CHAPTER IV

RESULTS AND DISCUSSION

In this study, the lithium grease for rolling bearing grade 1 (penetration no. 220-250) was prepared using two base oils (TMP-ester oil and paraffin oil) and lithium stearate. Then the lithium greases were blended with one type of the following additives; zinc dialkyldithiophosphate (ZDDP), molybdenum dialkyldithiocarbamate (MDTC) and diphenylamine (DPA). Their properties were tested according to Japanese Industrial Standard (JIS) and American Society for Testing and Materials (ASTM) **[31-32]**.

The test results of TMP-ester greases and paraffin greases were compared with comparative three types of additives. The test results were evaluated following JIS K-2220 specification (see Appendix 1), and compared to commercial lithium grease.

4.1 Synthesis of lithium stearate

Lithium stearate was prepared by the reaction of stearic acid and a solution of lithium hydroxide monohydrate at 90 ^{o}C. The reaction is illustrated as the equation:

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

After removal of water, the lithium stearate was obtained in approximately 98% as a white powder.

The synthesized lithium stearate was characterized by FT-IR as presented in Appendix 2. The FT-IR spectrum shows C-H stretching at 2,932-2,860 cm^{-1}, C=O stretching of carbonyl group at 1,738 cm^{-1} and C-O stretching at 1,174 cm^{-1}.

The FT-IR spectrum shows that O-H stretching of stearic acid at 3,400- 2,400 cm^{-1} is disappeared for the product. This indicated that neither stearic acid nor water remained in the prepared lithium stearate.

Melting point and moisture content of the lithium stearate are shown in Table 4.1 (Appendix 3).

Table 4.1 Melting point and moisture content of lithium stearate

Items	Lithium stearate	
	Synthesized	Commercial
Melting point (^{o}C)	206	207
Moisture (%)	0.24	0.18

The melting point of the prepared and commercial lithium stearate was found to be similar. The prepared lithium stearate was found to have slightly higher moisture content than the commercial lithium stearate. However, the moisture content of prepared lithium stearate is still in the acceptable range for grease production (less than 1 %) **[16]**.

4.2 Production of base grease

The grease was prepared by blending the base oil and lithium stearate at 220 ^{o}C. The lithium grease was cooled to room temperature and homogenized by 3-roll mill machine. Lithium grease appearance was exhibited a smooth, stringy texture and white. The consistency of lithium grease was measured by the cone penetration test at 0 and 60 strokes (JIS K2220-5.3).

The penetration number was measured as the depth, in tenths of millimeters, which a standard cone sinks into the grease under the test condition. A worked penetration (60 strokes) is more considered than unworked penetration (0 stroke). The object is to observed whether or not the grease soften beyond acceptable limits.

Penetration values of prepared lithium base grease are shown in Table 4.2 (Appendix 4). The penetration number (after 60 strokes) was found to vary from 205 to 305 for TMP grease and from 170 to 288 for paraffin grease.

It was found that the penetration number of two greases increased with a decrease of the amount of lithium stearate. Each mixing ratio of paraffin greases showed the penetration number lower than TMP-ester grease because the viscosity of paraffin oil is higher than TMP-ester oil.

Table 4.2 Penetration of lithium base grease

Base oil (wt %)	Li stearate (wt %)	TMP-ester grease		Paraffin grease	
		0 stroke	60 strokes	0 stroke	60 strokes
80	20	200	205	166	170
82	18	220	225	189	194
85	15	247	252	219	224
90	10	300	305	283	288

From Table 4.2, the base grease having a penetration range of 220 to 225 was obtained by 82 % of TMP-ester oil mixed with 18 % of lithium stearate, or 85 % of paraffin oil mixed with 15 % of lithium stearate. Thus the consistency of grease depended on type, properties of base oil and the ratio of base oil and thickener.

4.3 Oxidation stability of grease

The effect of additives on oxidation stability was evaluated by the Norma-Hoffman bomb test (ASTM D-942, JIS K-2220 5.8). Grease oxidation test was measured as the rate at which grease absorbed oxygen at 99 °C for 100 hours. The oxygen pressure drop of TMP grease and paraffin grease using ZDDP, MDTC and DPA as additives are shown in Table 4.3.

Table 4.3 Oxygen pressure drop of grease (MPa)

Additives	TMP-ester grease*				Paraffin grease**			
	Amount of additive (%)				Amount of additive (%)			
	0%	1%	2%	3%	0%	1%	2%	3%
ZDDP	0.048	0.026	0.012	0.010	0.054	0.030	0.013	0.010
MDTC	0.048	0.025	0.012	0.010	0.054	0.030	0.014	0.011
DPA	0.048	0.023	0.010	0.009	0.054	0.028	0.011	0.009

* TMP-ester base grease comprising TMP-ester 82% and lithium stearate 18%

** Paraffin base grease comprising paraffin oil 85% and lithium stearate 15%

The results showed that TPM ester and paraffin lithium base grease without any additive had oxygen pressure drop at 0.048 and 0.054 MPa, respectively. All prepared greases without any additives showed good oxidation resistance property since the oxygen pressure drop of prepared grease is less than that of JIS specification (0.069 MPa).

As expected, the value of the oxygen pressure drop was found to decrease with an increase of the amount of additives. The effect of types of additive on the oxidation stability of prepared greases was considered. From Table 4.3, there are no difference of the oxygen pressure drop values of prepared greases using the same base oil and same amount of each additive. This indicates that ZDDP, MDTC and DPA have similar performance to improve oxidation stability of prepared greases.

At the same amount of additive, the greases prepared from TMP-ester oil was found to have oxygen pressure drop slightly less than the grease prepared from paraffin oil possibly because TMP-ester oil has oxygen stability better than paraffin oil.

TMP-ester oil is synthesized from acid and alcohol to provide certain predictable properties. This is contrast to refined petroleum oil, which are composed of many compounds of varying chemical composition, depending on the refining method and the crude oil. Paraffin oil contained aromatic and unsaturated compounds that have a negative influence on oxidation stability of base oils.

Oxidation stability of oils was tested by measurement of time (hour) to absorb 2 liters of oxygen **[23]**. The results shown paraffin oil used 45 hours to absorb 2 liters of oxygen, whereas TMP-ester oil used 70 hours. For this reason, paraffin oil showed slightly poorer oxidation stability than TMP-ester oil.

An increase amount of additive from 0 to 1 %, the oxygen pressure drop value of prepared grease was found to decrease by 50 %. Using 2 and 3 % additive, the oxygen pressure drop values of prepared grease were found to be insignificant difference. Thus 2 % additive is suitable to prevent oxidation of lithium base grease.

4.4 Work stability of grease

Work or shear stability of grease is its ability to withstand repeated working with a minimum change in its structure or consistency. The objective of this section is to see whether or not the grease softens or hardens beyond acceptable limits.

The work stability of grease was evaluated by work of the sample from 60 to 10,000 strokes, and compared as the percentage of a change in penetration with ASTM D-217 (±5 % is excellent, ±15 % is good and ±30 % is fair). Results are shown in Table 4.4.

Table 4.4 Penetration of finished grease after work stability test

Additives	Penetration number		
	60 strokes	10,000 strokes	%change
TMP ester grease			
No additive	225	245	8.9
ZDDP	228	249	9.2
MDTC	228	248	8.8
DPA	229	249	8.7
Paraffin grease			
No additive	224	245	9.4
ZDDP	227	248	9.3
MDTC	228	249	9.2
DPA	227	249	9.6
Commercial grease	240	261	8.8

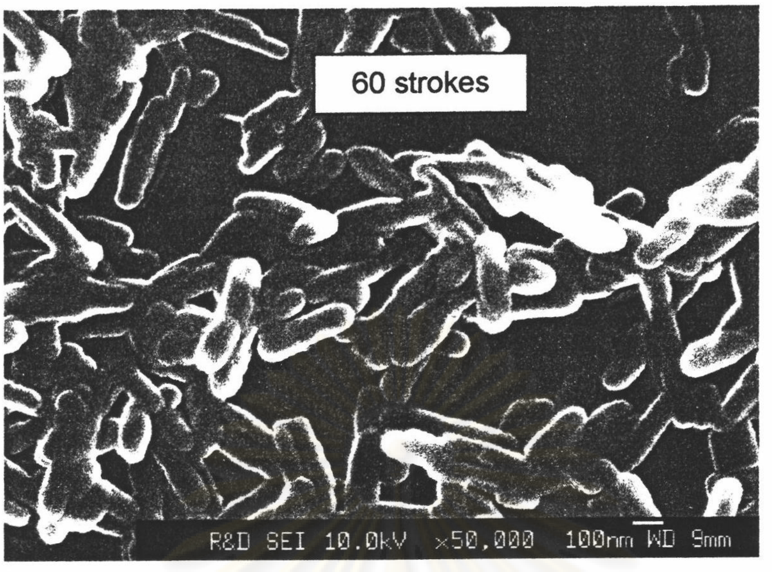
At 60 strokes testing, the prepared base greases mixed with 2 % additives (ZDDP, MDTC and DPA) were found to be softer than the base grease without additive. However the penetration of the prepared greases were still in a satifactory range NLGI#3 (penetration number 220-250).

At 10,000 strokes, the work stability of the prepared greases were studied. Results of the penetration changes, tested at 60 and 10,000 strokes, of the TMP-ester grease and the paraffin grease were found to be in range of 8.7-9.2 % and 9.2-9.6 % respectively. Thus the mechanical stability of TMP-ester grease was better than paraffin grease. However, both of the prepared greases and the commercial grease have good mechanical stability compared with ASTM D-217 (within $\pm$15 % change in penetration)

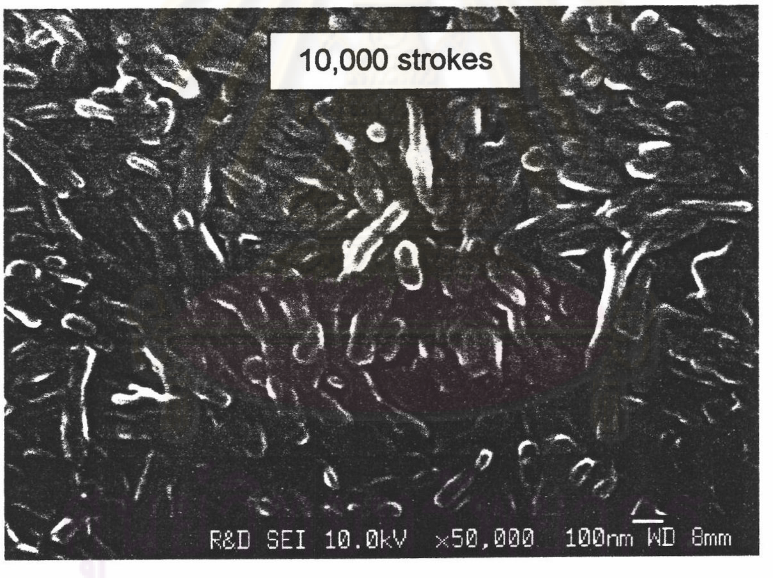
Structure of lithium soap by scanning electron microscopy (SEM)

The scanning electron microscopy was used to observe the fiber structure of the grease. The fiber structure depends on the thickener type **[17]**. For example, lithium 12-hydroxy stearate grease contains longer, visible twisted and well-tangled fibers. Lithium stearate grease contains smooth and straight fibers. The fiber size of lithium stearate is 0.2 μm or less in width and 0.5 to 20 μm in length.

From SEM data of prepared grease as shown in Figure 4.1, the shape of lithium stearate was found to exhibit a short fiber 0.1 μm in width and 0.5 μm in length. After the grease was worked from 60 to 10,000 strokes, the grease was softer than original, and electron microscopic results showed that the fibers of soap were smaller than the original fiber. Thus, a change of soap fibers to be smaller after working on heavy duty may be an important factor affecting penetration change.



Fiber structures before work stability test (60 strokes)



Fiber structures after worked stability test (10,000 strokes)

Figure 4.1 Fiber structures of lithium stearate before and after worked stability test (magnification 50,000).

4.5 Heat resistance of grease

Heat resistance of greases was evaluated by measurement of dropping point, evaporation loss and oil separation.

4.5.1 Dropping point of grease

Dropping point is the temperature at which grease changed from a semisolid state to a liquid state. This may due to either actual liquefaction of the thickener or to bleeding of oil. Dropping points of prepared greases were summarized in Table 4.5 (Appendix 5).

Table 4.5 Dropping point of grease with 2 % additive

Dropping point of grease (°C)					Commercial grease
Grease from	No additive	ZDDP	MDTC	DPA	
TMP-ester oil	197	197	197	196	195
Paraffin oil	195	195	196	196	

The dropping points of all greases were higher than the minimum (175 °C) dropping point of JIS K-2220 specification. In addition, the dropping points of the prepared greases were found to be similar to that of the commercial grease.

4.5.2 Evaporation loss of grease

In lubricating field, operations grease is exposed to long periods and temperature rises. It is important to avoid using the harden grease if oils are lost by evaporation. Normally, the smaller the evaporation loss, the better the grease is obtained.

The evaporation test (ASTM D-2595) was used to determine the loss of volatile materials from grease after run at 99 °C for 22 hours. The results are shown in Table 4.6 (Appendix 6).

Table 4.6 Evaporation loss of grease with 2 % additive

Evaporation loss (%)					Commercial grease
Grease from	No additive	ZDDP	MDTC	DPA	
TMP-ester oil	1.25	1.19	1.22	1.23	1.20
Paraffin oil	1.10	1.11	1.09	1.10	

All prepared greases were found to have evaporation loss in a range of 1.09 % to 1.25 %. For paraffin greases, evaporation loss was lower than both TMP-ester greases and commercial grease. According to JIS specification, the evaporation loss must be less than 2 %. Therefore, prepared TMP-ester greases and paraffin greases have good thermal stability.

4.5.3 Oil separated from grease

Oil separation test is useful to determine the stability of grease, especially for long-term storage. The test was run at 100 °C for 24 hours through a 60-mesh screen. The results are shown in Table 4.7 (Appendix 7).

Table 4.7 Oil separation of grease with 2% additive

Oil separation (%)					Commercial grease
Grease from	No additive	ZDDP	MDTC	DPA	
TMP-ester oil	3.32	3.31	3.32	3.29	3.29
Paraffin oil	3.29	3.28	3.25	3.26	

The amount of oil separated for prepared greases was in a range of 3.25 to 3.32 %, whereas that of commercial grease was 3.29 %. According to JIS specification, the amount of oil separated from grease must not exceed 5%.

Normally, the bleeding of oil will affect the lubrication properties of the grease, and also the consistency of grease. If % oil separation is higher than 5 %, the tendency of noise and vibration in bearing will increase and cause contaminated to other area on a spindle motor.

4.6 Corrosion resistance of grease

Corrosion resistances of grease were evaluated by measurement of copper corrosion test and corrosion preventive property test.

4.6.1 Copper corrosion test

According to JIS K2220-5.5 and ASTM D-4048, the tendency of the grease product to corrode copper metal was measured, and the color of copper metal after testing was observed and graded using Appendix 8.

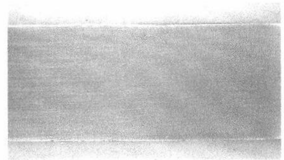
The results are summarized in Figure 4.4 and Table 4.8. It was found that the color of copper after copper corrosion test of the grease with 2% DPA and without additive and commercial grease were slightly tarnished with grade 1b. The copper metal was moderately tarnished (grades 2a to 2b) by grease with 2% MDTC and 2% ZDDP. At the test condition, the color of copper metal with uncoated grease was dark tarnished with grade 3b (dark tarnish is the first stage of rusting).

It is known that organo sulfur and phosphorus compounds possess a corrosive tendency toward copper metal. Thus, the grease containing ZDDP or MDTC tends to increase the copper corrosion.

Table 4.8 Grade of corrosion on copper from grease with 2% additive

Grade of corrosion on copper					Commercial grease
Grease from	No additive	ZDDP	MDTC	DPA	
TMP-ester oil	1b	2b	2a	1b	1b
Paraffin oil	1b	2b	2a	1b	

No grease
color = 3b



Commercial grease
color = 1b

TMP grease without additive
color = 1b

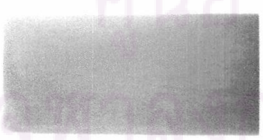
TMP grease with 2 % DPA
color = 1b

TMP grease with 2 % ZDDP
color = 2b

TMP grease with 2 % MDTC
color = 2a

Paraffin grease without additive
color = 1b

Paraffin grease with 2 % DPA
color = 1b



Paraffin grease with 2 % ZDDP
color = 2b

Paraffin grease with 2 % MDTC
color = 2a

Figure 4.2 The color of copper metal after copper corrosion test.

4.6.2 Corrosion preventive property test

The corrosion resistance property of the grease was measured by ASTM D-4048. In this test, two types of base grease with three types of additives were applied in bearing then spun for 1 minute at 1,750 rpm. The bearing was stored in a closed container with water for 48 hours at 52 ^{o}C. After cleaning, the bearing was observed for evidences of corrosion using a microscope.

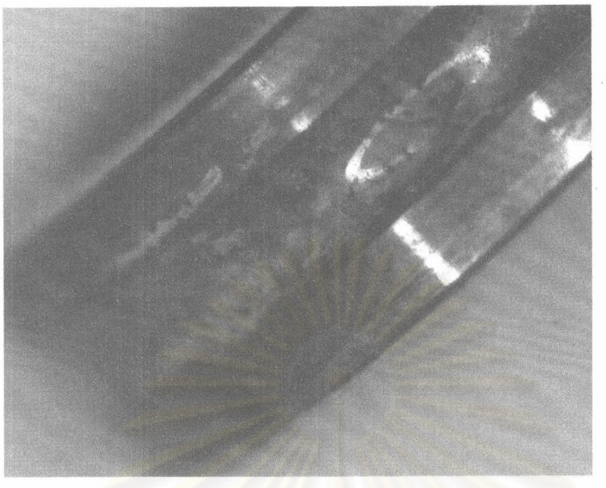
The corrosion were determined in three rating numbers; 1, 2, and 3 refer to corrosion free, maximum of 3 spots, and more than 3 spots, respectively.

The corrosion preventive property of all greases was investigated, and the results are shown in Table 4.9 and Figure 4.5. The bearings were not corroded (rating number 1) by all types of the prepared and commercial grease.

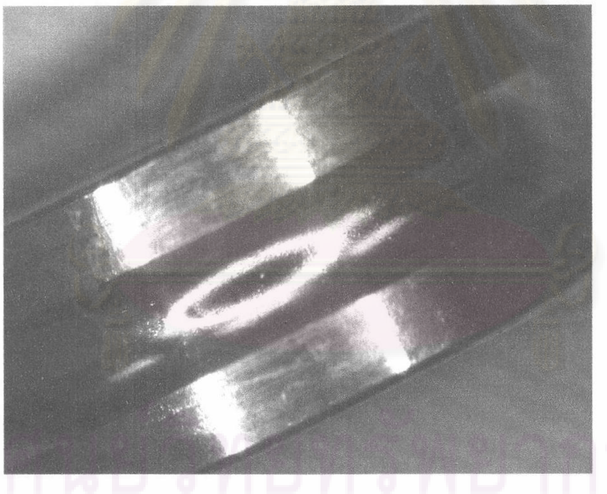
This indicated that the prepared and commercial grease could protect corrosion, but bearing without grease showed a line of corrosion (rating number 3).

Table 4.9 Grade of corrosion on bearing from grease with 2% additive

Grade of corrosion on bearing					Commercial grease
Grease from	No additive	ZDDP	MDTC	DPA	
TMP-ester oil	1	1	1	1	1
Paraffin oil	1	1	1	1	



Inner ring of bearing without lithium grease



Inner ring of bearing with lithium-TMP ester grease or
lithium-paraffin grease (with 2 % ZDDP or MDTC or DPA)

Figure 4.3 Inner ring of bearing after corrosion preventive property test.

4.7 Volatile organic compound of grease

The high-speed bearing was designed for a spindle motor (rotation speed more than 5,000 rpm). At bearing operating temperature (maximum 85 °C), the volatile materials will be limited, and must be determined. The volatile organic compounds or outgas of grease were measured by GC/MS using a dynamic headspace technique **[29-30]**. This method was applied at maximum temperature of computer condition (85 °C).

The total amount of outgases released from grease were calculated based on peak area of hexadecane as standard (Appendix 9). Chromatograms of outgas from TMP grease, paraffin grease and commercial grease are shown in Appendices A10-A12. From mass spectrum, the volatile compounds from paraffin grease are hydrocarbons (C_{10}-C_{25}) and benzene derivatives. The volatile compound from TMP-ester grease and commercial grease are hydrocarbons (C_{10}-C_{20}) and ester compounds.

Total outgas of grease is shown in Table 4.10. Paraffin grease released outgas lower than TMP-ester grease and commercial grease. All types of grease released outgas lower than the critical limit (20,000 ng/mg) for Hard Disk Drive (HDD). It was clear that when all types of grease were applied in a spindle motor, it released the fewer amounts of volatile materials at maximum operating temperature. Thus it is not enough to make striction between disk head and disk medium of a HDD's computer.

Table 4.10 Total volatile organic compounds of grease with 2 % additive

Total volatile compounds (ng/mg of grease)				Commercial grease
Grease from	No additive	ZDDP	MDTC	
TMP-ester oil	6,813	6,737	6,854	5,833
Paraffin oil	4,513	4,280	4,341	

4.8 Characterization of additive in commercial grease

Additive in commercial grease was characterized by FT-IR and XRF. The interpretation of results from these techniques can identify the functional group and composition of additives. The FT-IR spectrum of commercial grease (Appendix 15) showed the functional group of C-H stretching at 2,920 cm^{-1}, C-H bending at 1,450 and 1377 cm^{-1}, C-P at 815 and 720 cm^{-1}, P=S at 560 cm^{-1} and P-S at 512 cm^{-1}. It was found to be similar to those of the grease prepared with 2% ZDDP.

The elemental composition in commercial grease was measured by XRF (Appendices 16-17). From XRF spectrum, the commercial grease was found to contain 0.49 % zinc , 0.59 % phosphorus and 1.21 % sulfur. While the grease prepared with 2% ZDDP contained 0.34 % zinc, 0.43 %phosphorus and 0.85 % sulfur.

Therefore, the additive in commercial grease is ZDDP and the amount of ZDDP in commercial grease is more than 2 %.