for stearic acid. The other acids present in tallow react in a similar manner.

Stearic Acid (or tallow) + Lime = Calcium Di-Stearate + Water



$$2C_{17}H_{35}\overset{O}{\overset{\|}{C}}OH + Ca(OH)_2 = (C_{17}H_{35}COO)_2Ca + 2H_2O$$

The equation used to determine the amount of lime required for reacting with an acid in neutral formulation, which can be calculated as follows:

$$Ca(OH)_2\ (g) = \frac{(\text{wt. acid, g})(\text{Equivalent wt. } Ca(OH)_2)(\text{Sap. No.})}{561^*(\text{Assay of } Ca(OH)_2)}$$

The weight of the acid is dictated by the desired thickness of the grease. The molecular weight of $Ca(OH)_2$ is 74.095. However because $Ca(OH)_2$ reacts with two acid molecules, therefore, its equivalent weight is half that or 37.05.

Sap. No. is saponification number of the acid. The assay of the $Ca(OH)_2$ present in the lime (the purity is normally listed on a specification sheet provided by the supplier). It is common to add an excess of lime in order to ensure that all of the acids have completely reacted [1].

Water is required to stabilize these greases [8]. The inclusion of water generally up to about the 2 wt. % is needed to help solubilize and stabilize the soap in the oil. If this water is driven off during manufacture or end used, the soap fibers become insoluble in the oil with subsequent de-gelling of the grease. Other stabilizers such as alcohols and esters can also are used. These greases have dropping point of about 93-104 C°, and have a useable upper temperature range of approximately 65 C°. Hydrate calcium soap greases have excellent water resistance characteristics and are relatively low production cost [1].

2.8.2 Manufacturing

Lime and tallow are dissolved in a small amount of oil. The temperature is increased about 130 C°. Water is periodically added throughout the saponification reaction. The function of water is to modify the structure so that oil can be incorporated into the soap. After the saponification reaction is completed the heating process is discontinued and reduction oil is slowly added to the mixture. When the temperature reaches about 100 C°, the mixture should be hydrate again. Oil can be added at a faster rate. Antioxidants are commonly incorporated into hydrated caladium grasses. Hydrate calcium soap quickly discolors (turn orange/brown) if additives are not present to inhibit the oxidation process. Extreme pressure and antiwar additive are less common since other grease types are more appropriate for severe service applications [3].

2.9 Literature review

Cibular considered the main characteristics of grease to be structure, hardness, consistency and lubricity of these, he said, only hardness (penetration) could be measured. He also pointed out that low V.I. naphtenic oil gave more stable grease than high V.I. Paraffinic oil [7].

Sproule and Pattenden defined calcium grease as a three-component system consisting of a dispersion of calcium soap of higher fatly acid in mineral oil, which stabilized by a small quantity of water. Using an electron microscope for their studies, they concluded that when calcium soap is stirred in mineral oil at elevated temperatures, it become dispersed in the form of minute, nondescript particles. The addition of water to this system orients the particles in the form of fibers having a wavy or loosely coiled form. The shearing action associated with mixing causes the fibers to become tightly coiled [7].

Lawrence found that when water is added to an oil dispersion of calcium stearate, at a temperature above the gelation point, the soap will be hydrolyzed. The liberated acids then act as a structure modifier. When excess lime is present, this action will not occur [7].

Bryant and Giordano said that greases formed in this way were adequate for the axles of wagons, but when used on machinery, and friction heats the grease causing water to evaporate, and the "tie water" is lost, syneresis occurs (i.e., the soap separates form the oil). Early grease makers knew the presence of water was essential, but did not know its function [7].

Rhodes and Wannamaker stated that the water present in the grease plays an important in determining its lubricating characteristics; for maximum lubricating power the proper ratio of water to soap is essential. The glycerol formed during the process of manufacture may have a distinct effect on the effectiveness of the grease [7].

Hans Backstrom reported that in the manufacture of grease, naphthenic base oil have great adventages compared with paraffinic oil. The basis for these adventage lies in the favourable solubility properties of naphthenic oil. The ways of measuring solubility properties are aniline point and VGC (Viscosity Gravity Constant). The aniline point is determined by mixing equal part of oil and aniline and stirring vigorously while the temperature is raised. The aniline point is the temperature at which it becomes possible for both liquids to become wholly mixed. VGC is calculated from the values for viscosity and density. The main characteristic to consider when choosing which oil to use is the solubility. The metal soap in grease is a compound with strong polar characteristic. Oil's ability to dissolve soap is dependent on the degree of polarity possessed by the molecule in the oil. Aromatic molecules are most polar, after which come naphthenic molecules, while paraffinic are the least polar [9].

Bo Jacobson reported that naphthenic oil give the best results for actual cooking of the grease. But paraffinic oil is better able than naphthenic oil to remain fluid under high pressure. On the other hand, due to their chemical properties, maphthenic oils have a positive influence on the steel if and reduce the risk of carck propagation [10].

Luo Ruibin, Wang Ping and Liu Fusheng study of composition and technology of complex lithium grease. They reported that under pressure sapanification process, only the dicarboxilic fatty acids with more that 6 carbon atom can complex with 12-hydroxy stearic acid to form grease with dropping point higher than 300°C. The dropping points of grease do not exceed 300°C until the mole ratio of sebaic acid to 12- hydroxy stearic acid reaches over 0.25:1. Paraffinic base, naphthenic base. Intermediate base and PAO oil can be used to prepare complex lithium grease with high dropping point using 12-OHSt and sebaic acid. As for mechanical stability of complex greases prepared by different base oil, paraffinic base oil is best, naphthenic base oil is slightly poor. And intermediate base and PAO oil fall in between [11].

S. Hurley and P.M. Cann study grease structure by Scanning electron microscopy (SEM) and atomic force microscope (AFM) techniques. SEM and AFM examination has been carried out on grease thickener as bulk sample and rolled films. In these investigations, the base oil was removed by solvent washing. For AFM technique, the fibers appeared to be twisted and had similar overall dimensions to those found in the washed studies. However, in some cases the washed samples have greater width fiber than unwashed samples because there was a thickener / solvent interaction swelling the fiber. Also the fibers were more evenly dispersed and there was less evidence of fiber clumping and the formation of the thick twisted ropes that has been reported for the wash samples. It might be that this phenomenon is a consequence of the solvent washing method [12].

Vold studied grease structures by using X-ray diffraction orientation analysis and the electron microscope. He found that molecular layers of calcium soap fibers were arranged perpendicularly to the thickness of the fiber [13].

Bird and Rooney, using the electron microscope found two types of fibers : (1) small, so-called twisted fiber, and (2) ribbons of larger dimensions having no twist. In both types they found striations running parallel to the length of the fibers. They concluded that these were due to the "edge on" view of the layers of metal atom in the soap structure, which ran approximately parallel to the direction of thickness and length [14].