CHAPTER IV
RESULTS AND DISCUSSION

In this study, the calcium di-stearate was synthesized from saponification reaction of calcium hydroxide and fatty acid at 130 ^{o}C in an opening process system; the total soap content was 27.25%. Then calcium di-stearate was blended with one type of base oil, such as naphthenic oil, paraffinic oil and mixed base oil of naphthenic oil and paraffinic oil in various ratios; 80:20, 70:30 and 60:40 which properties are shown in Table 4.1.

The 70:30 ratio of naphthenic to paraffinic was used for studying the effect of water content by varying water content in hydration step.

Saponification rate was studied by preparing calcium grease with varying the heating rate, such as 2.0, 2.5 and 3.0^{o}C / min. Finally, the effect of surfactant was studied by using paraffinic oil and mixed base oil in ratio naphthenic to paraffinic of 60:40 and varying surfactant content in base oil.

Then the prepared calcium greases were tested for its consistency, dropping point, water content and water washout by following standard methods of Japanese Industrial Standard (JIS) and American Society for Testing and Materials (ASTM) [15-18].

4.1 Synthesis of calcium di-stearate

The calcium di-stearate was synthesized from saponification reaction of calcium hydroxide and fatty acid at 130 ^{o}C (Saponification reaction step). The reaction is illustrated as follows :

$$2C_{17}H_{35}COOH + Ca(OH)_2 \rightarrow C_{17}H_{35}COO\text{-}Ca\text{-}OOCC_{17}H_{35} + 2\,H_2O$$

After the water was removed in dehydration step, the calcium di-stearate was obtained as a brown solid. It was tested for free alkali following the standard method ASTM D128. Calcium di-stearate was alkali 0.42 mgKOH/g. This indicates that all of the acids have been completely reacted.

4.2 The effect of base oil type on properties of calcium grease

In the component of grease, base oil accounts for 75-95% of total mass. Therefore, the performance of grease is largely determined by the characteristics of base oil. The experiment uses respectively paraffinic base, naphthenic base and mixed base oil of naphthenic and paraffinic which properties are shown in Table 4.1.

Table 4.1 *The physical and chemical properties of base oils*

ITEM	TEST METHOD	BASE OIL TYPE				
		100 % N	N:P 80:20	N:P 70:30	N:P 60:40	100 % P
Density @15 °C; g/cm^3	ASTM D4052	0.9321	0.9244	0.9204	0.9167	0.8945
Viscosity @40 °C; cSt.	ASTM D445	180.3	178.6	178.2	179.0	189.9
Viscosity @100 °C; cSt.	ASTM D445	11.76	12.72	13.22	13.75	17.25
Viscosity Index	ASTM D2270	16	42	53	62	97
Aniline Point	ASTM D611	83.8	90.7	94.1	97.1	113.6
Hydrocarbon Type	ASTM D2140					
C_A, %		16.24	14.11	13.47	12.08	6.98
C_P, %		46.58	49.73	50.98	53.13	60.18
C_N, %		37.18	36.16	35.55	34.79	32.84

Remark *: N=naphthenic oil, P=paraffinic oil*

It is generally known that the main characteristic to consider when choosing oil is the solubility. The metal soup in grease is a compound with strong polar characteristics. The ability of oil to dissolve soap is dependent on the degree of polarity possessed by the molecules in the oil. Aromatic molecules are the higher polarity than naphthenic molecules, while paraffinic are the least polar.

Two of the most common ways of describing solubility are by using the aniline point and the Viscosity–Gravity–Constant (VGC). The aniline point is determined by mixing equal parts of oil and aniline and stirring vigorously the increasing temperature. The aniline point is the temperature at which it becomes possible for both liquids to become wholly mixed. Therefore, lower aniline point has the higher solubility, whereas, higher aniline point has the lower solubility. The results from Table 4.1 showed that 100 %N has lower aniline point than N:P ratios of 80:20, 70:30 and 60:40, respectively, while 100 %P is the highest aniline point.

VGC is calculated from the values of viscosity and density. Both of these characteristics correlate with solubility since they are linked to the oil composition. Oil contains a mixture of aromatic, naphthenic and paraffinic molecules. These three groups of molecules have different densities at the same molecular weight. Aromatic molecules have higher density than naphthenic molecules, which have higher density than paraffinic molecules. Therefore, aromatic molecules have higher solubility than naphthenic molecules, which have also higher solubility than paraffinic. The results from Table 4.1 showed that 100%N has higher density than N:P ratio 80:20, 70:30, 60:40, respectively, while 100%P has the lowest density. From results discussed above, 100 % N has a higher solubility than N:P ratios of 80:20, 70:30 and 60:40, respectively, while 100 %P has the lowest solubility.

Calcium greases, which prepared from different kinds of base oil, were tested for its consistency, dropping point, water washout and water content by following the standard methods of ASTM and JIS. The results are shown in Table 4.2.

Table 4.2 The effect of base oil type on properties of calcium greases

ITEM	TEST METHOD	BASE OIL TYPE				
		100 % N	N:P 80:20	N:P 70:30	N:P 60:40	100 % P
Appearance	Visual Inspection	smooth & clear	smooth & clear	smooth & clear	slightly rough	very rough & grainy
Penetration; Unworked	ASTM D1403	227	218	221	221	291
Penetration; Worked	ASTM D1403	243	236	235	227	243
Dropping Point; °C	ASTM D566	110	110	111	110	109
Water Washout (38 °C/1 h), mass %	ASTM D1264	2.19	0.86	0.76	1.01	3.57
Water Content, mass %	JIS K2275 (4)	0.68	0.65	0.64	0.65	0.66

***Remark** : N = Naphthenic Oil ; P = Paraffinic Oil*

4.2.1 The effect of base oil type on the consistency

The consistency of calcium grease is a measure for its softness or stiffness by the cone penetration test at 0 (unworked) and 60 strokes (worked) by following standard method ASTM D1403[20].

The penetration number was measured in depth, tenths of millimeters, which a standard cone sinks into the grease under the test condition. The results are shown in Table 4.2 and Figure 4.1.

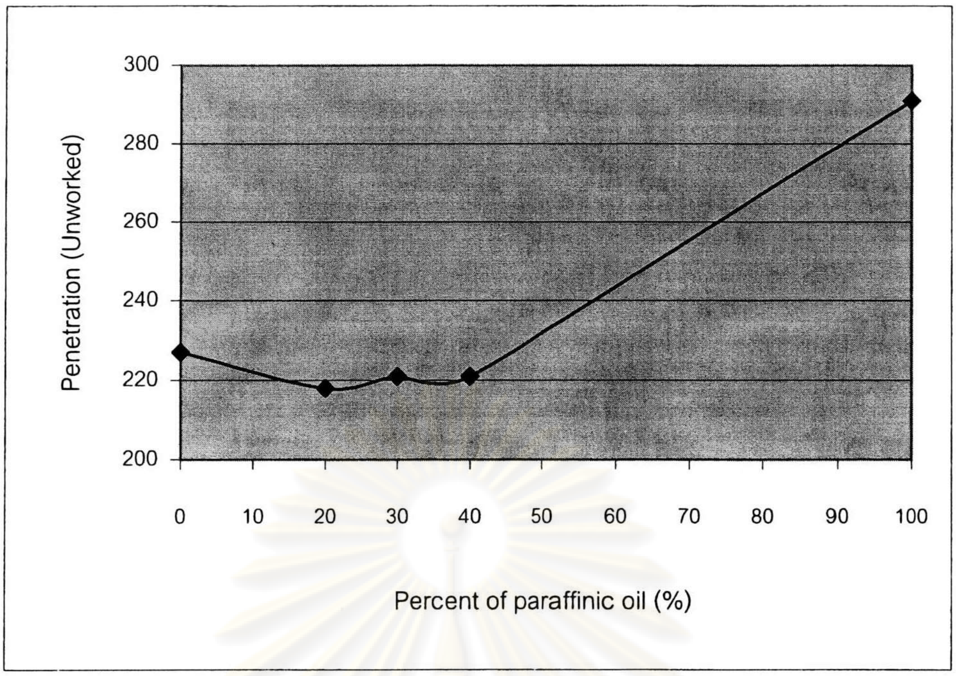

***Figure 4.1** Unworked penetration number at 1 day in varying base oil type*

The penetration number (unworked) of calcium grease prepared from 100% P (291) has higher than prepared 100% N, 80:20, 70:30 and 60:40 (218-227). Therefore, calcium grease prepared from 100%P has lower yield than it was prepared from 100% N and mixed base oil. When consider the difference between unworked and worked penetration numbers, calcium grease prepared from 100%P is more different than 100%N and mixed base oil. Thus, 100% N and mixed base oil in various ratios of 80:20, 70:30 and 60:40 can prepare stable calcium grease, whereas, 100%P is not proper for preparing calcium grease.

Consistency of the stability of calcium grease was studied by storing for 30 days and tested the penetration number at 1 day, 7 days and 30 days. The results are shown in Table 4.3 and Figure 4.2.

Table 4.3 The penetration number at 1, 7 and 30 days in varying base oil type

BASE OIL TYPE	PENETRATION (UNWORKED/WORKED)		
	1 Day	7 Days	30 Days
100 % N	227/243	233/246 (+3)	222/237 (-6)
N:P = 80:20	218/236	218/227 (-9)	217/227 (-9)
N:P = 70:30	221/235	212/225 (-10)	221/225 (-10)
N:P = 60:40	221/227	226/230 (+3)	216/223 (-4)

Remark : N = Naphthenic Oil ; P = Paraffinic Oil

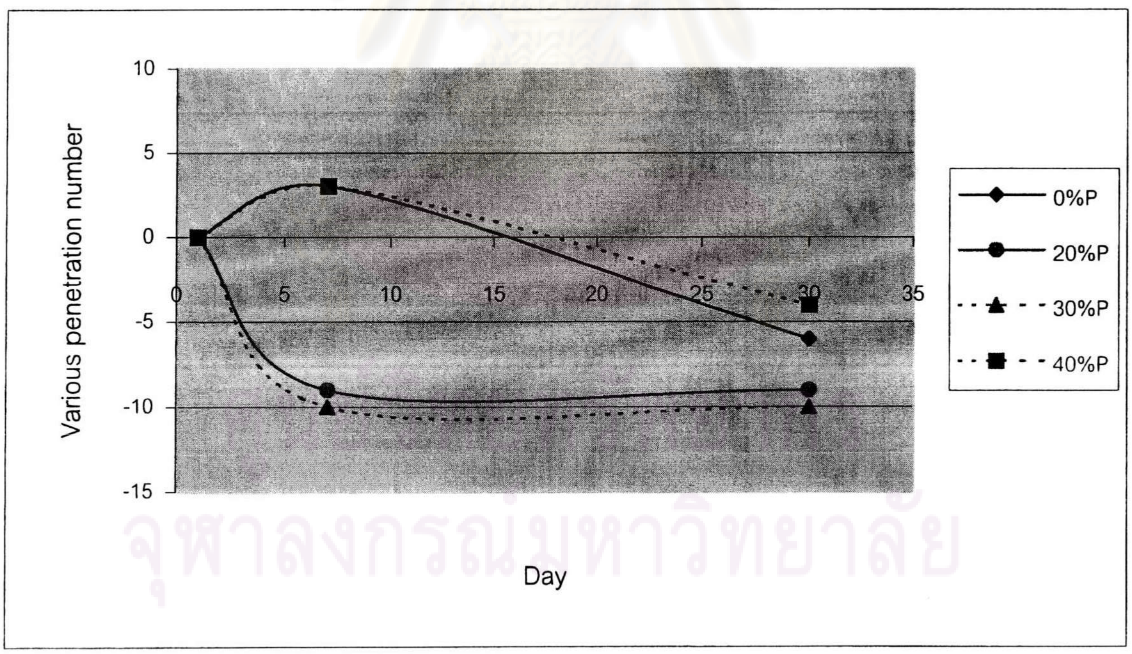

Figure 4.2 The consistency stability in varying base oil type

The penetration numbers (worked) of grease prepared from 100%N, 80:20, 70:30 and 60:40 can vary slightly varied from 3 to 10 penetration when storage for 30 days. However, the penetration number of calcium grease was still in the acceptable range for NLGI Grade No.3 (220-250) (APPENDIX 3). Thus, base oil type is not affect to consistency stability of calcium grease.

4.2.2 The effect of base oil type on dropping point

Dropping point is the temperature at which grease changed from a semisolid state to a liquid state. The results are shown in Table 4.2 and Figure 4.3. The dropping points of all greases were varied from 109 - 110 °C. However, it was still in acceptable range of JISK-2220 specification (APPENDEX 3). Therefore, base oil type is not affect on the dropping point of calcium grease.

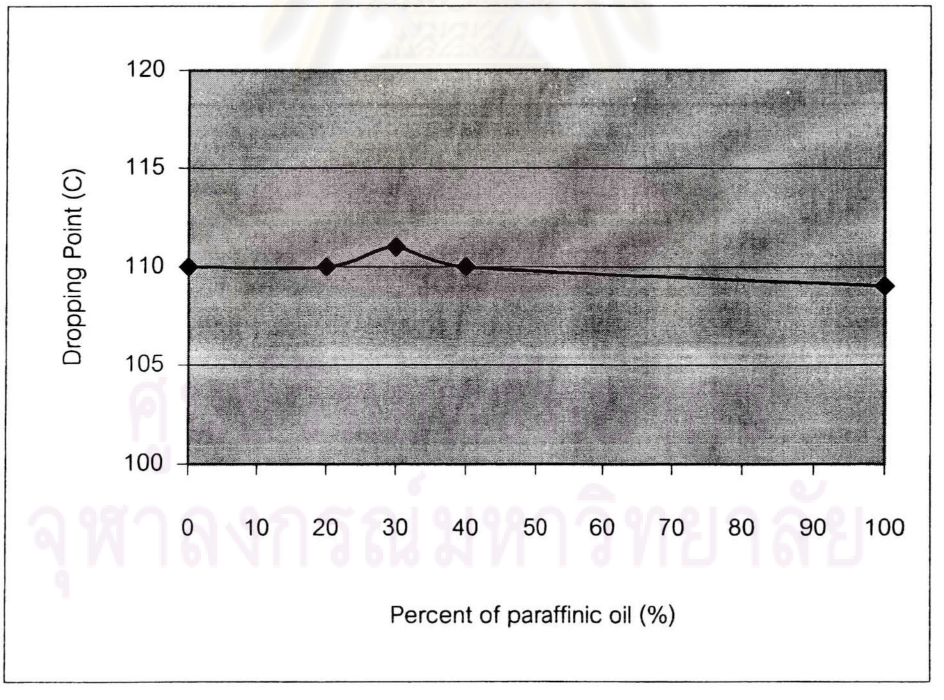

Figure 4.3 The effect of base oil type on dropping point

4.2.3 The effect of base oil type on water washout resistance

The loss of a sample was measured after a specified ball bearing with the sample was revolved at 600 RPM, and 38 °C distilled water was sprayed onto the housing of the ball bearing at 5 ml/s for 1 hour. The results are shown in Table 4.2.

All prepared calcium greases have water washout resistance in a range of 0.76% to 3.57%. Calcium grease prepared from 100%P has higher water washout resistance than the other oils. However, it was still in acceptable range of JIS K2220 specification. Therefore, all prepared calcium greases have good water washout resistance.

4.2.4 The effect of base oil type on appearance

The results from Table 4.2 showed that calcium greases prepared from 100%N, 80:20 and 70:30 were smooth and clear, whereas, the ones prepared from 100%P were rough and grainy. This was due to the lower solubility of paraffinic oil than that of naphthenic oil. Therefore, base oil type affects to grease's appearance.

4.2.5 The effect of base oil type on grease structure

Calcium soap fibers, which prepared from naphthenic oil and paraffinic oil were showed to have similar to appearance as a two stranded rope. The results are shown in Figure 4.4 and Figure 4.5.

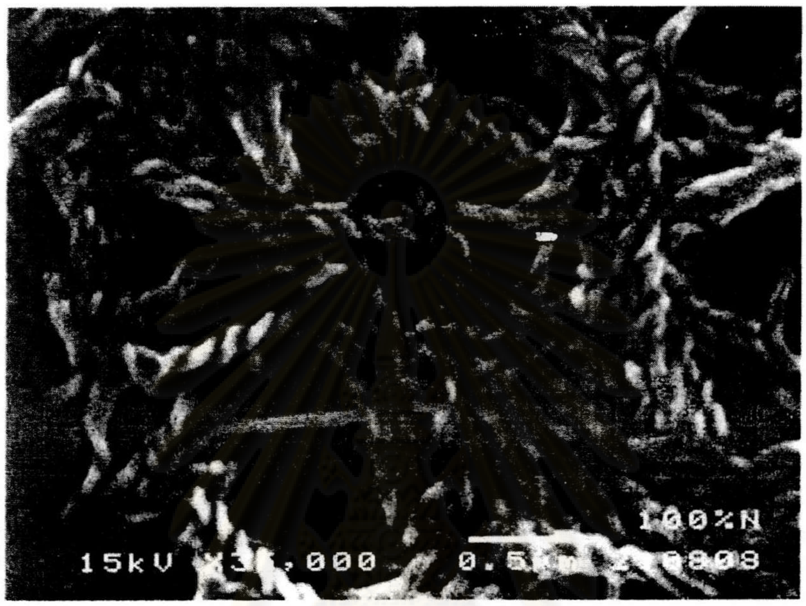

Figure 4.4 Calcium soap fibers prepared from naphthenic oil

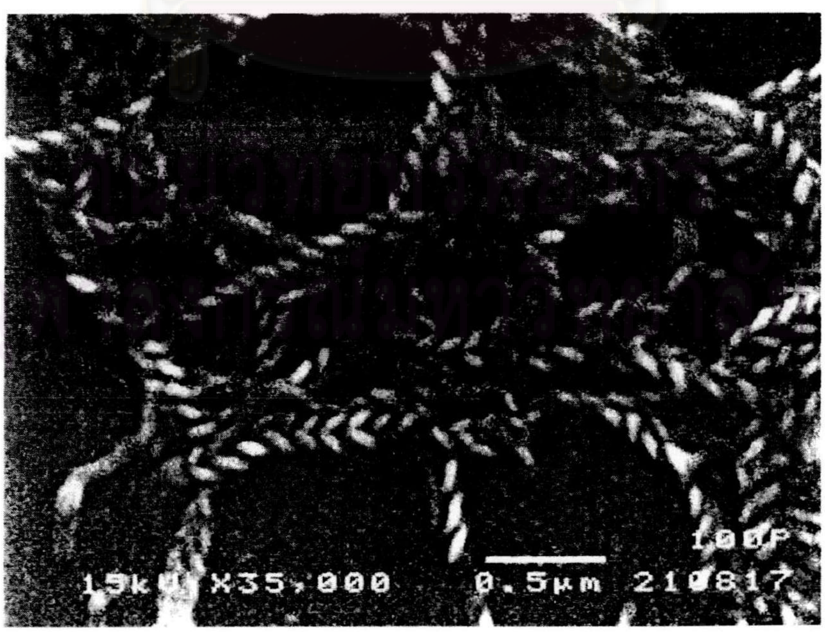

Figure 4.5 Calcium soap fibers prepared from paraffinic oil

4.3 The effect of water content on properties of calcium grease

It is generally known that water is important part in calcium grease. Calcium soap is not stable in most mineral oils and require the third component to produce stability. Water is most often used as stabilizing agent in calcium grease.

Using mixed base oil of naphthenic oil to paraffinic oil of 70:30 and varying the percentage of water content in hydration step prepared calcium grease. The results are shown in Table 4.4.

Table 4.4 The effect of water content on properties of calcium grease

ITEM	TEST METHOD	WATER CONTENT (%)				
		6 %	8 %	10 %	12 %	14 %
Appearance	Visual Inspection	smooth & very clear	smooth & clear	smooth & clear	smooth & clear	smooth & clear
Penetration; Unworked	ASTM D1403	265	230	222	233	223
Penetration; Worked	ASTM D1403	270	233	236	240	235
Dropping Point; °C	ASTM D566	110	112	111	111	111
Water Washout (38 °C/1 h), mass %	ASTM D1264	0.73	0.69	0.76	1.21	1.46
Water Content, mass %	JIS K2275 (4)	0.30	0.54	0.65	0.87	1.12

4.3.1 The effect of water content on the consistency

The results from Table 4.4 and Figure 4.6 showed that the penetration number (worked) of 6% water content (265) has higher than 8%, 10%, 12% and 14% water content (233-240). If calcium grease has a lot of water, it will be hard. Whereas, the lower content of water will lead to soft calcium grease. Therefore, the proper water content for prepared calcium grease no.3 was no less than 8% (0.54 mass %) of soap weight.

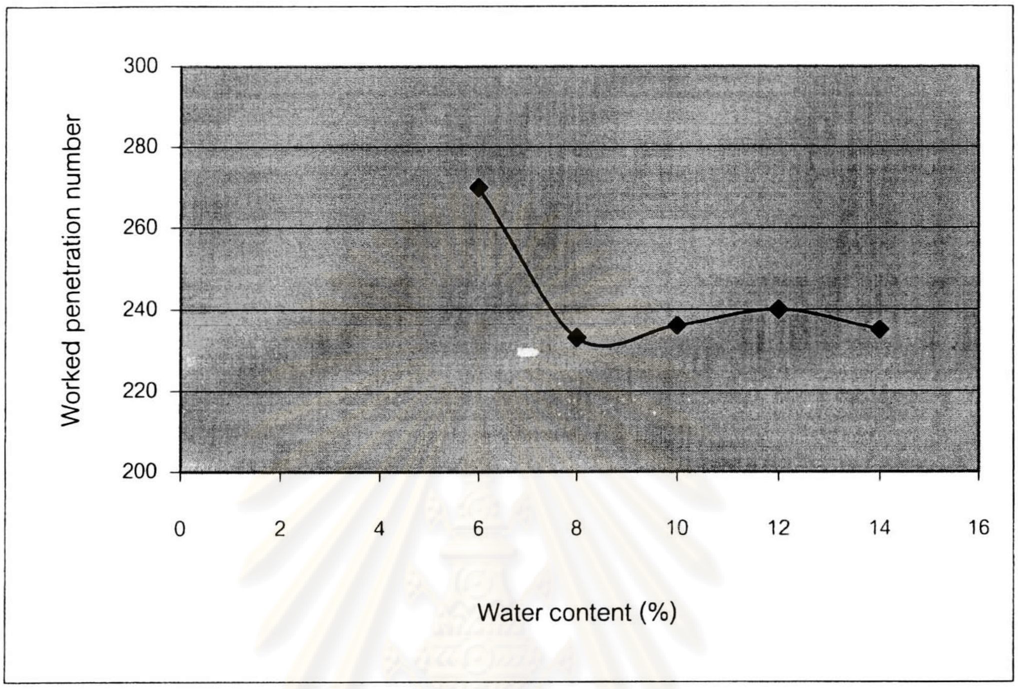

Figure 4.6 Worked penetration number at 1 day in varying water content

Consistency stability of calcium grease was studied by storing for 30 days and tested the penetration number at 1 day, 7 days and 30 days. The results are shown in Table 4.5 and Figure 4.7.

Table 4.5 The penetration number at 1, 7 and 30 days in varying water content

WATER CONTENT (%)	PENETRATION (UNWORKED/WORKED)		
	1 Day	7 Days	30 Days
6 %	265/270	251/254 (-16)	259/251 (-19)
8 %	230/233	242/242 (+9)	243/238 (+5)
10 %	222/236	227/243 (+7)	228/239 (+3)
12 %	233/240	247/247 (+7)	242/240 (0)
14 %	223/235	227/231 (-4)	225/236 (+1)

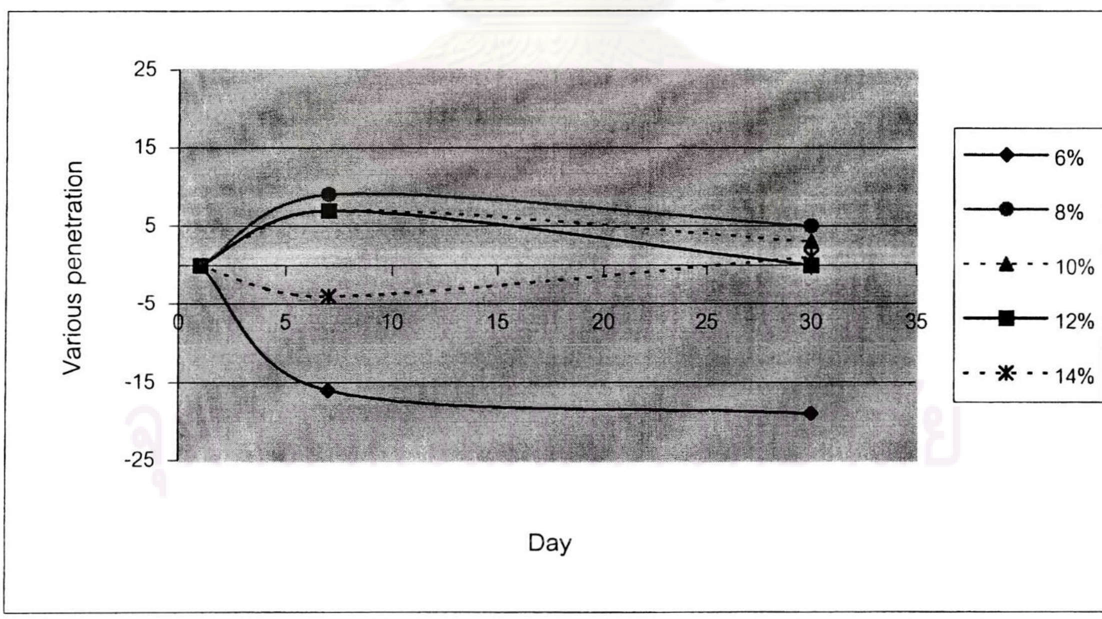

Figure 4.7 The consistency stability in varying water content

When storing calcium grease for 30 days, the penetration number (worked) of 8%, 10%, 12% and 14% water content have slightly varied from 0 to 9 penetrations, whereas, the penetration number (worked) of 6% water content has varied for 19 penetrations. Therefore, if calcium grease has little water content, it will not be stable. Thus, the proper water content for prepared calcium grease No.3 can not be less than water content 8% of soap weights (0.54 mass%).

4.3.2 The effect of water content on dropping point

The results from Table 4.4 showed that dropping points of all greases (110 - 112 ^{o}C) were higher than the minimum specification of JIS K-2220 (APPENDIX 3). Therefore, the water content is not affect to dropping point of calcium grease.

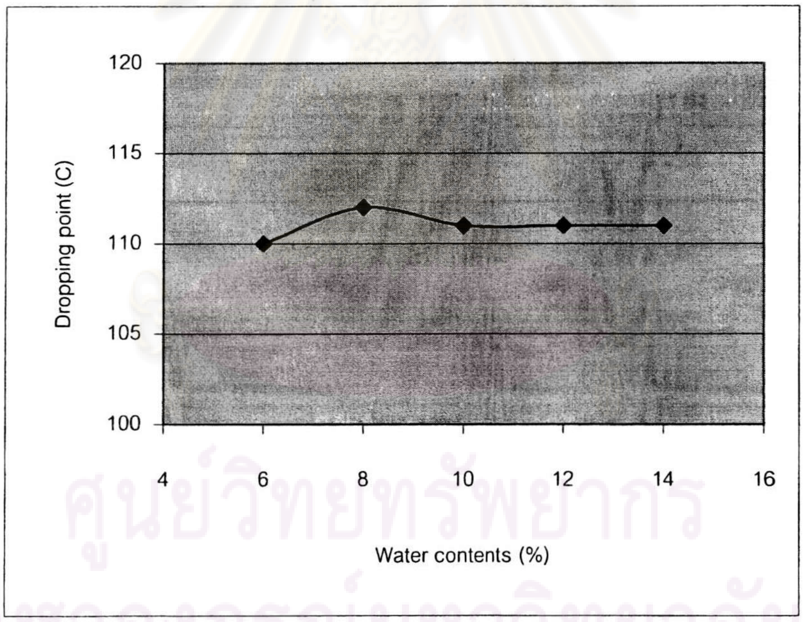

Figure 4.8 *The effect of water content on dropping point*

4.3.3 The effect of water content on water washout resistance

The results from Table 4.4 showed that all prepared calcium greases have water washout resistance in a range of 0.69 to 1.46%. Calcium grease prepared from 14% water content has a higher water washout resistance than the other, but it was still in an acceptable range according to JIS K2220 specification (APPENDIX 3). Therefore, water content is not affect to calcium greases.

4.3.4 The effect of water content on appearance.

Calcium greases were prepared from 6%, 8%, 10%, 12% and 14% water content have smooth and clear, but 6% water content was the clearest.

4.3.5 The effect of water content on grease structure

Calcium soap fibers appear as a rope. It is known that a stabilizer must be presented in calcium grease. If that stabilizer is water, the calcium soap fibers twist into a rope-like structure. The results are shown in Figure 4.9 and Figure 4.10. When water content in calcium grease is 0.3 mass % (6% water content addition), the fibers untwist and lose their structure. To maintain the twisted fiber, calcium soap greases must have water content at least 0.54 % (8 % water content addition).

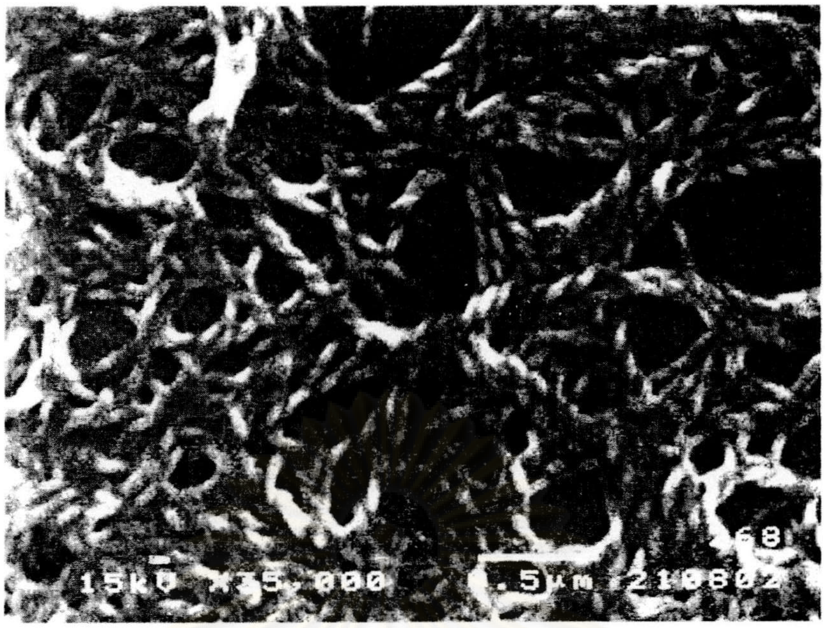

Figure 4.9 Calcium grease structure in 6% water content

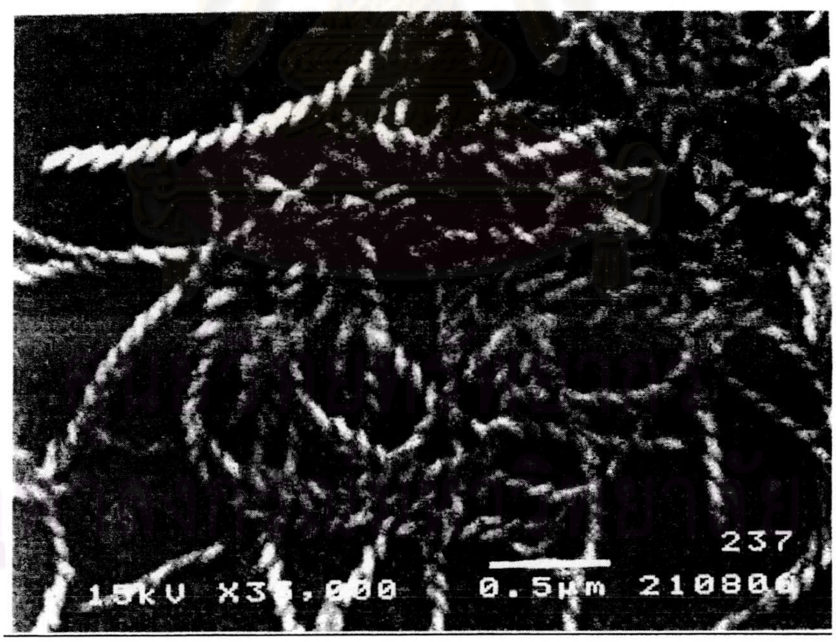

Figure 4.10 Calcium grease structure in 8% water content

4.4 The effect of saponification rate on properties of calcium grease

Saponification reaction is a reaction between of calcium hydroxide and fatty acid at 130°C to form calcium di-stearate. Calcium grease was prepared by using the ratio of naphthenic oil to paraffinic oil; 70:30, 8% water content and varying heating rate during saponification reaction step, such as 2.0, 2.5 and 3.0°C / min. Then prepared calcium grease was tested for consistency, dropping point, water washout and water content. The results are shown in Table 4.6.

Table 4.6 The effect of saponification rate on properties of calcium grease

ITEM	TEST METHOD	RATE OF SAPONIFICATION (°C/min)		
		2.0	2.5	3.0
Apearance	Visual Inspection	Smooth & Clear	Smooth & Clear	Smooth & Clear
Penetration; Unworked	ASTM D1403	237	223	237
Penetration; Worked	ASTM D1403	234	227	234
Dropping Point; °C	ASTM D566 / JIS K2220 (5.4)	111	111	111
Water Washout (38 °C/1 h), mass %	ASTM D1264 / JIS K2220 (5.12)	0.85	0.78	0.91
Water Content, mass %	JIS K2275 (4)	0.60	0.58	0.55

4.4.1 The effect of saponification rate on the consistency

The results from Table 4.6 showed that the penetration number (worked) of all greases were found in range 227 to 234 (NLGI grade No.3). Therefore, the saponification rate is not affect to the consistency of calcium grease.

The consistency stability of calcium grease was studied by storing for 30 days and tested the penetration number at 1 day, 7 days and 30 days. The results are shown in Table 4.7 and Figure 4.11.

Table 4.7 The penetration number at 1, 7 and 30 days in varying saponification rate

RATE OF SAPONIFICATION (°C/min)	PENETRATION (UNWORKED/WORKED)		
	1 Day	7 Days	30 Days
2.0	237/234	242/243 (+9)	247/244 (+10)
2.5	223/227	233/234 (+7)	225/226 (-1)
3.0	237/234	246/243 (+9)	246/242 (+8)

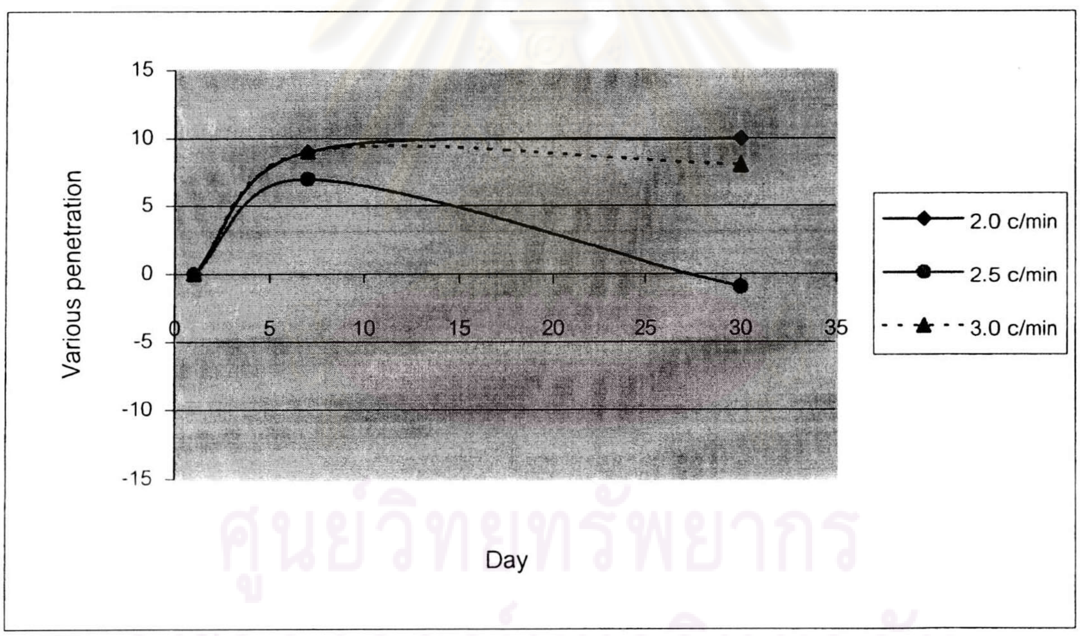

Figure 4.11 The consistency stability in varying saponification rate

When the grease had stored for 30 days, the penetration number (worked) of all greases have slight variation from 1 to 10 penetration. However, the penetration number was still in acceptable range for NLGI Grade No.3 of JIS K2220 specification (APPENDIX 3). Therefore, saponification rate does not effect on consistency stability of calcium grease.

4.4.2 The effect of saponification rate on dropping point

The results from Table 4.6 showed that dropping point of all greases (111^{o}C) were higher than the minimum of JIS K-2220 specification (85^{o}C min.) (APPENDIX 3). Therefore, saponification rate does not affect on the dropping point of calcium grease.

4.4.3 The effect of saponification rate on water washout resistant

The results from Table 4.6 showed that all prepared calcium greases have water washout resistance in a range of 0.78 to 0.91%, but they were still in acceptable range of JIS K2220 specification (APPENDIX 3). All prepared calcium greases have good water washout resistance. Therefore, saponification rate does not affect on water washout resistance of calcium grease.

4.4.4 The effect of saponification rate on appearance

All prepared calcium greases have smooth and clear. Therefore, saponification rate does not affect on calcium grease's appearance.

4.5 The effect of surfactant on properties of calcium grease

Some water is necessary in the formation of calcium grease because soap is not soluble in oil; water dissolves some of the soap to emulsify it with the oil. The water added in the manufacturing of calcium grease also be called the emulsifier.

It is known that calcium grease prepared from 100% P was rough and grainy and prepared from N:P; 60:40 was slightly rough. Since parafinic oil has low solubility, so the soap can slightly dissolved in oil. Therefore, surfactants added to base oil can perhaps the help smoothness of grease.

Calcium grease was prepared by using 100% P and N:P ratio; 60:40, and varying surfactant content in base oil. Then prepared calcium greases were tested consistency, dropping point, water washout and water content as the results showed in Table 4.8 and Table 4.9

Table 4.8 *The effect of surfactant in 100%P on properties of calcium greases*

ITEM	TEST METHOD	SURFACTANT (%)			
		0 %	1 %	2 %	3 %
Appearance	Visual Inspection	Very rough & Grainy	Very rough & Grainy	Rough & Grainy	Rough & Grainy
Penetration; Unworked	ASTM D1403	291	303	288	274
Penetration; Worked	ASTM D1403	243	285	273	269
Dropping Point; °C	ASTM D566 / JIS K2220 (5.4)	109	108	108	108
Water Washout (38 °C/1 h), mass %	ASTM D1264 / JIS K2220 (5.12)	3.57	3.48	3.53	3.50
Water Content, mass %	JIS K2275 (4)	0.66	0.61	0.65	0.72

Table 4.9 The effect of surfactant in N:P ratio; 60:40 on properties of calcium greases

ITEM	TEST METHOD	SURFACTANT (%)			
		0 %	1 %	2 %	3 %
Appearance	Visual Inspection	Slightly Rough	Smooth & Clear	Smooth & Clear	Smooth & Clear
Penetration; Unworked	ASTM D1403	221	205	250	260
Penetration; Worked	ASTM D1403	227	250	278	297
Dropping Point; °C	ASTM D566 / JIS K2220 (5.4)	110	108	108	106
Water Washout (38 °C/1 h), mass %	ASTM D1264 / JIS K2220 (5.12)	1.01	2.02	2.23	2.40
Water Content, mass %	JIS K2275 (4)	0.65	0.87	0.85	0.79

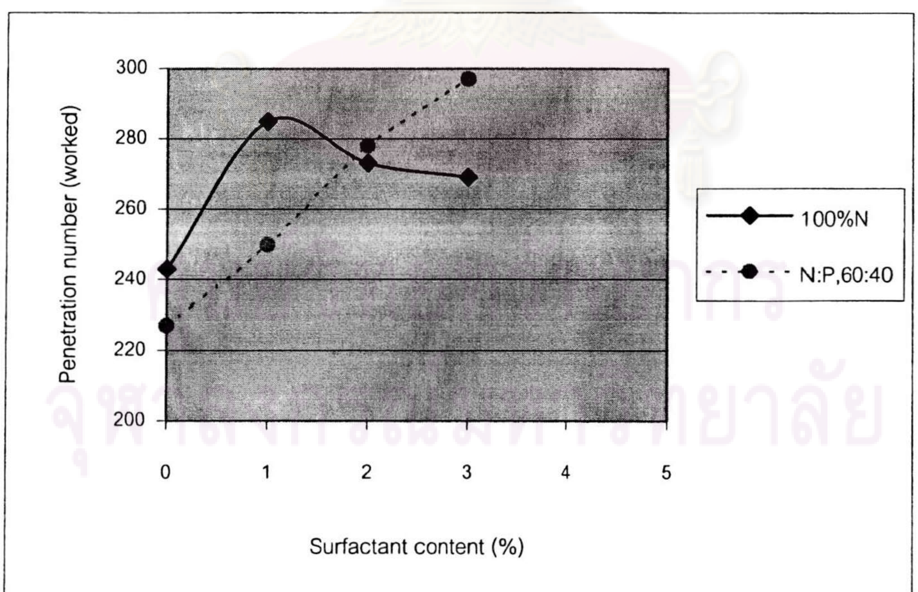

Fig 4.12 The effect of surfactant in paraffinic oil and N:P ratio 60:40 on penetration number

4.5.1 The effect of surfactant on the consistency

The results from Table 4.8, Table 4.9 and Figure 4.12 showed that the penetration number (worked) of all greases varied from 243 to 285 for 100%P and 227 to 297 for N:P ratio 60:40. The penetration number of grease, surfactant was added, was higher (or softness) than calcium grease was not added surfactant. Therefore, adding surfactant is not proper for preparing calcium greases, which leads to a low yield of calcium grease.

When consider the difference between unworked and worked penetration number, it was found that calcium greases prepared from adding surfactant have higher difference (28 to 52 penetration) than surfactant was not added (6 penetration). Therefore, surfactant affect to stability of calcium grease.

4.5.2 The effect of surfactant on dropping point

The results from Table 4.8 and table 4.9 showed that the dropping point of all greases prepared by adding surfactant are slightly lower than greases without surfactant. However, the dropping point of all greases was still in the acceptable range of JISK 2220 Specification (APPENDIX 3).

4.5.3 The effect of surfactant on water wash out resistance

The results from Table 4.8 and table 4.9 showed that all prepared calcium greases have water washout resistant in a range of 1.01% to 3.57%. It was still in acceptable range of JIS K2220 specification (APPENDIX 3).

4.5.4 The effect of surfactant on appearance

The results from Table 4.8 and Table 4.9 showed that calcium greases prepared from 100% P with added surfactant were still rough and grainy. Whereas, it prepared from N:P ratio; 60:40 with added surfactant are smooth. Therefore, surfactant affect the calcium grease has more smooth appearance.

4.5.5 The effect of surfactant on grease structure

Calcium grease was prepared from mixed base oil of N:P ratios; 60:40 was studied for grease structure. The results are shown in Figure 4.13 and Figure 4.14.

Figure 4.13 *Calcium soap fiber of N:P ratio; 60:40*

Figure 4.14 *Calcium soap fiber of N:P ratio; 60:40 with 3 % surfactant*

The calcium soap fiber were shown to appear as twist into a rope-like structure for N:P ratio; 60:40. Whereas, it showed to appear as fiber untwist, short fibers and lose their structure when 3 % surfactant was added. Therefore, adding surfactant is not proper to preparing calcium grease.