CHAPTER III

EXPERIMENT

3.1 Materials

1. Diisopropylnaphthalene, MW 212 Product-No. 124008 (Kureha Chemical Industry Co. Ltd., Japan).
2. Leuco dye CVL (Yamada Chemical Co. Ltd., Kyoto, Japan).
3. Hexamethylene diisocyanate (HDI) and Diphenylmethylene diisocyanate (MDI) (Sumitomo Bayer Urethane Co. Ltd., Ehime Pref, Japan).
4. Poly(vinyl alcohol) (Kuraray POLYTRADE Co. Ltd., Japan).
5. Ethanol (BDH Laboratory Supplies, Poole, England).
6. Ethylene diamine (EDA) or 1,2-diaminoethan; ($C_2H_4N_2H_4$) (Dow Chemical Company, Michigan, U.S.A.).
7. Acetone (Batch No. 0070242, Fisher Chemicals, England).
8. Benzene (Batch No. E001097G, Carlo Erba, Italy).

3.2 Equipment

Major instruments used are listed below:

1. Ultrasonicator (Model 2210, Branson, Canada).
2. pH Meter (Model F21, Horiba, Japan).
3. Four-necked flask (Model U-34727-00, ACE Glass, Germany).
4. Scanning Electron Microscope (JEOL JSM 5800LV, Japan).
5. Densitometer (R710, IHARA Electronic IND. Co. Ltd., Japan).

6. Fourier Transform IR Spectrophotometer FTIR (Nicolet Impact 400, Thermo Nicolet Corporation, Madison, United States).
7. Thermogravimetric Analyzer (STA 490 C, NETZSCH, Germany).
8. Laser Diffraction Particle Size Analyzer (SALD 2000, Shimadzu, Japan).
9. UV Visible spectrophotometer (UV-1601, Shimadzu, Japan).
10. Homo Mixer (Mark II 2.5, Tokushu Kika Kogyo Co. Ltd., Japan).

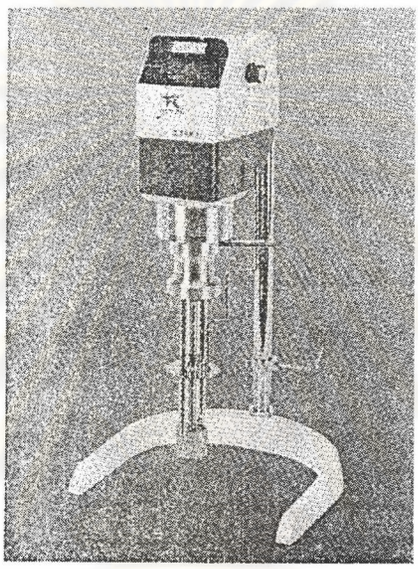

Figure 3.1 Homo Mixer (Mark II 2.5)

3.3 Experimentals [40]

3.3.1 Preparation of Poly(vinyl alcohol)

PVA 97% solid was dissolved in cool water for 15 min then it was heated up until it reached 90°C and kept for 30 min to cool down to 12°C. After that the concentration was adjusted to 2.6%.

3.3.2 Preparation of Leuco Dye Solution

Diisopropylnaphthalene was heated to 90°C, the CVL was poured to the solvent and it was stirred for 10 min to make it completely soluble. The leuco dye solution was cooled down to 20°C. The different weight ratios of TDI and HDI were added into oily solutions and were stirred until completely soluble.

3.3.3 Preparation of Microcapsule Emulsion

An organic-water (o/w) emulsion was formed by adding the organic solution into an aqueous solution with 2.6% PVA as stabilizer and was stirred strongly by 9000 rpm at room temperature for 4 min by homomixer. The buffle plate was adjusted to the surface of solutions. Polyurea microcapsules with different wall membranes and core-to-wall materials were prepared by interfacial polymerization for 5 hr. After 80°C was reached and its reaction took place for 1.5 hr. Distilled water (100 ml) was added into the microcapsules slurry to maintain the monodispersed microparticles. Slow stirring was administrated to the microcapsules slurry until reaching room temperature. The microcapsule slurry obtained was decanted and washed with 30% ethanol to remove oil and unreacted isocyanate on the surface, and dried at ambient temperature for 24 hr. The flow chart of the experiment is illustrated in Figure 3.2.

3.3.4 CB Coating Color and CB Coated Paper Preparation

Microcapsules slurry was mixed up with the binder in the ratio 1.6 to 1 and diluted to 15% concentration. The solution is named CB coating color. CB coating color was coated on a plain substrate with a grammage 50 g/m^2 using a wire bar No.

12 and kept in an oven at 105°C for 2 min. Coating weight was controlled at 3.0 g/m^2 to obtain a CB coated paper with a grammage of 54-56 g/m^2.

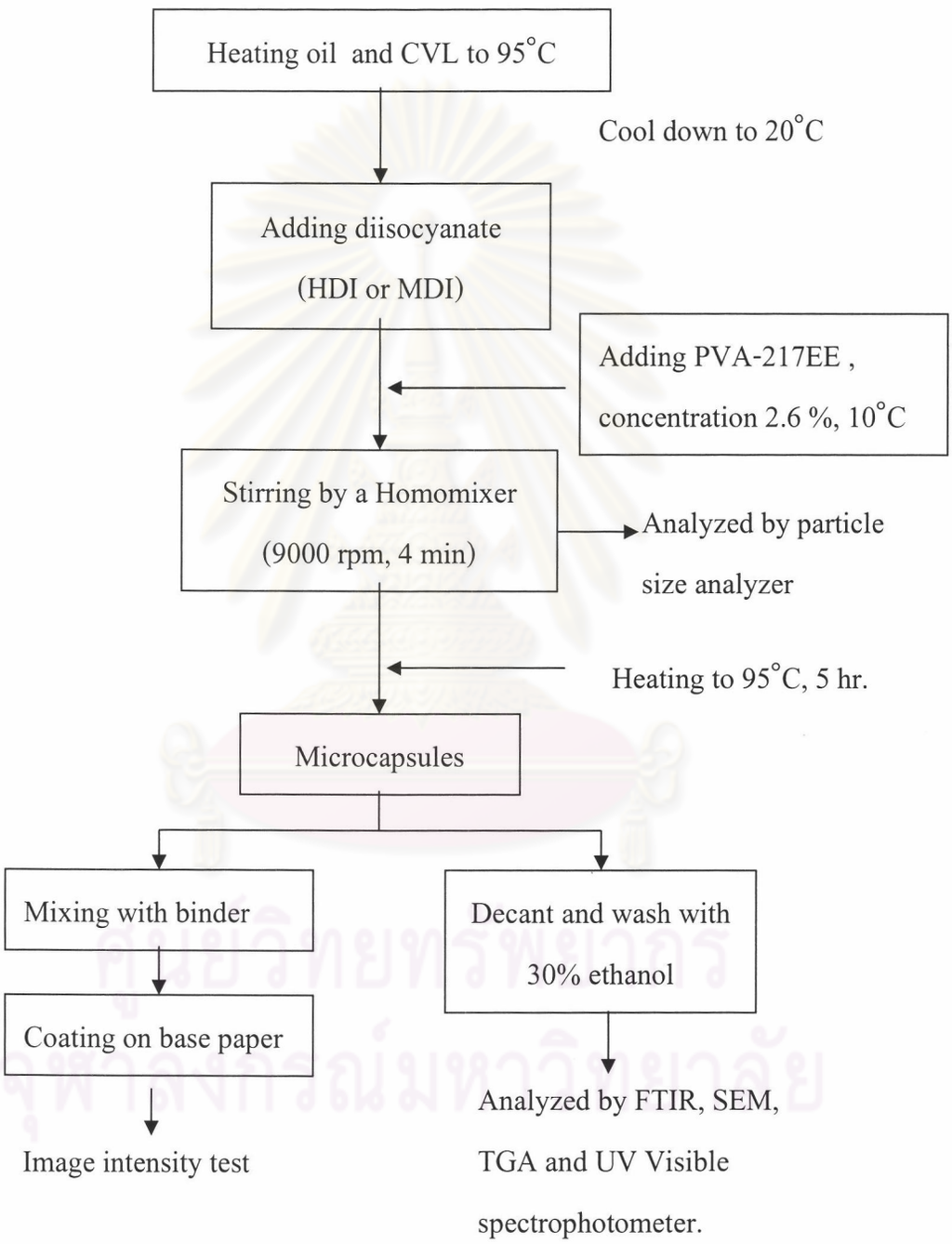

Fig 3.2 Flow chart of experiment

3.4 Influential Parameters on Microencapsulation

3.4.1 Effect of Core-to-Wall Ratio and Type of Diisocyanate

The following microcapsules were prepared using the above procedure to investigate the effects of formulation variables on properties of polyurea microcapsule containing leuco dye by varying amounts of the wall material, HDI and MDI, and keeping amounts of the core material, solvent and leuco dye as constant. The other factors were controlled in the same condition. The emulsifier used was 2.6% concentration. The core-to-wall ratios and the appropriate HDI to MDI ratios were chosen to evaluate the effect of EDA in section 3.4.2. The concentration of the core-to –wall ratio and the concentration ratio of HDI and MDI are summarized in Table 3.1.

Table 3.1 Conditions of the microencapsulation.

Formulation No.	Oil (g)	CVL (g)	Wall material (mole)	HDI:MDI (mole ratio)
1	150	9	0.10	0.10:0.00
2	150	9	0.10	0.08:0.02
3	150	9	0.10	0.06:0.04
4	150	9	0.10	0.03:0.07
5	150	9	0.10	0.00:0.10
6	150	9	0.07	0.07:0.00
7	150	9	0.07	0.06:0.01
8	150	9	0.07	0.04:0.03
9	150	9	0.07	0.02:0.05

Table 3.1 Continued conditions of the microencapsulation.

Formulation No.	Oil (g)	CVL (g)	Wall material (mole)	HDI:MDI (mole ratio)
10	150	9	0.07	0.00:0.07
11	150	9	0.05	0.00:0.05
12	150	9	0.05	0.04:0.01
13	150	9	0.05	0.03:0.02
14	150	9	0.05	0.02:0.03
15	150	9	0.05	0.00:0.05

3.4.2 Effect of EDA

The microcapsules were prepared as the procedure shown in Figure 3.2. The amount of EDA studied were 10, 20 and 30% mole of the wall materials, HDI and MDI. The formulations of polyurea microcapsules by adding EDA are shown in Table 3.2.

Table 3.2 The formulation of polyurea microcapulses in the presence of EDA

Formulation No.	Oil (g)	CVL (g)	HDI (mole)	MDI (mole)	EDA (mole)
16	150	9	0.08	0.02	0.01
17	150	9	0.08	0.02	0.02
18	150	9	0.08	0.02	0.03

Table 3.2 Continued the formulation of polyurea microcapulses in the presence of EDA

Formulation No.	Oil (g)	CVL (g)	HDI (mole)	MDI (mole)	EDA (mole)
19	150	9	0.06	0.04	0.01
20	150	9	0.06	0.04	0.02
21	150	9	0.06	0.04	0.03
22	150	9	0.03	0.07	0.01
23	150	9	0.03	0.07	0.02
24	150	9	0.03	0.07	0.03

3.5 Characterization of Microcapsules

3.5.1 FTIR

FTIR peaks were identified after they were recorded on a Nicolet Impact 400 FTIR Spectrometer using cast films from the solution onto KBr discs. The spectra data were acquired by using Omnic 2.0 software.

3.5.2 Scanning Electron Microscopy (SEM)

Scanning of the microcapsules by electron microscopy was performed using JSM-5400 (JEOL Co. Ltd., Japan). Microcapsules were sprinkled onto a double sided tape, sputteringly coated with gold and examined in the microscope. Microcapsules of formulations 1-5 were frozen about 4°C for 4 hours and pressed under pressure 75 kg/cm^2 for 30 seconds. The pressed microcapsules were viewed by SEM technique.

3.5.3 Microcapsule Size and Particle Size Distribution.

Laser Diffraction Particle Size Analyzer of SALD-2001 (Shimadzu Co. Ltd., Japan) was used to characterize the microcapsule particle size and size distribution. Microcapsule emulsion was diluted and added in an agitator bath for ultrasonic dispersion at the optimum measuring conditions at the absorbance range of 0.80-0.95. The particle size distribution was calculated from the light intensity distribution data.

3.5.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on a STA 409 C (NETZSCH). Microcapsules powder of about 12-17 mg each were heated at the rate of 10°C /min up to 500°C under constant N_2 flow.

3.5.5 UV/Visible Spectrophotometer

3.5.5.1 Standard Curve of CVL

Benzene was used for preparing the standard CVL solution as well as the samples. This vehicle was found to stabilize CVL over the entire period of assay. About 35 mg of CVL was accurately weighed in a 100-ml volumetric flask. CVL was dissolved and adjusted to the volume using benzene. Six appropriate dilutions were then made with the same vehicle to obtain the standard solutions with various concentrations ranging from 15 to 90 μg/ml. The absorbances of these solutions were determined at a wavelength of 353 nm, which was the λ_{max} of CVL in this vehicle, using UV/Visible spectrophotometer and using benzene as a blank. The

relationship between absorbances and concentrations was fitted using a linear regression analysis.

3.5.5.2 Standard Curve of Developed CVL

CVL was accurately weighed, dissolved in benzene and reacted with 5 ml of 2% zinc salicylic acid. Blue color was developed from the reaction. Six appropriate dilutions were then made with the same vehicle to obtain the standard solutions with various concentrations ranging from 0.20 to 3.0 μg/ml. The absorbances of these solutions were determined at a wavelength of 610 nm, which was the λ_{max} of developed CVL in this vehicle, using UV/Visible spectrophotometer and using benzene as a blank. The relationship between absorbances and concentrations was fitted using a linear regression analysis.

3.5.5.3 Validation of CVL Assay

Microcapsules powder was accurately weighed in the range of 300-350 mg. Grinding by mortar was used to break microcapsules and 100 ml of acetone was added to extract the core material. The residue was cleaned by 80 ml benzene. Acetone was evaporated and microcapsules were dissolved by filtrated benzene, then the solution was adjusted into a 100 ml volumetric flask. The absorbances of the diluted solutions were determined at a wavelength of 353 nm, which was the λ_{max} of CVL in this vehicle, using UV/Visible spectrophotometer and using benzene as a blank. The regression equation of the standard solution was used to calculate the amount of CVL in the microcapsules.

Residue from the extraction was kept to examine the remaining CVL by dissolving 25 ml of benzene and 5 ml of 2 % zinc salicylic acid was then

added. The absorbance of the diluted solutions was determined at a wavelength of 610 nm, using UV/Visible spectrophotometer and using benzene as a blank. The regression equation of the standard solution was used to calculate the amount of CVL in the residue.

3.5.6 Image Density of CB Coated Paper

The CB coated paper (18 cm x 3 cm) was set in such a way that the "back side" was contacted with the front side of standard CF coated color and the pressure of 20 kg/cm^2 was applied at 3 positions, each 15 cm^2, for 1 min by a testing instrument manufactured by Riken Seiki K., and the image was examined on the dye acceptor coating paper (CF) by a reflection densitometer.