

CHAPTER III

EXPERIMENTAL

3.1 General information

3.1.1 Instrumentals

- NMR
- IR
- Friction & wear test machine; Model Falex Timken
- Pour point analyzer; Herzog
- Flash point analyzer; Stanhope-Seta
- Optifix titrier 50/0.01 millitre.
- Viscosity bath
- Viscometer
- Vacuum pump

3.1.2 Materials

Palm oil	LUM SOON
Powdered sulfur	Aldrich
Silicone oil	Aldrich
Nitrogen gas	Thai Industrial Gas
Air	Thai Industrial Gas
Base oils	ShellCo. (Thailand)

- Oil A: "HVI 60," viscosity 4.7 cSt.
at 100 °C, viscosity index (VI) 100
- Oil B: "HVI 160B," viscosity 10.8 cSt.
at 100 °C, viscosity index (VI) 97
- Oil C: "HVI 650," viscosity 31.5 cSt.
at 100 °C, viscosity index (VI) 95

The above base oils, A, B, and C, are typically commercial paraffinic base oil refined from crude oil for use as a blending component of lubricating oil and greases.

3.1.3 Test methods

Sulfur content	IP 242
Timken load extreme pressure	ASTM D-2782
Viscosity, Kinematic	ASTM D-445
Viscosity index	ASTM D-2270
Pour point	ASTM D-97
Flash point	ASTM D-93
Copper corrosion	ASTM D-130
Solubility	

3.2 Procedure

3.2.1 Synthesis of sulfurized plam oil

3.2.1.1 Typical sulfurization

Palm oil was charged in to a 500 ml round bottom 3-neck flask equipped with mechanical stirrer and heated to 150 °C for 5 minutes under light nitrogen blanket. Powdered sulfur was added slowly for 10 minutes with constant stirring. In the course of the next 30 minutes, the temperature was raised and held at $200 \pm 2^\circ\text{C}$ for 2 hrs. There action mixture was cooled to about $150 \pm 2^\circ\text{C}$. Then air was blown through the reaction mixture for 5 hrs. to purge any volatile sulfur-containing compounds. Some H_2S was evolved. At the end of the air blowing period, lead acetate paper gave a negative test on the outgoing air. After the final step, the product was allowed to stand for 3 days at room temperature, and filtered with suction through Whatman #1 paper to remove unreacted sulfur. The final product of the reaction was a mobile, dark reddish brown oil.

3.2.1.2 Variation of reaction temperature

190 g. of palm oil and 10 g. of powdered sulfur were added into reaction flask. While the reaction time was constant for 2 hrs., the reaction temperatures were varied at 160, 180, 200 and 220 °C. The final product should have 5 % by weight of total sulfur.

3.2.1.3 Variation of reaction time

190 g of palm oil and 10 g of powdered sulfur were added into a reaction flask. The reaction times were changed from 2, 4, 8 and 10 hrs, while the reaction temperature was constant at 200 °C and the final product should have 5 % by weight of total sulfur.

3.2.1.4 Variation of sulfur concentration

The reaction was carried out with various concentration of sulfur from 3-25 % by weight in palm oil. In each reaction, reaction temperature and reaction time were constant at 200 °C and 2 hrs, respectively.

3.3 Characterization of palm oil and sulfurized palm oil

3.3.1 Nuclear magnetic resonance (NMR) measurement

The ^1H -NMR spectra of palm oil and sulfurized palm oil were taken by using Fourier transform NMR spectrometer, Bruker ACF200. The samples were dissolved in CDCl_3 to make the solution of 5 % concentration.

3.4 Analysis of physical properties of sulfurized palm oil

3.4.1 sulfur content (IP 242)

Sulfur content of products was determined using a flask combustion method. The sample, absorbed on a filter paper, was rapidly and completely burnt in a closed flask filled with oxygen at atmospheric pressure. The combustion products were absorbed in a hydrogen peroxide solution and the amount of sulfuric acid formed was determined by titration with standard barium perchlorate solution, using thordin as an indicator. The total sulfur content of the sample was calculated by means of the following equation

$$\text{sulfur, \% w} = \frac{(V-v) \times N \times 1603}{W}$$

W

where V = volume of barium perchlorate solution used for sample titration

v = volume of barium perchlorate solution

used for blank titration

N = normality of the barium perchlorate solution

W = weight of sample in milligrams

3.4.2 Viscosity, kinematic (ASTM D-445)

See the Appendix section for the viscosity determination.

3.4.3 Solubility tests

Solubilities of sulfurized products in base oils were evaluated by stirring to dissolve at 40-45 °C, followed by storing 24 hrs at room temperature (RT), 16 hrs at 4 °C, and then again at RT for 24 hrs.

3.5 Analysis of physical properties of sulfurized palm oil in base oils

3.5.1 Timken load extreme pressure (ASTM D-2782)

A modification procedure was used in a test using additives in oils by operating a lubricated test ring rotating against a loaded stationary test block. Test speed was 800 rpm. The temperatures were ranged from 28-35 °C. After a 2-min warm up at 50 lbs

load, the load was allowed to walk up to failure, but on the way up was held constant for 1 min at each increment of 10 lbs.

3.5.1.1 Variation of concentration of sulfurized palm oil in base oil A

The sulfurized palm oil additive no. S₃ was added in various concentration from 0, 1.5, 3, 15 and 30 g., while the volume of base oil A was constant at 3 litres. The fail load of the samples was measured.

3.5.1.2 Variation of viscosity of base oils

The sulfurized palm oil additive no. S₃, with 3 different concentrations, was added into various types of base oils having different viscosities as detailed in Table 3.1. In each sample, the volume of each base oil was constant at 3 litres. The fail load was measured.

Table 3.1 EP Properties of sulfurized palm oil with various viscosity of base oil.

Sample No.	amount of SPO in base oil (g)	viscosity of base oil (cts)
EP ₁	0.0	A
EP ₂	1.5	A
EP ₄	15.0	A
EP ₆	0.0	B
EP ₇	1.5	B
EP ₈	15.0	B
EP ₉	0.0	C
EP ₁₀	1.5	C
EP ₁₁	15.0	C

3.5.1.3 Variation of concentration of sulfurized palm oil.

The various additives were added in 3 litres of base oil A, as detailed in Table 3.2.

Table 3.2 EP Properties of sulfurized palm oil with various concentration of sulfurized palm oil

sample no.	concentration of SPO (% by weight)	amount of SPO in base oil (g)
EP ₁	0	0
EP ₁₂	6.8	1.5
EP ₂	10.87	1.5
EP ₁₃	12.14	1.5
EP ₁₄	15.07	1.5

3.5.2 Copper corrosion

A polished copper strip is immersed in a given quantity of sample and heated at a temperature and for a certain time of characteristics of the material being tested. After the end of this period the copper strip is removed, washed, and compared with the ASTM copper strip corrosion standards.

3.5.2.1 Variation of concentration of sulfurized palm oil.

The sulfurized palm oil additive no. S₁₃ was added in various concentration from 0.05, 0.5, 1.0, 5.0 %w in base oil A. This test method was heated at 100 °C for 2 hrs. and compared with the ASTM copper strip corrosion standards.

3.5.3 Viscosity, kinematic

See the Appendix for the testing of viscosity.

3.5.4 Flash point

See the Appendix for the determination of flash point.

3.5.5 Pour point

See the Appendix for the determination of pour point.

