

## CHAPTER III

### EXPERIMENT

#### 3.1 Materials

- 3.1.1 Salicylaldehyde ( $C_7H_6O$ ) from Fluka
- 3.1.2 Ethylenediamine ( $C_2H_8N_2$ ) from Fluka
- 3.1.3 Diethylenetriamine ( $C_4H_{13}N_3$ ) from Fluka
- 3.1.4 Triethylenetetramine ( $C_6H_{18}N_4$ ) from Fluka
- 3.1.5 *p*-Nitroaniline ( $C_6H_6N_2O_2$ ) from Fluka
- 3.1.6 2-Chloro-4-nitroaniline ( $C_6H_5ClN_2O_2$ ) from Fluka
- 3.1.7 4-Chloro-2-nitroaniline ( $C_6H_5ClN_2O_2$ ) from Fluka
- 3.1.8 2-Methoxy-4-nitroaniline ( $C_7H_7NO_3$ ) from Fluka
- 3.1.9 Methanol ( $CH_4O$ ) from Merck
- 3.1.10 Dichloromethane ( $CH_2Cl_2$ ) from J.T. Baker
- 3.1.11 Hydrochloric acid (HCl) from BDH Chemicals, Ltd.
- 3.1.12 Ethylene glycol ( $C_2H_6O_2$ ) from Fluka
- 3.1.13 Propylene glycol ( $C_3H_8O_2$ ) from Fluka
- 3.1.14 Acetone from Merck
- 3.1.15 Anhydrous sodium sulfate from Merck
- 3.1.16 Toluene ( $C_7H_8$ ) from Merck
- 3.1.17 Sodium nitrite ( $NaNO_2$ ) from Fluka
- 3.1.18 Potassium hydroxide (KOH) from Fluka

#### 3.2 Instrument and apparatus

##### 3.2.1 Fourier Transform Infrared Spectrophotometer

The FT-IR spectrophotometer model Nicolet (Impact 410) from Perkin Elmer was used for characterization the infrared spectra of synthetic azo dyes.

### 3.2.2 Nuclear Magnetic Resonance Spectrophotometer

NMR spectrometer model Bruker AC-F 200 MHz was used for characterization  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of synthetic azo dyes.

### 3.2.3 Mass Spectrophotometer

Fisons Instrument model VG Trio 2000 of mass spectrometer was used for confirmed molecular weight of synthetic azo dyes.

### 3.2.4 Ultraviolet / Visible Spectrophotometer

The UV/VIS spectrophotometer model Lamda-2 from Perkin Elmer was used to measure the maximum wavelength and the absorbance of each maker dye.

### 3.2.5 Digital Melting Point Apparatus

The digital melting point apparatus from Electrothermal was used to determine the melting point of solid azo dyes.

### 3.2.6 Petrochemical Tintometer

The petrochemical tintometer model PFX 990/P from Lovibond was used to determine color by using ASTM D1500 method.

### 3.2.7 Automatic Sulfur Content

Antex 9000 series automatic sulfur content was used to determine sulfur content of marked and unmarked diesel oil by using ASTM D5453 method.

### 3.2.8 Automatic Distillation Apparatus

Herzog (M626) automatic distillation apparatus was used to determine the boiling point and percent recovery by using ASTM D86 method.

### 3.2.9 Automatic Flash Point Apparatus

ISL (PMFP 93) automatic flash point apparatus model was used to determine flash point of marked and unmarked diesel oil by using ASTM D93 method.

### 3.2.10 Automatic Pour Point Apparatus

ISL (CPP 92) automatic pour point apparatus was used to determine the pour point of marked and unmarked diesel oil by using ASTM D97 method.

### 3.2.11 Total Acid Number Apparatus

Mettler Toledo DL50 graphix (Tritator 5118429209) was used to determine the total acid number of marked and unmarked diesel oil by using and ASTM D664 method.

### 3.2.12 Automatic Viscosity Apparatus

Cannon automatic viscosity was used to determine viscosity of marked and unmarked diesel oil by using ASTM D445 method.

### 3.2.13 API Gravity Apparatus

### 3.2.14 Specific Gravity Apparatus

### 3.2.15 Copper Strip Corrosion Apparatus

## 3.3 Experimental procedure

### 3.3.1 Synthesis

#### 3.3.1.1 Preparation of imine compounds [10]

##### 3.3.1.1.1 Preparation of imine from ethylenediamine

Salicylaldehyde (10.47 cm<sup>3</sup>, 0.1 mole) was added dropwise and with stirring to ethylenediamine (6.7 cm<sup>3</sup>, 0.1 mole) in methanol solution. The reaction mixture was cooled using an icebath. When the addition had been completed, stirring was continued for 1 hour and then an aqueous layer was separated at the end of the reaction. The reaction was allowed to crystalline and the yellow solid was filtered off with suction on a Buchner funnel. The solid was washed well with water and drained as completely as possible; it was then washed once with toluene and drained again. Recrystallised from dichloromethane and hexane to obtain 24.29 g (91% yield) of pure bis (salicylaldehyde) N-N'-ethylenediimine, m.p. 120-120 °C.

##### 3.3.1.1.2 Preparation of imine from diethylenetriamine

The procedure was the same as that described for the preparation from ethylenediamine. Salicylaldehyde (10.47 cm<sup>3</sup>, 0.1 mole) and diethylenetriamine (10.86 cm<sup>3</sup>, 0.1 mole) in methanol solution were used. The solution was extracted with dichloromethane, the combined extracts washed with water, and the

dichloromethane layer with anhydrous sodium sulfate was dried. The solution was filtered the dichloromethane removed on a rotary evaporator to obtain bis (salicylaldehyde) N, N'-diethylenetriamine (26.76 g, 86% yield) as a yellow liquid.

### 3.3.1.1.3 Preparation of imines from triethylenetetramine

The procedure was the same as that described for the preparation from ethylenediamine. Salicylaldehyde (10.47 cm<sup>3</sup>, 0.1 mole) and triethylenetetramine (14.9 cm<sup>3</sup>, 0.1 mole) in methanol solution was used to obtain 25.77 g (73.5% yield) of bis (salicylaldehyde) N, N'-triethylenetetramine as a yellowish orange solid, m.p. 166-167 °C.

## 3.3.1.2 Synthesis of azo dyes [7]

### 3.3.1.2.1 Diazotization

#### a) Diazotization of *p*-nitroaniline

A mixture of 1.38 g (0.01 mole) of *p*-nitroaniline, 3 cm<sup>3</sup> of water, and 3 cm<sup>3</sup> of concentrated hydrochloric acid, was heated and stirred until the solution was completed. The solution was cooled to room temperature, 8 g of ice was added, and 10 cm<sup>3</sup> of 1 N sodium nitrite was dropped slowly with vigorous stirring. Stirring was continued until most of the precipitated material had redissolved, and the mixture was allowed to stand for about 30 minutes in ice. Any residual undissolved material was removed by filtration. The residue should be very small; the filtrate should be clear and almost colorless and no cloudiness should reappear.

#### b) Diazotization of 2-chloro-4-nitroaniline

2-Chloro-4-nitroaniline was diazotized in the same procedure as *p*-nitroaniline except that of 1.73 g (0.01 mole) of 2-chloro-4-nitroaniline which was used.

**c) Diazotization of 4-chloro-2-nitroaniline**

4-Chloro-2-nitroaniline was diazotized in the same procedure as *p*-nitroaniline except that of 1.73 g (0.01 mole) of 4-chloro-2-nitroaniline which was used.

**d) Diazotization of 2-methoxy-4-nitroaniline**

2-methoxy-4-nitroaniline was diazotized in the same procedure as *p*-nitroaniline except that of 1.68 g (0.01 mole) of 2-methoxy-4-nitroaniline which was used.

**3.3.1.2.2 Preparation of phenolated diimine ions****a) Preparation of phenolated diimine ion from bis (salicylaldehyde) N-N'-ethylenediimine**

Potassium hydroxide (0.56 g, 0.01 mole) was dissolved in 5 cm<sup>3</sup> of methanol. The solution was cooled to 0 °C, and 2.68 g (0.01 mole) of bis (salicylaldehyde) N-N'-ethylenediimine was added into the solution to give a pale yellow solution.

**b) Preparation of phenolated diimine ion from bis (salicylaldehyde) N-N'-diethylenetriimine**

The procedure of a) was repeated except that of 3.11 g (0.01 mole) of bis (salicylaldehyde) N-N'-diethylenetriimine which was used. Yellow solution of diphenolated diimine ion was obtained.

**c) Preparation of phenolated diimine ion from bis (salicylaldehyde) N-N'-triethylenetetriimine**

The procedure of a) was repeated except that of 3.54 g (0.01 mole) of bis (salicylaldehyde) N-N'-triethylenetetriimine which was used. Dark yellow solution of diphenolated diimine ion was obtained.

### 3.3.1.2.3 Coupling reaction of diazonium salts

Pale yellow solution of aniline diazonium salt was added dropwise into monophenolated diimine ion with vigorous stirring, while the temperature of the reaction mixture was controlled to below 0°C. The reaction mixture was continued stirring at the temperature below 0°C for 1 hr. The azo dye product was extracted from the reaction mixture by treating with dichloromethane and washing the combined extracts with water for 3-4 times. The dichloromethane layer was dried with anhydrous sodium sulfate. The mixture was filtered and the solvent was removed on a rotary evaporator to obtain an azodiimine.

### 3.3.2 Characterization of synthetic marker dyes

Synthetic marker dyes were characterized by spectroscopy techniques e.g. FT-IR, <sup>1</sup>H, <sup>13</sup>C-NMR and MS.

### 3.3.3 The use of marker dyes in diesel oil

#### 3.3.3.1 Preparation of marker dye stock solution

Each 1,000 ppm marker dye stock solution was prepared by dissolving 0.1g of each marker dye in toluene, and made up to 100 ml in a volumetric flask with toluene.

#### 3.3.3.2 Suitable extracted system for the detection of marker dyes in diesel oil

The extracted systems were divided into two systems consisting of system A, which is amine in various solution, and system B, 10% of HCl in various solution. All synthetic azo dyes were used to determine the suitable extracted system. The concentration of each dye in marked diesel was 5 ppm. This was done by pipetting 0.25 ml of 1,000 ppm marker dye stock solution into a 50 ml volumetric flask, and made up with unmarked high-speed diesel.

System A was comprised of 2% KOH in ethylene glycol, 10% and 20% ethylenediamine in ethylene glycol, 10% and 20% ethylenediamine in propylene glycol, and 10% and 20% diethylenetriamine in propylene glycol. Each marked diesel oil (6 ml) was pipetted into a 10 ml screw cap vial, and then 1 ml of the extracted solution was added into the vial, capped, and shaken for a while. The color in the extracted phase was observed after the two phases were separated.

System B was comprised of 10% HCl aqueous solution, 10% HCl in methanol, 10% HCl in ethylene glycol, 10% propylene glycol, and 10% HCl in a solution of 3:2 propylene glycol and methanol. Each marked diesel oil was carried out in the same manner as the extraction in system A. The color in the extracted phase was observed after the two phases were absolutely separated. All of the extracted solutions are tabulated in Table 3-1.

The suitable extracted system was considered using many reasons, such as toxicity, cost, time of phase separation, appearance, and extracted color.

**Table 3-1: Extracted solution of system A and B**

System A	System B
2% KOH in EG	10% HCl (aq)
10% ED in EG	10% HCl in EG
20% ED in EG	10% HCl in PG
10% ED in PG	10% HCl in MeOH
20% ED in PG	10% HCl in 3:2 PG-MeOH
10% DET in PG	---
20% DET in PG	---

### 3.3.3.3 The optimum shaking time for the extraction

Dye 12 was used to determine an optimum shaking time of the extraction with suitable extracted solution. The shaking time was varied from 10 to 50

seconds by pipetting 5 ml of 1,000 ppm marker dye stock solution into 5 screw cap vials, then adding 5 ml of suitable extracted solution and shaking for 10, 20, 30, 40, and 50 seconds, respectively. The absorbance was measured by using UV/VIS spectrophotometer. The optimum shaking time for the extraction was selected, which gave the highest absorbance.

#### **3.3.3.4 The suitable concentration of each marker dyes in diesel oil**

After the suitable extracted solution was obtained, there was a further study to monitor the suitable concentration of each marker dyes in diesel oil. The extraction was done in a volume ratio of 6 parts marked diesel oil and 1 part extracted solution.

#### **3.3.3.5 The maximum wavelength and the absorbance of each marker dye**

Each marker dye 5 ppm was prepared by pipetting 0.25 ml of 1,000 ppm marker dye stock solution into a 50 ml volumetric flask, and made up with unmarked diesel oil. The oil was extracted with suitable solution in a volume ratio of 6 parts marked diesel to 1 part extracted solution and measuring the maximum wavelength and its absorbance by using UV/VIS spectrophotometer were carried out.

#### **3.3.3.6 Recovery percentage of marker dye in the extracted phase**

Pipetting 1,000 ppm marker dye stock solution of dye 6 into the suitable extracting solution at 5 different concentrations (0, 4, 5, 6, and 7 ppm) to make the standard calibration curve between absorbance and concentration of marker dye at its maximum wavelength was carried out. The absorbance of the extracted phase of marked diesel oil was measured and calculated for the percent recovery of the extracted marker dye in the extracted phase.



### 3.3.4 Effects of marker dyes on physical properties of marked diesel oil

The 5 ppm of dye 1 was prepared in order to study the effects of marker dye on physical properties of marked diesel oil according to ASTM methods. The results were compared with unmarked diesel oil. Test items and their methods are listed in Table 3-2.

**Table 3-2: Test items and ASTM test methods for monitoring the physical properties of marked diesel oil.**

Test items	ASTM Test methods
Flash point, °C	D 93
Sulfur content, %wt	D 5453
Copper strip corrosion (3hrs., 50 °C)	D 130
Distillation	D 86
Total acid number, mg KOH/g	664
Color	D 1500
API 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

### 3.3.5 Quantitative determination of marker dyes in high-speed diesel

Each 5 ppm of synthetic azo dye was prepared and extracted with suitable extracted solution. The extracted phase was then removed and the absorbance at the maximum wavelength of the extracted phase was measured using UV/VIS spectrophotometer. After the maximum wavelength of each marker dyes was obtained, the marked diesel oils was prepared at 5 different concentrations and the standard calibration curves were plotted between absorbance and concentrations using UV/VIS spectroscopic technique to monitor the quantities of marker dyes.

### **3.3.6 Stability of marker dyes in diesel oil**

All marker dyes were studied for their stability in diesel oils during three months of storage. Each 5 ppm of marked diesel oil was prepared by pipetting 5 ml of 1,000 ppm marker dye stock solution into a 100 ml volumetric flask, and made up to volume with unmarked diesel oil. The quantities of marker dyes that contained in diesel oils were determined monthly using UV/VIS spectrophotometer.