

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals used in this research were the analytical reagent grades. They were obtained from Fluka : methylsalicylate, chloronitroanilines, ethylene glycol, n-hexane, salicylic acid, methylamine, diisopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine, 1-hexanol, 1-octanol, methanol and ammonium hydroxide; from BDH : sodium nitrite, sodium bicarbonate, sodium sulfate anhydrous, concentrated hydrochloric acid, concentrated sulfuric acid and potassium hydroxide; from Merck : ferric chloride. The cashew nut shells were obtained from Phuket province.

3.2 Apparatus

The IR absorption spectra were obtained with FT-IR spectrophotometer (model 2000 series, Perkin Elmer) using KBr cell. The NMR spectra were recorded in CDCl_3 solution on a Bruker spectrometer (model ACF 200) operated at 300 MHz for ^1H -NMR and 75 MHz for ^{13}C -NMR. The quantitative determinations were determined by UV-VIS spectrometer (Model Lamda-2, Perkin Elmer). The physical properties of diesel oil were tested following ASTM test methods.

3.3 The experimental procedures

3.3.1 Esters

A) Methylsalicylate from Fluka

B) Octylsalicylate

Esterification of salicylic acid :

Salicylic acid (0.01 mole, 13.81 g.), excess 1-octanol (24 ml.) and toluene were placed in 250 ml. round-bottomed flask. The concentrated sulfuric acid (2 ml.) was added into the flask. The mixture was stirred continuously. A Dean-Stark trap, a condenser, and a water trap were fitted, respectively. This mixture was refluxed for 24 hours in an oil bath. Then the temperature of the mixture was cooled down. This solution was poured into a separatory funnel containing 75 ml. of water and shake it vigorously. The aqueous layer was removed. The organic layer was rinsed with 75 ml. of water and saturated sodium bicarbonate solution to remove the remaining acid until the solution was neutral. Then the organic layer was filtered into a dry distilling flask. A few boiling chips were added. The remaining water and toluene were distilled off.

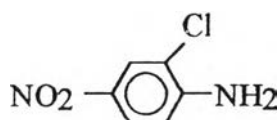
C) Esterification of cashew nut shell liquid

The cashew nut shells were removed from dust and crushed into small pieces. n-Hexane was added to extract the cashew nut shell liquid and then distilled off to recover it. The cashew nut shell extract (0.1 mole, about 34.00 g.), excess 1-hexanol (20 ml.) and toluene were placed in a 250 ml.

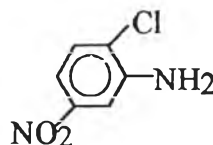
Erlenmeyer flask. Concentrated sulfuric acid (3ml.) was added into the flask. Stirring was continued with refluxing for ten hours in an oil bath. The mixture was cooled down and poured into a separatory funnel containing 75 ml. of water. It was shaken gently and the aqueous layer was removed. The organic layer was rinsed with 75 ml. of water to remove the remaining acid until the solution was neutral. It was filtered into a dry distilling flask. A few boiling chips were added and the remaining water and toluene were distilled off.

3.3.2 Preparation of diazonium salts of chloronitroaniline derivatives

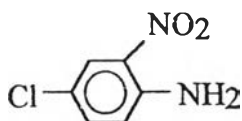
The chloronitroaniline derivatives use in this research are listed below :



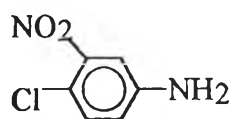
2-chloro-4-nitroaniline



2-chloro-5-nitroaniline



4-chloro-2-nitroaniline



4-chloro-3-nitroaniline

The concentrated hydrochloric acid (3 ml), crushed ice (10 g.) and a magnetic bar were added into a 50 ml. Erlenmeyer flask. Then, 2-chloro-4-nitroanilines (0.01 mole, 1.73 g.) were gradually added to obtain the paste form and 1 N. NaNO_2 (20 ml.) was slowly dropped into the mixture. Stirring was continued for 20 minutes. The mixture was kept cold until it was clear solution. Then it was filtered to remove the remaining traces of nitrite. The diazonium salt solution was kept lower 5°C .

These procedures were used for 2-chloro-5-nitroaniline, 4-chloro-2-nitroaniline and 4-chloro-3-nitroaniline, as well.

3.3.3 Preparation of phenolate ion of the esters

A) The phenolate ion of methylsalicylate (ester A) :

Potassium hydroxide (1.12 g.) was dissolved in methanol (10 ml.). This solution was kept cold and gradually dropped into methyl salicylate (0.01 mole, 1.28 ml.). The solution was cooled below 5°C.

B) The phenolate ion of octylsalicylate (ester B) :

Potassium hydroxide (1.12 g.) was dissolved in methanol (10 ml.). This solution was kept cold and gradually dropped into octylsalicylate (0.01 mole, 2.50g.). The solution was cooled below 5°C.

C) The phenolate ion of the esterified CNSL (ester C) :

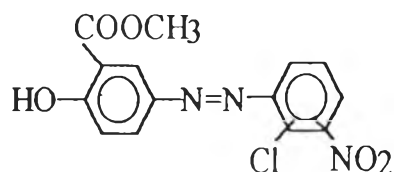
Potassium hydroxide (1.12 g.) was dissolved in methanol (10 ml.). This solution was kept cold and gradually dropped into the esterified CNSL (0.01 mole, about 4.30 g.). The solution was cooled below 5°C.

3.3.4 Coupling reactions

The diazonium salt solutions of chloronitroanilines in Section 3.3.2 were gradually dropped into the solution of phenolate ion of the ester A-C in Section 3.3.3. Continuous stirring should be used and the temperature of the mixtures should not rise above 8°C. After 20 minutes, the product was poured into a separatory funnel and the organic layer was rinsed with water (5 ml.) to remove the remaining acid.

The obtained marker dyes were listed below :

Set A



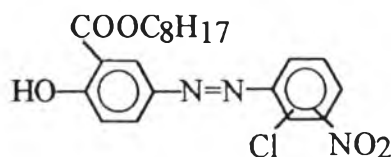
Dye A₁ : The diazonium salt of 2-chloro-4-nitroaniline coupled with the phenolate ion of methylsalicylate.

Dye A₂ : The diazonium salt of 2-chloro-5-nitroaniline coupled with the phenolate ion of methylsalicylate.

Dye A₃ : The diazonium salt of 4-chloro-2-nitroaniline coupled with the phenolate ion of methylsalicylate.

Dye A₄ : The diazonium salt of 4-chloro-3-nitroaniline coupled with the phenolate ion of methylsalicylate.

Set B



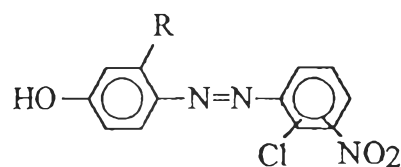
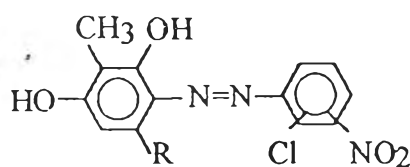
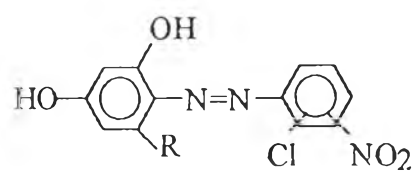
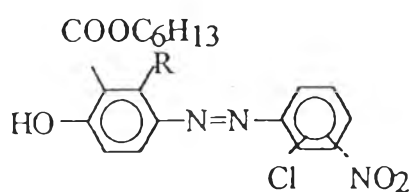
Dye B₁ : The diazonium salt of 2-chloro-4-nitroaniline coupled with the phenolate ion of octylsalicylate.

Dye B₂ : The diazonium salt of 2-chloro-5-nitroaniline coupled with the phenolate ion of octylsalicylate.

Dye B₃ : The diazonium salt of 4-chloro-2-nitroaniline coupled with the phenolate ion of octylsalicylate.

Dye B₄ : The diazonium salt of 4-chloro-3-nitroaniline coupled with the phenolate ion of octylsalicylate.

Set C



Dye C₁ : The diazonium salt of 2-chloro-4-nitroaniline coupled with the phenolate ion of the esterified cashew nut shell liquid.

Dye C₂ : The the diazonium salt of 2-chloro-5-nitroaniline coupled with the phenolate ion of the esterified cashew nut shell liquid.

Dye C₃ : The diazonium salt of 4-chloro-2-nitroaniline coupled with phenolate ion of the esterified cashew nut shell liquid.

Dye C₄ : The diazonium salt of 4-chloro-3-nitroaniline coupled with the phenolate ion of the esterified cashew nut shell liquid.

3.3.5 Acid reduction of the marker dyes

Stannous chloride (about 0.5 g) was dissolved in concentrated hydrochloric acid (1 ml). A small amount of the marker dyes (about 0.1 g) was added and then the solution was heated. A colorless solution should result and no precipitate should form on adding water.

3.3.6 The appropriate solvent extraction systems for the marker dyes in diesel oil

10 ppm of each marker dyes in diesel oil (25ml) were extracted with the various types of solvents (5 ml.) in the list below using the vial glasses, shaken vigorously and allowed to two phase separation. The hue of aqueous phase, the interphase area, the hue of oil phase and the efficiencies of each solvent were observed.

Table 3-1 : The appropriate solvent extraction systems used for the detection procedures

No.	Solvent extraction system
1	5% wt KOH in Methanol
2	10% wt KOH in Methanol
3	5% wt KOH in Ethylene glycol
4	10% wt KOH in Ethylene glycol
5	5% wt KOH in 10% vol. Methanol + 90% vol. Ethylene glycol
6	30% wt Ethylene glycol + 40% vol. Methanol + 30% vol. Methylamine
7	30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Diisopropylamine
8	30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Ethylenediamine
9	30% vol. Ethylene glycol + 40% vol. Methanol + 30% vol. Morpholine
10	2.5% Ferric chloride in methanol
11	2.5% Ferric chloride in ethylene glycol
12	90% vol. Ethylene glycol + 10% vol. Ethylenediamine
13	80% vol. Ethylene glycol + 20% vol. Ethylenediamine
14	70% vol. Ethylene glycol + 30% vol. Ethylenediamine
15	60% vol. Ethylene glycol + 40% vol. Ethylenediamine
16	60% vol. Ethylene glycol + 40% vol. Ammonium hydroxide
17	60% vol. Ethylene glycol + 40% vol. Ethylenediamine
18	60% vol. Ethylene glycol + 40% vol. Diethylenetriamine
19	60% vol. Ethylene glycol + 40% vol. Triethylenetetramine
20	60% vol. Ethylene glycol + 40% vol. Morpholine

3.3.7 Preparation of stock solution marker dyes B₁- B₄

A) Preparation of 1% marker dyes B₁- B₄ in toluene.

The marker dyes B₁- B₄ (0.25 g.) were added into 25 ml. volumetric flask and made up volume with toluene. They were shaken well to obtain good mixing.

B) Preparation of 1000 ppm marker dyes B₁- B₄ in toluene.

The 1 % stock solutions of marker dyes B₁- B₄ (10 ml.) were pipetted into 100 ml. volumetric flask and made up volume with toluene. They were shaken well to ensure good mixing.

C) Preparation of marker dyes B₁- B₄ standard solution in diesel .

The 1000 ppm of marker dyes B₁- B₄ stock solutions in Section 3.3.7 B) were pipetted into 100 ml. volumetric flask following the list below and made up volume with diesel oil.

Standard solution (ppm)	Volume of 100 ppm stock solution (ml.)
3	0.30
5	0.50
7	0.70
9	0.90

3.3.8 Preparation of stock solution marker dyes C₁- C₄.

A) Preparation of 10% marker dyes C₁- C₄ in toluene.

The marker dyes C₁- C₄ (2.50 g.) were added into 25 ml. volumetric flask and made up volume with toluene. They were shaken well to obtain good mixing.

B) Preparation of 1000 ppm marker dyes C₁- C₄ in toluene.

The 10 % stock solution of marker dyes C₁- C₄ (1 ml.) were pipetted into 100 ml. volumetric flask and made up volume with toluene. They were shaken well to ensure good mixing.

C) Preparation of marker dyes C₁- C₄ standard solution in diesel.

The 1000 ppm of marker dyes C₁- C₄ stock solutions in Section 3.3.8 B) were pipetted into 100 ml. volumetric flask following the list below and made up volume with diesel oil.

Standard solution (ppm)	Volume of 100 ppm stock solution (ml.)
3	0.30
5	0.50
7	0.70
9	0.90

3.3.9 Detection procedures for the marker dyes in the series of chloronitroaniline derivatives in diesel oil

Each of standard solution marker dyes in Section 3.3.8 C), 3.3.9 C) (25 ml.) and the appropriate solvent extraction systems ; solvent 1(5 ml.) were pipetted into the vial glasses. The vial glasses were shaken vigorously and allowed for phase separation. The solvent phases were drawn into the VIS-cuvettes. The absorption at the maximum wavelengths were measured by UV-VIS spectrophotometer. The ratio of oil phase to aqueous phase was 5:1. A blank test carried out on unmarked diesel oil (25 ml.) under similar conditions was compared.

For the ratio 7:1, each of standard solutions (35 ml.) and the solvent 1 (5 ml.) were pipetted into the vial glasses, respectively. They were shaken vigorously and allowed for phase. A blank test carried out on unmarked diesel oil (35 ml.) under similar conditions was compared.

For the ratio 9:1, each of standard solutions (45 ml.) and the solvent 1 (5 ml.) were pipetted into the vial glasses, respectively. They were shaken vigorously and allowed for phase separation. A blank test carried out on unmarked diesel oil (45 ml.) under similar conditions was compared.

In this section, the appropriate concentration and ratio of oil phase to aqueous phase were chosen by the visual color of their aqueous phases. These suitable conditions were subjected to the quantitative determinations.

3.3.10 Property tests for marker dyes in diesel oil compared with the unmarked diesel oil

The marked diesel oil containing 5 ppm marker dyes B₁- B₄ and marker dyes C₁-C₄ were provided in 1,000 ml. volumetric flask to test for the physical properties according to the ASTM test methods as shown in Table 3.2:

Table 3-2 : The ASTM test method

Test item	Test method ASTM
API gravity @ 60°F	D 1298
Specific gravity @ 15.6/15.6°C	D 1298
Calculated cetane index	D 976
Kinematic viscosity @ 40°C, cSt	D 445
Pour point, °C	D 97
Sulfur content, % wt	D 4294
Copper strip corrosion, 3hrs @ 50°C	D 130
Flash point (P.M.), °C	D 93
Distillation (Correct temp.)	D 86
IBP	
10% rec, °C	
50% rec, °C	
90% rec, °C	
Color	D 1500

3.3.11 Quantitative determinations of the marker dyes in diesel oil for the series of chloronitroaniline derivatives (marker dyes B₁- B₄ and marker dyes C₁-C₄)

All standard solutions in Section 3.3.8 C) and 3.3.9 C) were extracted with the suitable solvent extraction systems (solvent 1-3). The appropriate ratio of oil phase to aqueous phase was 9:1. Each of aqueous phases (solvent phases) were drawn into the VIS-cuvettes. The absorption at maximum wavelengths in Section 3.3.10 were used. A blank test carried out on unmarked diesel oil (45 ml.) under similar conditions was compared.

The standard calibration curves plotting between their absorptions and concentrations were shown with the maximum wavelength. Furthermore, the examples of dilutions and adulterations were investigated.

3.3.12 Stability tests for the marker dyes in the series of chloronitroaniline derivatives in diesel oil

The marked diesel oil containing 5 ppm marker dyes B₁- B₄ and marker dyes C₁-C₄ were subjected to the stability tests. In the period of every week for 3 months, these marked diesel oil (45 ml.) and the solvent 1(5 ml.) were pipetted into the vial glasses and shaken vigorously. Each of aqueous phases was drawn into the VIS-cuvettes. The concentrations of the marker dyes in diesel oil were measured using corresponding calibration curves. The experiment was carried out in triplicate.