CHAPTER III

EXPERIMENTAL

3.1 Chemical

3.1.1 Calcium hydroxide ($Ca(OH)_2$) premium grade was purchased from Siam Lime Product Co., Ltd.

3.1.2 Palm Fatty acid was purchased from P.S. Pacific Co., Ltd.

3.1.3 Base oil was purchased from Thai Petroleum Industry Co., Ltd. and Nynas Co., Ltd.

3.1.4 Toluene, n-Hexane and Ethanol analytical grade was purchased from Chemical House and Lab Instruments Co., Ltd.

3.1.5 Nonionic Surfactant (NP-9)

3.2 Instrument and apparatus

3.2.1 Penetrometer: Model -, Manufacture Rigosha

3.2.2 Dropping point Tester: Model 852-02, Manufacture Rigosha

3.2.3 Water washout Tester: Model -, Manufacture Stansope Seta

3.2.4 Apparatus for distillation is distillation flask, cooler, water measuring tube and heater.

3.2.5 Scanning Electron Microscope (SEM): Model JSM 5410LV, Manufacture Jeol

3.2.6 Density Meter: Model AMD 4500, Manufacture Anton Pacer

3.2.7 Automatic Viscometer: Model CAV 2000, Manufacture CANNON

3.2.8 Clevelan open cup test unit: Model CL1, Manufacture Petrotest

3.2.9 Fourier Transform Infrared Spectrometer. (FTIR): Model Paragon 1000 PC, Manufacture Perkin Elmer

3.3 Procedure

3.3.1 Preparation of Calcium Grease

Calcium Hydroxide ($Ca(OH_2)$) 13.6 g was dissolved in 50 ml distilled water and 30 g base oil in 2 liters stainless steel pot at room temperature. Then the pot was placed on a hot plate at $80^{\circ}C$. Palm fatty acid 110 g was transferred into a 250 ml beaker and heated on hot plate at $60^{\circ}C$. The palm fatty acid solution was slowly poured into the pot and the mixture was heated at $130^{\circ}C$ and stirred at the same time (Saponification step). When temperature reached $130^{\circ}C$, it was maintained at that temperature for 15 minutes and the water was evaporated on the hot plate (Dehydration step). After the saponification reaction was completed, the heating process was discontinued and 100 g of oil was slowly poured into the mixture. When the temperature reached $100\ ^{\circ}C$, water was added into the mixture (Rehydration step). After that, 200 g of oil was added at a faster rate. Calcium greases are generally not milled or dearated. Calcium grease was obtained as a smooth and butter.

3.3.2 The effect of base oil type

3.3.2.1 Preparation of Base Oil Blend

The effect of base oil type was studied by prepared calcium grease with different kinds of base oil. Naphthenic oil (N) and paraffinic oil (P) were mixed in 3000 ml beaker. The ratios of base oil blend between naphthenic oil and paraffinic oil are show in Table 3.1.

Table 3.1 *Ratio of mixed base oil of naphthenic oil and paraffinic oil*

Ratio of N : P	100 : 0	80 : 20	70 : 30	60 : 40	0 : 100
Wt. of N (g)	1000	800	700	600	0
Wt. of P (g)	0	200	300	400	1000

3.3.3 The effect of water content

Calcium grease was prepared from base oil blend in ratio N:P equal 70:30 and vary water content in rehydration step as following Table 3.2.

Table 3.2 Water content in rehydration step

Water Content (% of wt. Acid)	6	8	10	12	14
H_2O (ml)	7	10	12	15	17

3.3.4 The effect of saponification rate

Calcium grease was prepared by using base oil blend ratio N:P equal 70:30, water content 10 % and vary heat rate for 2.0, 2.5 and 3.0 °C/min.

3.3.5 The effect of surfactant

Calcium grease was prepared by using 100% paraffinic oil and ratio of nathenic and paraffinic oil was 60:40 which mixed with nonionic surfactant (NP-9) in various ratio 1%, 2% and 3% respectively, as following Table 3.3.

Table 3.3 Surfactant content in base oil

%Surfactant in base oil	1	2	3
Amount of surfactant (g)	10	20	30
Amount of base oil (g)	990	980	970

3.3.6 Test method of cone penetration of lubricating grease using one-quarter and one-half scale cone equipment (ASTM D1403)

Test method was used for measuring the consistency of small samples of lubricating greases by penetration of ¼ - scale cone or a ½ - scale cone of unworked and worked penetrations [15].

The penetration was determined at 25°C by releasing ¼ - scale or ½ - scale cone assembly from the penetrometer and allowed to drop freely into the grease for 5 seconds.

3.3.6.1 Procedure of unworked penetration

The empty grease worker cup and sample in a container were placed in the temperature bath at 25°C for sufficient time to bring the temperature of the sample and the worker cup to 25 ± 0.5°C. The sample was transferred into an overfilled the cup of the grease. The cup was jarred to release trapped air and the grease was packed with the spatula to without air pockets. The excess grease was scrape off extending above the rim by moving the blade of the spatula.

The cup was placed on the penetrometer table and the mechanism was set to hold the cone in the zero position of the indicator dial. Then the tip of the cone was adjusted to touch the surface at the center of the test sample. The cone was released shaft rapidly into the test sample and allow it to drop for 5.0 ± 0.1s. The indicator shaft was gently depressed until stopped and read the penetration to nearest 0.1 mm from the indicator. A total of three tests on the specimen and reported in the average value, to nearest 0.1 mm, as the ¼ - scale or ½ - scale unworked penetration of the sample [15].

3.3.6.2 Procedure of Worked Penetration

Sample was filled to the cup of the clean grease worker and mounded up about 7 mm at the center. The sample was packed using a spatula and jarred in a cup to avoid trapped air. The worker was placed in the temperature bath at 25°C until the temperature of the worker and contents reached 25 ± 0.5°C. Then the worker was removed from the bath. Grease was worked 60 full double strokes of the plunger, completed in 1 min ± 5 s. After that, the plunger was returned to its top position and the vent cock was opened for remove the top and plunger. The

cup was jarred and packed the grease with a spatula to fill the holes and remove air pockets. Moving the blade of the spatula with a 45° angle to scrap off the excess grease at the rim of the cup. The worked penetration was measured same the unworked penetration [15].

Calculation

The penetration value which obtained from ¼ - scale or ½ - scale cone equipment shall be full – scale penetration (Test Methods D217) by the equation :

¼ Scale :

$$P = 3.75p + 24$$

P = cone penetration by test method D 217

p = cone penetration by ¼ - scale equipment

½ Scale :

$$P = 2r + 5$$
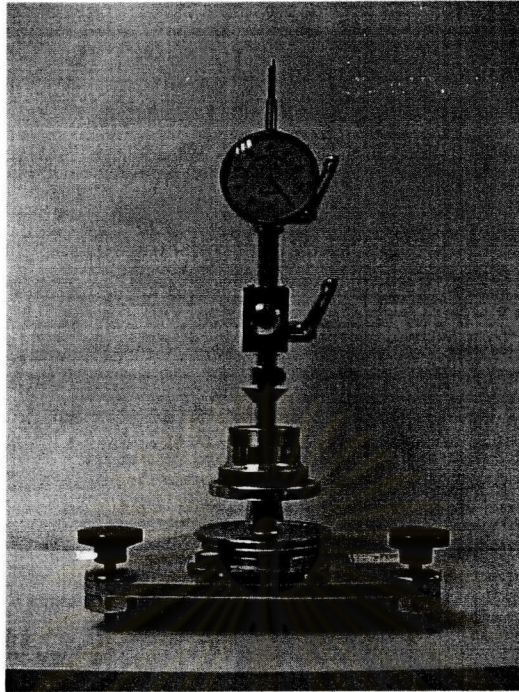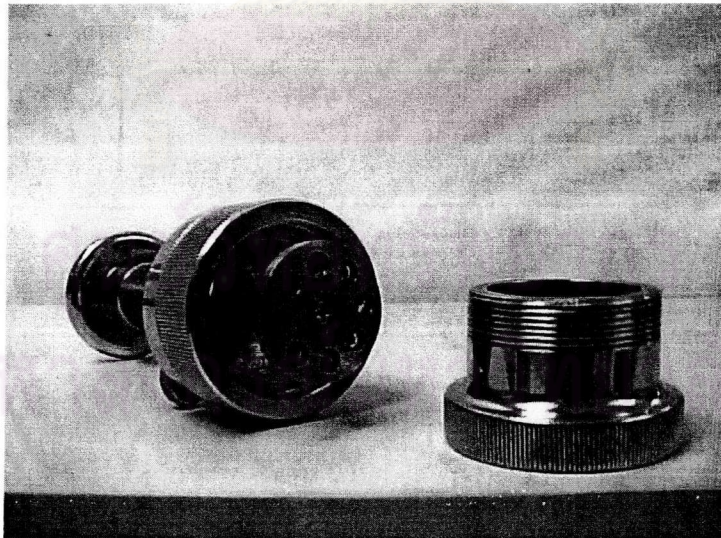
P = cone penetration by test method D 217

p = cone penetration by ½ - scale equipment

Figure 3.1 Penetrometer

Figure 3.2 Apparatus for grease worker

3.3.7 Test Method for Dropping Point (JIS K2220 (5.4)/ASTM D566)

The bigger month of cup was filled with the sample without air trapped and the sample was extruded from both ends by a spatula. The metallic rod was inserted from the smaller mouth to protrude about 25 mm and the rod was push to the cup to allow the rod contact the rims of upper and lower edges. The cup was spirally turned while pressing the rod. Then the sample was removed in conical form the cup. The cup was put in the air bath and inserts the thermometer into the cup. After that the air bath was put in heating bath and started heating to raise the temperature at a rate of 5-7.5°C /min until the heating bath reached 20°C lower than the expected dropping point of the sample. Then temperature was raised at a rate of 1-2°C/min by the difference of the temperature between the air bath and the heating bath was within 1-2 $^{\circ}$C. When the sample dropped from the rim of the cup, the both thermometers was recorded by average value of indications [16].
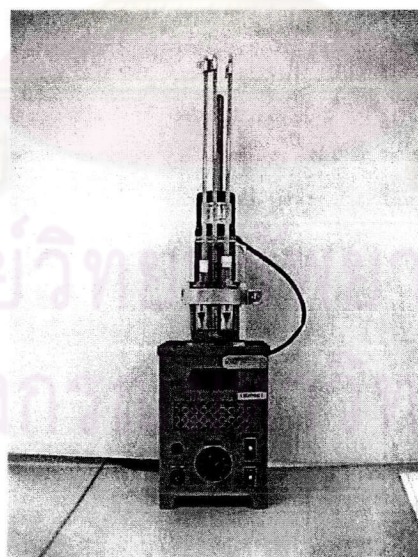
Figure 3.3 Apparatus for dropping point

3.3.8 Test method for water washout resistance (ASTM D1264/JIS 2275 (5.12))

The ball bearing was packed by known mass with 4.0 ± 0.05 g of sample into the housing. The minimum 750 ml of distilled water was added into the bath and the water was kept at 38 ± 2°C or 79 ± 2°C and droved the motor. After that, the water was adjusted the flow rate of 5 ± 0.5 ml/s. The ball bearing was rotated at 600 ± 30 RPM for 60 ± 1 min. The test ball bearing was detached from the housing, and was placed on a pre-weight watch glass. Then they were dried in the thermostatic air bath at 77 ± 6 $^{\circ}$C for 15 hours. After drying, they were left in a desiccators for cooling to room temperature. The mass of the test ball bearing was measured to nearest 0.01 g, and obtained the loss in mass of the sample [17].

Calculation

$$A = \frac{C}{B} \times 100$$

A = water washout resistant (mass %)

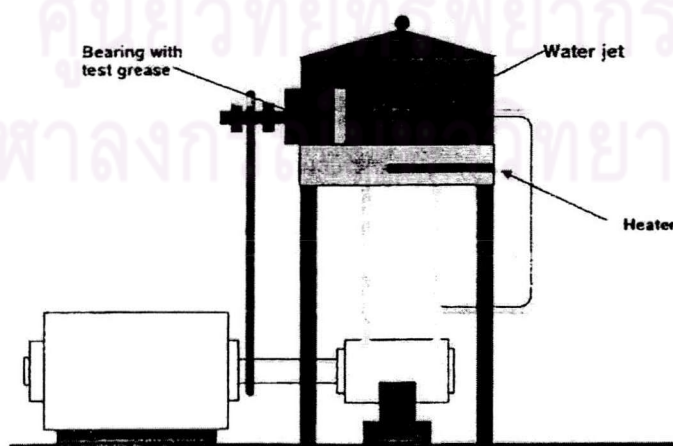C = loss in mass of sample (g)

B = mass of sample (g)

Figure 3.4 Apparatus for water washout resistance

3.3.9 Test Method for water content (JIS K 2275)

The sample 50 g was weighted in a distillation flask and glass beads was added to prevent bumping. 100 ml of toluene solvent was added into distillation flask and refluxed using heat. The heater was adjusted for the condensed liquid to fall at a rate of 2 to 5 drops per second from the lower end of the cooler. The heating distillation was continued until no water was observed. When the distillation of water ceases, the water measuring tube and its content were allowed to cool to room temperature. The volume of the water in the water measuring tube was read and calculated by equation as following [18].

Calculation

$$W = \frac{100A}{M}$$

W = water content in sample (mass %)

A = quantity of water (ml)

M = quantity of sample taken (g)

Figure 3.5 Apparatus for water content in grease

3.3.10 Study of Calcium soap structure by Scanning Electron Microscopy (SEM)

Thin film of grease was smeared onto a glass slide. The glass slide was dipped in hexane for 15-30 min. to remove the base oil. Then thickener on slide glass was dried and coated with gold by Ion Sputter machine, and then analyzed by Scanning Electron Microscope (SEM) at magnification 20,000 to 50,000.

3.3.11 Test Methods for Analysis of Lubricating Grease (ASTM D128-98) : Free alkali

The sample 10-30 g was completely dissolved in 75 ml of n-hexane by stirring with spatula in 250 ml Erlenmeyer flask and added 50 ml of 95% ethanol into it. Then a few drops of phenolphthalein solution were added into the flask and shake the content vigorously. If the alcoholic layer, after setting for a few seconds, is pink, 10 ml 0.5 N HCl was added, the solutions were boiled on a hot plate for 10 min to expel CO_2 , and titrate the excess acid back with 0.5 N alcoholic KOH solution. Blank was tested by following exactly the above procedure described, but omitted the sample. Calculate the free alkalinity in terms of hydroxide of the predominating base by equation as following:

$$\text{Free alkalinity (mgKOH/g)} = \frac{(B-V)*N*56.1}{W}$$

B = volume of potassium hydroxide used in blank

V = volume of potassium hydroxide used in sample

N = normality of the potassium hydroxide

W = weight of sample, g