CHAPTER III

EXPERIMENTAL AND RESULTS

3.1 Synthetic Lubricant Materials.

Commercial Synthetic Lubricants were obtained from

Exxon (trade name Ultron)

Shell (trade name TMO)

BP (trade name BP)

Castrol (trade name Castrol)

Mobil (trade name Mobil)

3.2 Instrument and Equipments.

3.2.1 Rotatory Evaporator

Eyela type N-N rotary evaporator was used for the rapid removal of large amounts of volatile solvents.

3.2.2 Fourier Transform-Infrared Spectrophotometer (FT-IR)

The FT-IR spectra were recorded on a Perkin-Elmer Model 1760X Fourier Transform-Infrared Spectrophotometer.

3.2.3 ^{1}H- and ^{13}C-Nuclear Magnetic Resonance Spectrometer

The ^{1}H-NMR and ^{13}C-NMR spectra were obtained by using a Bruker Model ACF 200 Spectrometer operated at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C-nuclei. The chemical shift in (ppm.) was assigned with reference to the signal from the residual proton in deuterated solvent. Accordingly, the signal due to deuterated chloroform was assigned to be 7.24 ppm. with the reference to TMS.

3.2.4 GC-MS Spectrometer

The gas chromatogram and mass spectra were obtained by a Fisons Instruments GC-MS Spectrometer Model Trio 2000.

3.2.5 GPC- Evaporative Mass Chromatography

The GPC chromatogram were detected by Evaporative Mass Detector (EMD).

3.3 Chemical Reagents.

3.3.1 Solvents

All solvents used in this research were purified prior to use by distillation, except solvents that were reagent grade.

3.3.2 Merck silica gel

Merck silica gel 60 Art. 7734.1000 (70-230 mesh ASTM) was used as the adsorbent for column chromatography.

3.3.3 Merck's TLC silica gel

Merck TLC silica gel 60 F254 pre-coated 25 sheet, 20x20 $cm.^2$, layer 0.2 mm., was used for identifying the identical fractions.

3.4 Physical Separation techniques

3.4.1 Column Chromatography (CC)

Column Chromatography was performed as in reference 24.

3.4.2 Thin-Layer Chromatography (TLC)

Thin-Layer Chromatography was performed as in reference 30.

3.5 Extraction

Additives in synthetic lubricant (100.0g) were extracted with 150 ml of methanol for 1 day at room temperature for 3 times. After separation and evaporation of the solvent under reduced pressured, Crude MeOH extract was obtained.

Extraction obtained from this procedure were presented in Table 3.5.1

Table 3.5.1 Crude MeOH extract from MeOH extraction of Synthetic Lubricants

Lubricant	Weight (g)	Crude MeOH extract (g)	%
Exxon	101.92	5.40 (dark green oil)	5.3
Shell	98.90	5.83 (dark green oil)	5.9
BP	100.25	5.41 (brown oil)	5.4
Castrol	100.65	5.73 (brown oil)	5.7
Mobil	99.73	6.18 (brown oil)	6.2

3.6 Isolation of Chemical Constituents of Additives in Synthetic Lubricant.

Column chromatography was use for separating additives in methanol crude extract in to fractions.

The column (50 $cm.^3$) was eluted with hexane, hexane-chloroform, chloroform, chloroform-methanol, and methanol respectively.

After the eluent was collected (approximately 10 ml for each fraction) it was concentrated by rotary evaporator. Each fraction was monitored by thin-layer chromatography and the identical fractions were combined.

3.6.1 Separation of Base oil in Crude MeOH of Synthetic Lubricant.

Crude MeOH of synthetic lubricant was eluted with hexane to separate base oil in Crude MeOH.

The results of separation base oil in crude MeOH are presented in Table 3.6.1.

Table 3.6.1 The results of separation of base oil in crude MeOH extract of synthetic lubricant

Lubricant	Crude MeOH (g)	Base Oil in Crude MeOH (g)
Exxon	5.20	0.48 (ULT1)
Shell	5.80	0.52 (TMO1)
BP	5.38	0.15 (BP1)
Castrol	5.70	0.52 (CAS1)
Mobil	6.00	0.84 (MOB1)

3.6.2 Isolation of Antioxidants from Crude MeOH extract of Synthetic Lubricant.

Crude MeOH extract of synthetic lubricant was eluted with hexane to separate base oil which could interfere with the chromatographic identification, and washed with hexane-chloroform to desorb antioxidants.

Exxon

The results of isolation of antioxidants from the crude MeOH extract (5.20 g) are presented in Table 3.6.2.1.

Table 3.6.2.1 The results of isolation antioxidants from crude MeOH extract

Eluent	Fraction No.	Remark
100% hexane	1-6	colorless oil
5% $CHCl_3$-hexane	7-9	colorless oil
	10-13	yellow oil (ULT2, 0.70g)

Shell

The results of isolation of antioxidants in crude MeOH extract (5.80 g) are presented in Table 3.6.2.2.

Table 3.6.2.2 The results of isolation of antioxidants from crude MeOH extract

Eluent	Fraction No.	Remark
100% hexane	1-6	-
	7-13	colorless oil
5% $CHCl_3$-hexane	14-21	yellow oil
	22-29	red-brown oil (TMO2, 0.79g)
	30-33	yellow oil

BP

The results of isolation of antioxidants from crude MeOH (5.38 g) are presented in Table 3.6.2.3.

Table 3.6.2.3 The results of isolation antioxidant from crude MeOH extract

Eluent	Fraction No.	Remark
100%hexane	1-6	-
	7-13	colorless
5% $CHCl_3$-hexane	14-21	yellow oil
	22-29	yellow oil (BP2, 0.73g)
	30-37	yellow oil

Castrol

The results of isolation of antioxidant from crude MeOH (5.70 g) are presented in Table 3.6.2.4

Table 3.6.2.4 The results of isolation of antioxidant from crude MeOH extract

Eluent	Fraction No.	Remark
100%hexane	1-6	-
	7-13	colorless
5% $CHCl_3$-hexane	14-21	yellow oil
	22-29	yellow oil (CAS2, 0.78 g)
	30-37	yellow oil

Mobil

The results of isolation of antioxidant from crude MeOH (6.00 g) are presented in Table 3.6.2.5

Table 3.6.2.5 The results of isolation of antioxidant from crude MeOH extract

Eluent	Fraction No	Remark
100% hexane	1-6	
	7-13	colorless oil
	14-21	yellow oil
	22-29	yellow oil
	30-33	yellow oil

Table 3.6.2.5 (Continued)

Eluent	Fraction No	Remark
5% $CHCl_3$-hexane	34-41	yellow oil
	42-48	yellow oil
10% $CHCl_3$-hexane	49-54	yellow oil (MOB2, 1.94 g)
	55-60	yellow oil

The results of separation of antioxidant from crude MeOH of synthetic lubricants are summarized in Table 3.6.2.

Table 3.6.2 The results of separation of antioxidants from crude MeOH of synthetic lubricants

Lubricant	Crude MeOH (g)	Antioxidant in Crude MeOH (g)
Exxon	5.20	0.70 (ULT2)
Shell	5.80	0.79 (TMO2)
BP	5.38	0.73 (BP2)
Castrol	5.70	0.78 (CAS2)
Mobil	6.00	1.94 (MOB2)

3.6.3 Isolation Dispersant and Antiwear in Crude MeOH extract of Synthetic Lubricant

Crude MeOH extract of synthetic lubricants were eluted with hexane to separate base oil, washed with 5%chloroform-hexane to separate antioxidants which could interfere with the chromatographic identification, and washed with chloroform-hexane, to isolate dispersant or antiwear agent.

Exxon

The results of separation of additives from crude MeOH extract (5.20 g) are presented in Table 3.6.3.1.

Table 3.6.3.1 The results of isolation of additives from crude MeOH extract

Eluent	Fraction No	Remark
100% hexane	1-6	colorless oil
5% $CHCl_3$-hexane	7-9	colorless oil
	10-13	yellow oil
10% $CHCl_3$-hexane	14-16	yellow oil
	17-22	yellowish-green oil (ULT3, 0.55g)
20% $CHCl_3$-hexane	23-29	yellow oil

Table 3.6.3.1 (Continued)

Eluent	Fraction No	Remark
	30-36	red brown oil (ULT4, 0.54g)
50% $CHCl_3$-hexane	37-39	yellow oil
60% $CHCl_3$-hexane	40-46	yellow oil
70% $CHCl_3$-hexane	47-53	yellow oil
80% $CHCl_3$-hexane	54-60	yellow oil

Shell

The results of separation additives in crude MeOH (5.80 g) are presented in Table 3.6.3.2.

Table 3.6.3.2 The results of isolation additives from crude MeOH extract

Eluent	Fraction No	Remark
100% hexane	1-6	-
	7-13	colorless oil
5% $CHCl_3$-hexane	14-21	yellow oil
	22-29	red-brown oil
	30-33	yellow oil

Table 3.6.3.2 (Continued)

Eluent	Fraction No	Remark
10% $CHCl_3$-hexane	34-41	yellow oil (TMO3, 0.68g)
	42-48	yellow oil
20% $CHCl_3$-hexane	49-54	yellow oil
30% $CHCl_3$-hexane	55-60	yellow oil
40% $CHCl_3$-hexane	61-67	yellow oil
100% $CHCl_3$	68-74	yellow oil

BP

The results of separation of additives from crude MeOH (5.38 g) are presented in Table 3.6.3.3.

Table 3.6.3.3 The results of isolation of additives from crude MeOH extract

Eluent	Fraction No.	Remark
100%hexane	1-6	-
	7-13	colorless
10% $CHCl_3$-hexane	14-21	yellow oil
	22-29	yellow oil

Table 3.6.3.3 (Continued)

Eluent	Fraction No.	Remark
20%$CHCl_3$-hexane	30-37	yellow oil
	38-45	yellow oil (BP3, 0.67g)
30%CHCl-$_3$hexane	46-53	yellow oil
40%CHCl-$_3$hexane	54-61	blue oil (BP4, 0.49g)
100%$CHCl_3$	62-69	yellow oil

Castrol

The results of separation of additives from crude MeOH (5.70 g) are presented in Table 3.6.3.4

Table 3.6.3.4 The results of isolation additives from crude MeOH extract

Eluent	Fraction No.	Remark
100%hexane	1-6	-
	7-13	colorless
10% $CHCl_3$-hexane	14-21	yellow oil
	22-29	yellow oil
20%$CHCl_3$-hexane	30-37	yellow oil

Table 3.6.3.4 (Continued)

Eluent	Fraction No.	Remark
	38-45	yellow oil (CAS3, 0.65 g)
30%$CHCl_3$hexane	46-53	yellow oil
40%$CHCl_3$-hexane	54-61	blue oil (CAS4, 0.61 g)
100%$CHCl_3$	62-69	blue oil

Mobil

The results of separation of additives from crude MeOH (6.00 g) are presented in Table 3.6.3.5

Table 3.6.3.5 The results of isolation of additives from crude MeOH extract

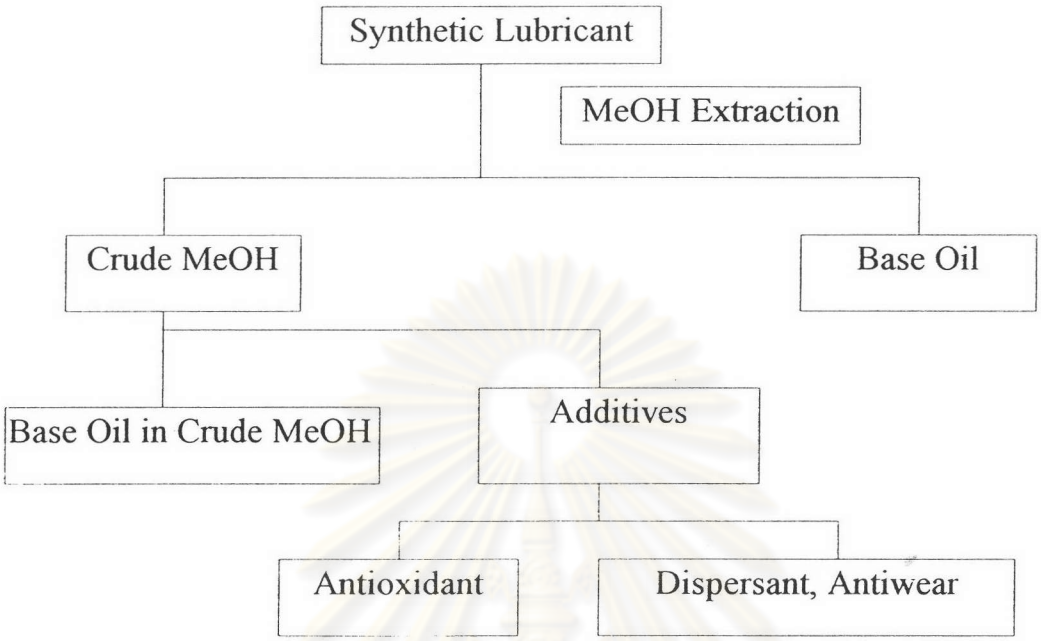
Eluent	Fraction No.	Remark
100% $CHCl_3$	1-6	yellow oil
10% MeOH-$CHCl_3$	7-13	yellow oil
	14-21	yellow oil
20% MeOH-$CHCl_3$	22-29	brown oil (MOB3, 3.15g)
30% MeOH-$CHCl_3$	30-36	yellow oil
40% MeOH-$CHCl_3$	37-44	yellow oil

The results of separation additives in crude MeOH of synthetic lubricant are summarizes in Table 3.6.3.

Table 3.6.3 The results of separation of additives from in crude MeOH extract of synthetic lubricants

Lubricant	Crude MeOH (g)	Additives in Crude MeOH (g)
Exxon	5.20	0.55 (ULT3) 0.54 (ULT4)
Shell	5.80	0.68 (TMO3)
BP	5.38	0.67 (BP3) 0.49 (BP4)
Castrol	5.70	0.65 (CAS3) 0.61 (CAS4)
Mobil	6.00	3.15 (MOB3)

The procedure of isolation chemical constituent of additives in synthetic lubricant is shown in Scheme 3.6.1



Scheme 3.6.1

3.7 Analyzing Molecular Weight of Base Oil in Synthetic Lubricant

Molecular weight of base oil in synthetic lubricant were analyzed by GPC-Evaporative Mass Detector (EMD).

The condition of GPC were as follow

Column 3 *u*m Mixed-E. 300x7.5mm

Solvent THF

Flow Rate 1.00 ml/min

In this study, the molecular weight (M_w) of polystyrene were varied from 500, 1050, 2630 and 5790. The log(M_w) of polystyrene comparing with retention volume (Vt.) were shown in Table 3.7.1 and Fig. 3.7.1

Table 3.7.1 The log(M_w) of polystyrene compared with retention volume (Vt)

M_w	log(M_w)	Vt 1 (ml)	Vt 2 (ml)	Average Vt (ml)
500	2.69897	7.890	7.876	7.883
1050	3.021189	7.488	7.479	7.483
2630	3.419956	6.851	6.832	6.841
5790	3.762679	6.168	6.157	6.162

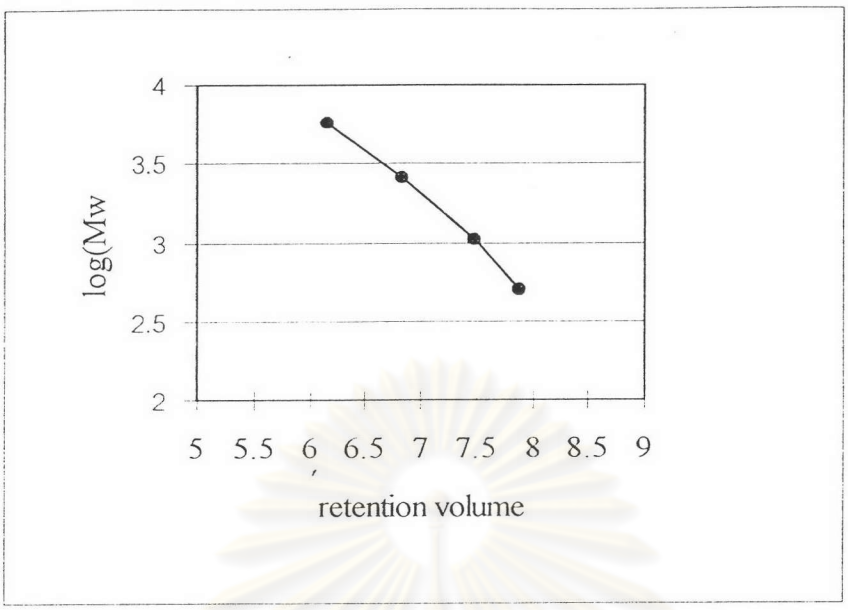


Figure 3.7.1 The calibration curve of log(M_w) versus retention volume

The retention volume of base oil in synthetic lubricants are shown in Table 3.7.2

Table 3.7.2 The retention volume of base oil in synthetic lubricant

Synthetic Lubricant	Vt. 1 (ml)	Vt. 2 (ml)	Average Vt. (ml)
Exxon	7.605	7.600	7.603
Shell	7.520	7.513	7.517
BP	7.712	7.708	7.710
Castrol	7.763	7.760	7.762

Table 3.7.2 (Continued)

Synthetic Lubricant	Vt. 1 (ml)	Vt. 2 (ml)	Average Vt. (ml)
Mobil	7.609	7.609	7.609

The calibration curve is given by the formula.

$$Y = (-0.61)X+7.56$$

where Y is log (M_w)

X is retention volume

The molecular weight of base oils in synthetic lubricants are shown in Table 3.7.3

Table 3.7.3 The molecular weight of base oil in synthetic lubricants

Synthetic Lubricant	Molecular Weight of Base Oil
Exxon	831
Shell	933
BP	707
Castrol	660
Mobil	812