

## CHAPTER III

### Experimental Procedures

#### Materials

- Bleached and unmercerised plain woven cotton fabric was used throughout this work.

#### Chemicals and a dye

- All chemicals used throughout this work were reagent grade.

Table 3.1 Chemicals used in this project.

<b>Chemicals</b>	<b>Company</b>
Cyanuric chloride	Fluka
Pyridine	Carlo-Erba
Sodium bicarbonate	Ferak
Sodium carbonate	Merck
Sodium chloride	Carlo-Erba
Ethylene diamine	Carlo-Erba
Tris-(2-aminoethyl)amine	Fluka
Urea	Fluka
Wetting agent	V.P.C. group
Non-ionic detergent	U.N.T.Chemical Co.,Ltd.

- Reactive dye, Cibacron Red F-B (kindly supplied by Ciba-Geigy)

### Equipment

1. Rotary dyeing machine & steel pots. , Ahiba Polymat<sup>®</sup>
2. Padding mangle
3. pH meter, Hanna model 400
4. Magnetic stirrer, Framo-Geratetechnik model M21/1
5. Reflectance spectrophotometer, Macbeth 7000
6. UV spectrophotometer, Milton Roy Spectronic 3000 Array
7. Fourier-Transform Infrared Spectrophotometer, Nicolet Impact 400D
8. High Performance Liquid Chromatograph, Shimadzu LC-3A
9. Elemental Analyzer, Perkin Elmer PE2400 series II
10. Nuclear Magnetic Resonance Spectrometer, Jeol JNM-A500
11. Magnetic bar
12. Thin Layer Chromatography plate, Fluka Switzerland
13. Ice bath
14. Glasswares
  - Beakers 250 and 500 ml.
  - Dropping funnel
  - Suction flask
  - Buchner funnel
  - Dropper
  - Volumetric flask 100 and 250 ml.
  - Pipette 1, 10 and 25 ml.

### 3.1 Synthesis of the modifying agent, 2,4-dichloro-6-pyridino-s-triazine (DCPT)

A 13.8 g (0.075 mole) of cyanuric chloride and 70 ml. of water were added into a beaker which was placed on a magnetic stirrer. The mixture was then stirred in ice bath at the temperature of 5°C. A solution of pyridine (5.9 g, 0.075 mole) and water (30 ml.) from a dropping funnel was added dropwise into the suspension over 30 min. as shown in Figure 3.1. The pH of reaction mixture was maintained between 6 to 7 by the addition of NaHCO<sub>3</sub> and the temperature being kept below 5°C throughout. Finally, the complete reaction would be obtained when clear solution was observed.

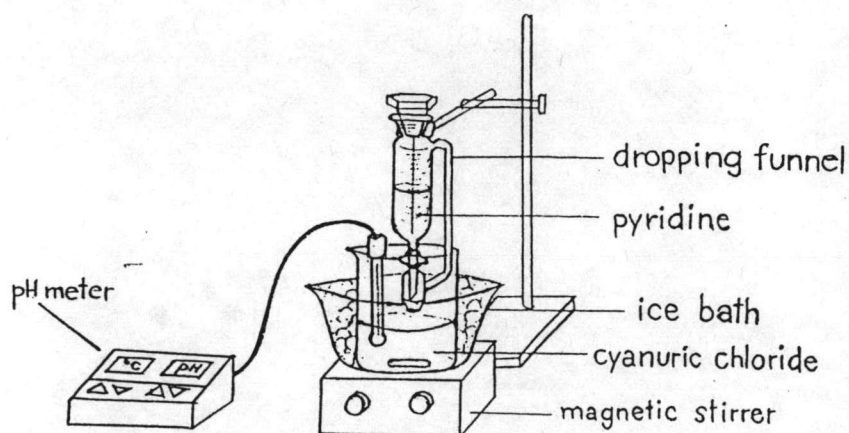
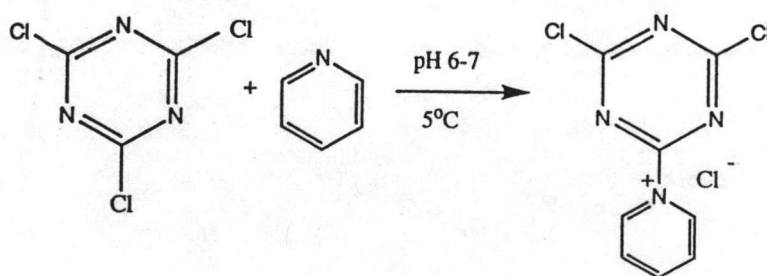


Figure 3.1 The method for synthesis of modifying agent.

The reaction scheme may be written as follows:



### 3.2 FT-IR Analysis

Principally, Infrared spectroscopy is based on the interaction of infrared radiation with molecular dipole moments in the sample. When a sample compound is placed in the IR beam, it absorbs particular frequencies.

Infrared spectroscopy is probably the most widely used technique for the identification of organic compounds. However, the disadvantage of the traditional spectrometer is found in the monochromator which separates the broad incident radiation into a frequency element before reaching the sample. The main components of a Fourier-transform infrared spectrophotometer consists of two parts:

1. An optical system which used an interferometer which can split a beam of radiation into two paths and recombine them so that the intensity variations of the exit beam can be measured by a detector as a function of path difference.
2. A sophisticated computer. The computer controls optical components, collects and stores data, performs computations on data (especially Fourier transforms of the interference patterns) and display spectra.

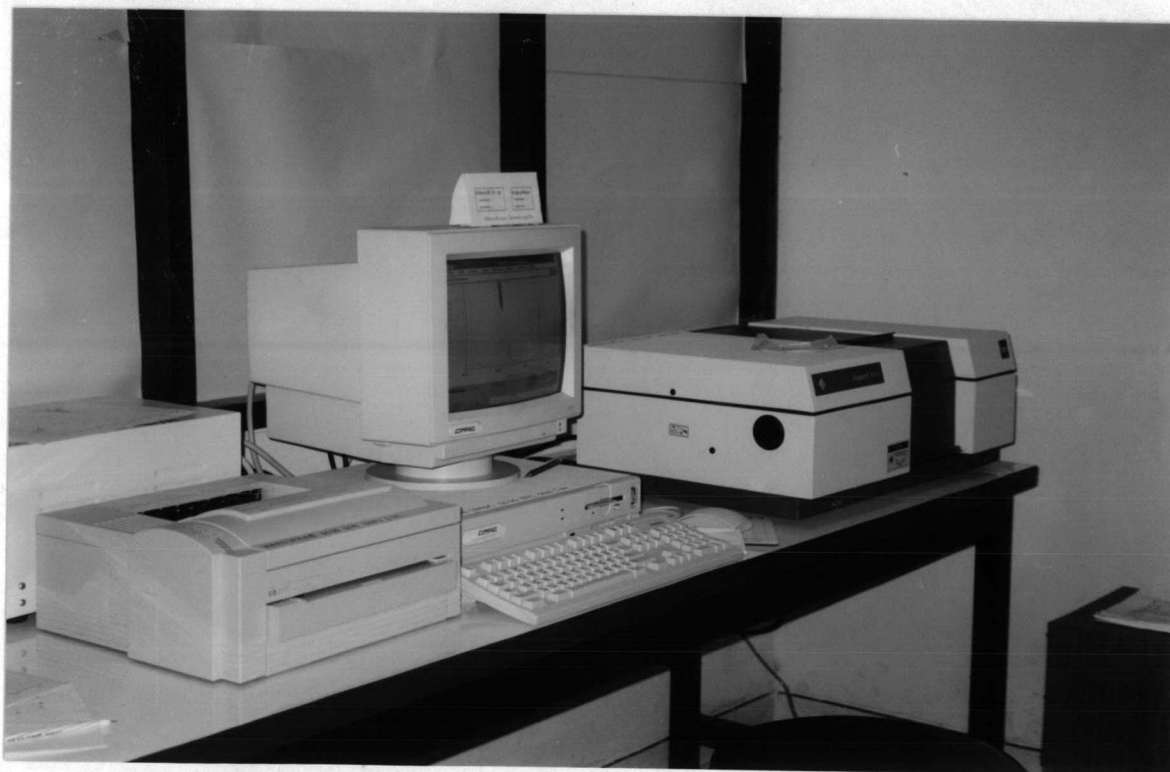


Figure 3.2 FT-IR spectrophotometer.

Identification of DCPT agent by FT-IR technique was carried out using the Nicolet Impact 400D FT-IR Spectrometer using the diffuse reflectance attachment to obtain transmission IR spectra. Resolution for the spectra presented was  $4\text{ cm}^{-1}$ . The scan number was 32. The method of sample preparation used in this experiment is pressed-disc technique by mixing sample in potassium bromide (KBr) at a ratio of 1:50.<sup>(24)</sup> All the spectra were transferred to the computer for further analysis and plotting by Omnic software.

### 3.3 HPLC Analysis

High Performance Liquid Chromatography (HPLC) is a technique that has arisen from the application to liquid chromatography (LC). There are other sorption mechanisms that can cause separation depending on choosing to use the stationary phase and mobile phase. Separation here is due to differences in the partition coefficients of solutes between the stationary and mobile phase. The stationary phase used are commonly uniform, porous silica particles with spherical or irregular shape and nominal diameters of 5-10  $\mu\text{m}$ . or using a bonded phase in which  $\text{C}_{18}$  alkyl groups are attached to the surface of silica particles.

HPLC system consists of the mobile phase reservoir, pumping system, guard column, analytical column and detector. This chromatographic method is an excellent method for the separation of mixtures, for instance, non-polar solutes are adsorbed relatively weakly and should be eluted with a non-polar solvent, whereas polar solutes are adsorbed more strongly and require a more polar solvent. If the sample contains a wide range of polarities, the separation could be done by changing the polarity of the solvent mixture during the separation. After passing through the column, the separated solutes are sensed by an in-line detector. The output of the detector is an electrical signal by measuring the time taken for the solute to pass through the chromatographic system called retention time.



Figure 3.3\_ HPLC instrument.

In this study, the identification was carried out using the Shimadzu LC-3A Liquid Chromatograph and UV-VIS detector (LDC Analytical 4100). The main conditions used were  $C_{18}$  column and mobile phase containing the required ratio of acetonitrile (ACN) and  $H_2O$ .

The application of HPLC in this work can be divided as follows:

### 3.3.1 Following the reaction of cyanuric chloride and pyridine.

The solution of reaction mixture was injected by microsyringe into the microsampling valve. The reaction mixture was taken at the beginning of the reaction and was then sent for HPLC analysis. The reaction between cyanuric chloride and

pyridine was followed by HPLC analysis until the reaction was completed. The mobile phase using 65:35 of ACN:H<sub>2</sub>O was pumped through the C<sub>18</sub> column at a flow rate of 1.6 ml/min and using UV detector at  $\lambda_{\text{max}}$  325 nm. Furthermore, the study of stability of DCPT product was also done by HPLC analysis.

### 3.3.2 Studying on stability of reactive dye in free-alkali dyebath.

This investigation was measured by sampling the dyebath before and after the dyeing process and was then analysed by HPLC techniques. The conditions employed for this case were using ACN:H<sub>2</sub>O mobile phase at a ratio of 55:45, flow rate of 1 ml/min and  $\lambda_{\text{max}}$  at 550 nm.

### 3.4 TLC Analysis

Another choice for studying on stability of reactive dye can be achieved by thin layer chromatography (TLC) technique. For this technique, the separation mechanism depends on the types of liquid mobile phase system uses. The stationary phase used today is silica gel. The differences in absorption by the stationary phase of every compounds are measured as R<sub>f</sub>-value which is the ratio between the distance of movable solute and the distance of movable solvent as shown in Figure 3.4<sup>(21)</sup>

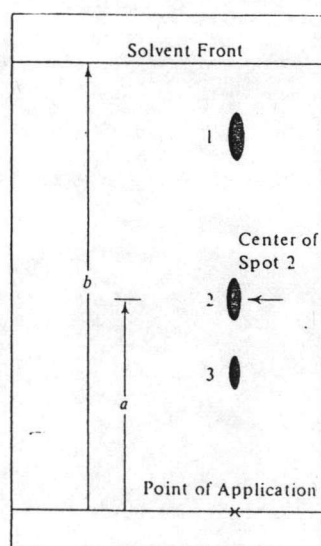


Figure 3.4 Thin layer chromatograph.[21]

In this work, TLC technique is used to identify  $R_f$ - value of dye solutions before and after dyeing processes in order to follow the hydrolysis reaction of dye. The mobile phase system used is water/ethyl acetate/ethyl alcohol (4:14:10).

### 3.5 NMR Analysis

Nuclear Magnetic Resonance Spectroscopy (NMR) technique is based on the measuring of difference energy level of nucleus under the influence of an external magnetic field. The important nuclei that exhibit the NMR phenomenon such as  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ , etc. The simplest NMR experiment consists in exposing the nuclei to a powerful external magnetic field, if these nuclei were irradiated with a beam of radiofrequency energy of the appropriate frequencies, the low-energy nuclei may absorb this energy and move to a higher energy state so this absorption of energy can be recorded in the form of an NMR spectrum, this gave rise to the term “chemical shift” because the professional frequency of nuclei in the same external applied field is not the same and the shift in frequency depended on chemical environment.

The basic features of the instrumentation needed to record an NMR spectrum are a magnet, a radiofrequency transmitter, a radiofrequency receiver and a data processor.

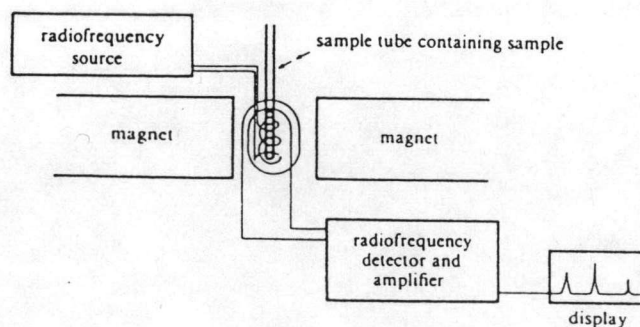


Figure 3.5 NMR spectrometer.[23]



For identification of the chemical structure of DCPT compound, the differences in frequency are measured with respect to some reference group of nuclei. For this case, the accepted reference is sodium salt of 4,4-dimethyl-4-silapentane sulphonic acid (DSS). The NMR sample tube containing a mixture of 2 ml. of DCPT solution and 0.5 ml. of DSS in D<sub>2</sub>O was placed in FT-NMR spectrometer and have a professional radiofrequency of 500 MHz. (Jeol JNM-A500) to obtain liquid state <sup>13</sup>C-NMR spectrum.

### 3.6 Treatment of cotton with the modifying agent

Application of the modifying agent was carried out using both exhaustion and pad-batch methods.

#### 3.6.1 Exhaustion method

Plain, bleached cotton fabric was cut into rectangles each of which had a weight of exactly 8.00 gram. and was treated in a solution containing different concentrations of the DCPT in the range from 5 to 30 g/l. using 100 ml. sealed stainless steel dyepots housed on an Ahiba Polymat<sup>®</sup> laboratory dyeing machine (Figure 3.7) at a liquor ratio of 10:1. Treatment was commenced at 55 °C for 15 min. and then Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> was added to dyepots. The temperature was kept at 55 °C for a further 45 min. The fabric was then taken out and rinsed. The rinsed fabric was further treated with ethylene diamine or tris-2-aminoethyl amine and the temperature was raised to 85°C and kept at this temperature for 45 min. Finally, the modified fabric was taken out and rinsed again. This so called “two-step” treatment process took long time to complete. Therefore, another option so called “one-step” treatment process was proposed; and eventhough it was found that the results obtained from one-step method gave a good color yield but it was difficult to obtain an even shade. Hence, the two-step method was used throughout in this project.

The diagram of treatment of cotton fabric using exhaustion method can be shown as follows :

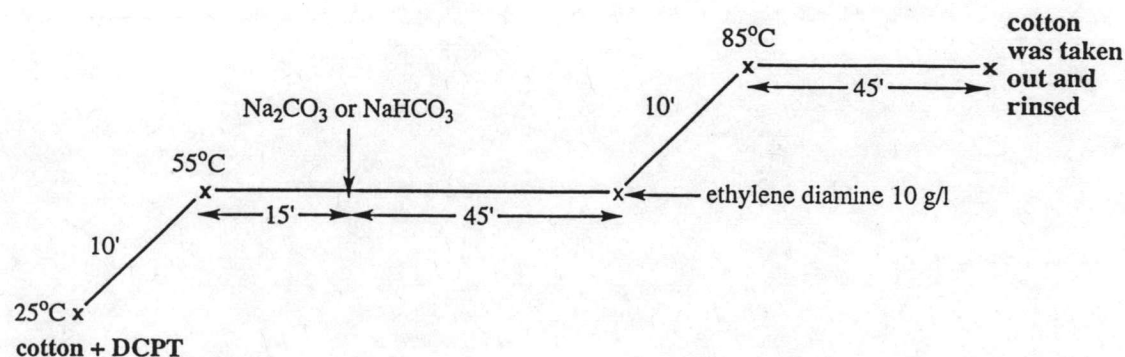


Figure 3.6 A two-step exhaust treatment of cotton fabric.



Figure 3.7 Laboratory dyeing machine.

### 3.6.2 Pad-batch method followed by steaming at 100°C

Cotton fabrics were wet and padded with a pad-liquor containing the 15 g/l of DCPT and followed by  $\text{Na}_2\text{CO}_3$  10 g/l. Padded fabric was squeezed in a pad mangle (Figure 3.9) at set pressure to remove excess liquid. After passing a pad mangle, 80% wet pick-up was obtained. The padded fabric was then batched at room temperature for 24 hours<sup>(35)</sup>; after 24 hours batching the batched fabric was padded again with a pad-liquor containing ethylene diamine 40 g/l and urea 100 g/l, before being steamed at 100°C for 4 min to allow the reaction of ethylenediamine taking place and after that, was washed thoroughly in running tap water. The diagram of treatment of cotton fabric using pad-batch method as shown below:

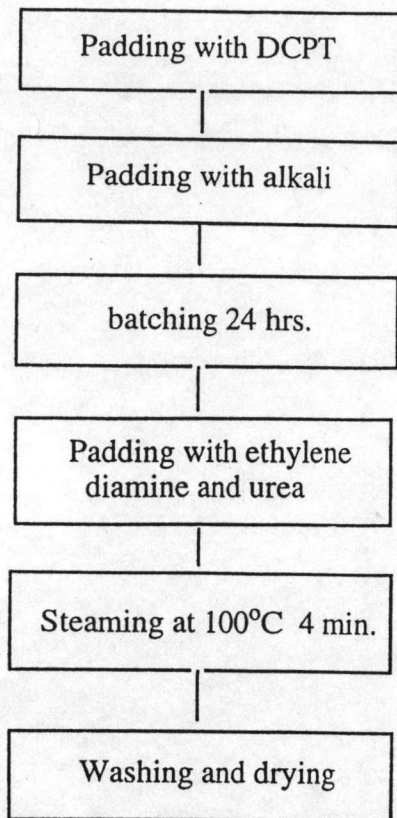


Figure 3.8 A pad-batch treatment followed by steaming at 100°C of cotton fabric.

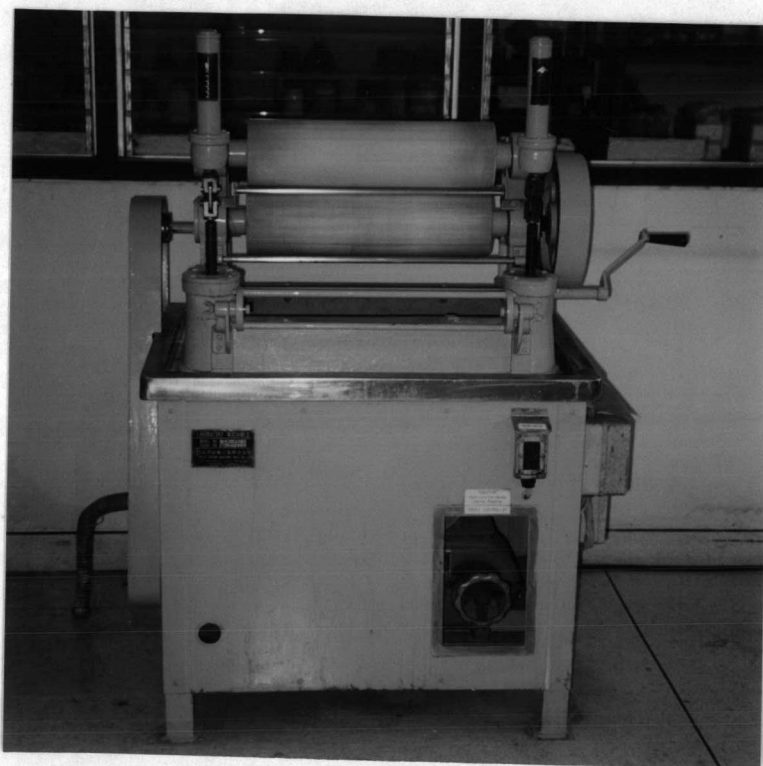
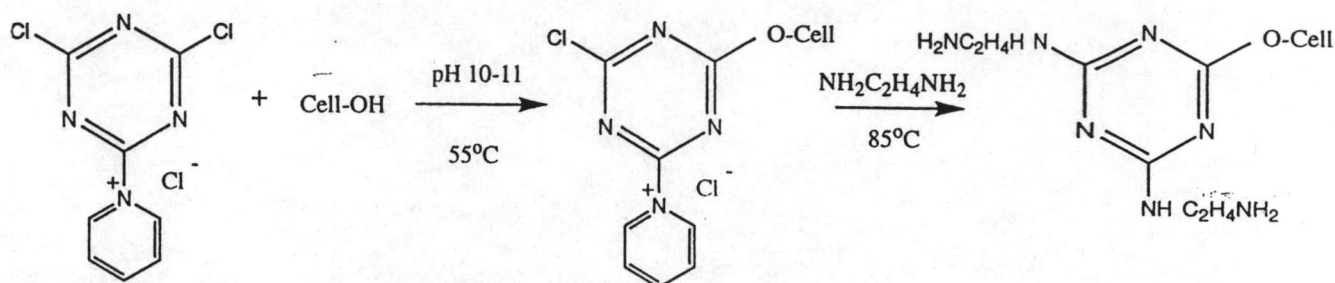


Figure 3.9 Padding mangle.

The reaction scheme between cotton fabric, DCPT and ethylenediamine may be written as follows:



### 3.7 General Dyeing Procedure

#### 3.7.1 Dyeing of modified fabric using exhaustion method

Modified cotton fabric was dyed in a solution containing commercial monofluorotriazinyl dye, Cibacron Red F-B and the electrolyte, NaCl. All dyeings were carried out in 100 ml. sealed stainless steel dyepots housed in the Ahiba Polymat<sup>®</sup> laboratory dyeing machine, at a liquor to goods ratio (L:R) of 10:1. In any dyeing, no alkali was made. Dyeing of modified cotton was commenced at 85°C for an hour. The dyed cotton was taken out and rinsed thoroughly in tap water and cut into equal portions. One of these portions was soaped in a solution containing non-ionic detergent (5 g/l) at the boil for 15 min (liquor ratio 20:1).<sup>(5)</sup> The diagram of exhaust dyeing can be shown as follows:

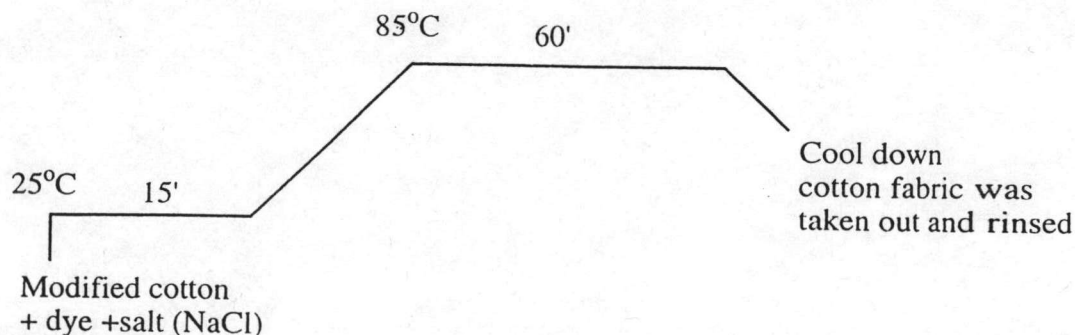


Figure 3.10 Exhaust dyeing of modified fabric.

In this work, the various factors that affected the degree of dye fixation for exhaust dyeing were investigated.

#### 3.7.1.1 The effect of DCPT concentrations on the degree of dye fixation

The DCPT concentrations in dye bath were varied from 5 to 30 g/l, and the cotton fabrics prepared in this way were then dyed (2% o.w.f.) at 85°C for 1 hour in the presence of NaCl 20 g/l. This investigation was classified into two processes, one-step and two-step methods.

#### 3.7.1.2 The effect of salt concentrations on the degree of dye fixation

In this case, cotton fabric was pretreated with 15 g/l DCPT and 10 g/l of  $\text{Na}_2\text{CO}_3$  and was then dyed (1% o.w.f.) at different salt concentrations in a range of 10-40 g/l.

#### 3.7.1.3 The effect of dye concentrations on the degree of dye fixation

Cotton fabrics were pretreated using 15 g/l DCPT and 10 g/l  $\text{Na}_2\text{CO}_3$  and were then dyed by varying the dye concentration in the range of 1-4% o.w.f. in the presence of 20 g/l NaCl.

#### 3.7.2 Dyeing of unmodified cotton fabric by conventional exhaust method

Dyeings of unmodified cotton fabrics at four depths of shade, 1%, 2%, 3% and 4% o.w.f (on weight of fabric) were carried out in similar manner to the dyeing of modified fabric except, in this case, addition of alkali was required. As indicated in the dyeing diagram, the electrolyte, NaCl (x g/l) was added into the dye solution at the beginning of dyeing to promote dye exhaustion. The temperature was raised to 85°C and  $\text{Na}_2\text{CO}_3$  was added to the dyepot. The dyeing was continued for 1 hour. After that, the dyed cotton was taken out and then washed-off in the solution of non-ionic detergent (5 g/l) at the boil for 15 min. to remove unfixed dyes. The washed-off fabric

was dried and the degree of dye fixation was measured. The results obtained were used later for comparison.

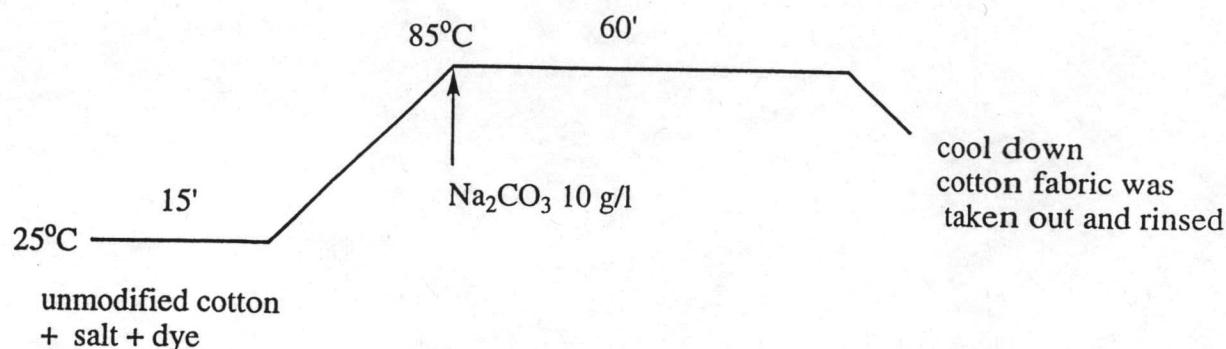


Figure 3.11 Exhaust dyeing of unmodified fabric.

### 3.7.3 Dyeing of modified fabric by pad-dry-cure (thermofixation method)

The thermofixation method involved padding the modified fabric in a pad liquor containing Cibacron Red F-B dye, drying the padded fabric to remove water and then curing the padded fabric at high temperature. Pad-liquors containing 10, 20, 30 and 40 g/l of dye, respectively, were prepared. Each pad liquor was made-up with 100 g/l of urea and 1 g/l of wetting agent. Padding of modified fabrics in pad liquor was carried out in pad mangle at a set pressure to obtain 80% wet pick-up. Padded fabrics were dried at 100°C for 10 min. and followed by baking at 160°C for 3 min. The dyed fabrics were then subjected to washing-off at the boil in the solution of 5 g/l of non-ionic detergent for 15 min. The diagram of dyeing by thermofixation method as shown below:

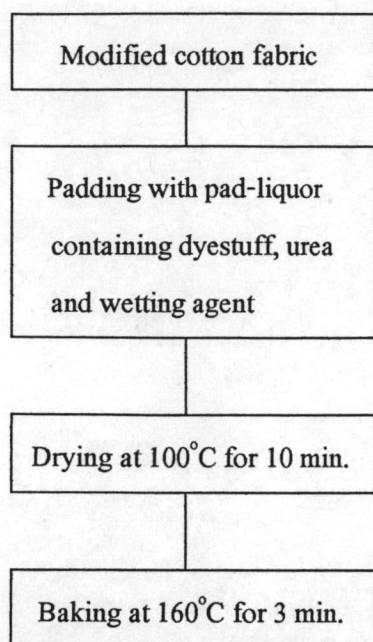


Figure 3.12 Thermofix dyeing method of modified fabrics.

#### 3.7.4 Dyeing of unmodified cotton fabric by thermofixation method

Dyeings of unmodified fabrics were carried out in similar manner to the thermofix dyeing of modified fabric except, in this case, addition of alkali in pad liquor was required. Pad-liquors containing 10, 20, 30 and 40 g/l of dye, respectively were prepared. Each pad liquor was made up with 100 g/l urea, 1 g/l wetting agent and 20 g/l  $\text{Na}_2\text{CO}_3$ . Cotton fabric was then padded in the prepared pad-liquor followed by passing through the mangle which was set the pressure to give 80% wet pick-up. Padded fabrics were dried, baked and soaped in the same conditions according to the conventional thermofixation dyeing.

#### 3.8 Measurement of dye exhaustion

The total amount of dye taken by both modified and unmodified cotton was measured by sampling the dye bath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption ( $\lambda_{\text{max}} = 540$ ) using a UV-visible spectrophotometer (Milton Roy Spectronic



3000 Array). Percentage of dye exhaustion (%E) was calculated using the following equation:

$$\%E = 100 (1 - A_1/A_0)$$

where  $A_0$  and  $A_1$  are the absorbances of dye solution before and after the dyeing process, respectively.



Figure 3.13 UV-visible spectrophotometer.

### 3.9 Measurement of dye fixation for exhaustion dyeing method

To find out how much the amount of dye fixed onto the fiber, the extraction of any unfixed dye from the dyed material was carried out by stripping of dyed fabric in the solution of non-ionic detergent at the boil for 15 min. By using an I.C.S. Micromatch colour measurement system (Macbeth 7000); the reflectance values ( $R$ ) at  $\lambda_{\max}$  (550) of dyed fabrics before and after stripping were obtained. The colour strength of the dyed fabrics were expressed as K/S values calculated by the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R}$$

where  $K$  is the absorption coefficient.

$S$  is the scattering coefficient.

$R$  is the reflectance of the fabric at the wavelength of maximum absorption ( $\lambda_{\max}$ )

Assuming  $K/S$  was proportional to dye concentration on the fiber, the extent of fixation of dye could be calculated using the following equation :

$$\text{Degree of fixation of dye absorbed (\%F)} = \frac{K/S \text{ after soaping} \times 100}{K/S \text{ before soaping}}$$

$$\text{Total dye fixation (\%T)} = \frac{K/S \text{ after soaping} \times (\%E)}{K/S \text{ before soaping}}$$



Figure 3.14 I.C.S Micromatch spectrophotometer.

### 3.10 Measurement of dye fixation for thermofix dyeing method

In thermofixation, different approach for calculation method of total dye fixation from exhaustion method was undertaken.

Method of measurement:

#### 3.10.1 Preparation of standard dye solutions for calibration curve

The dye solutions which had concentrations of exactly 0.004, 0.008, 0.012, 0.016, 0.020 and 0.024 g/l, respectively, were prepared. The absorbance value of each standard dye concentration was measured by using UV-visible spectrophotometer. The determined absorbance was plotted against the corresponding dye concentration. The calibration curve was then established in Figure 3.15.

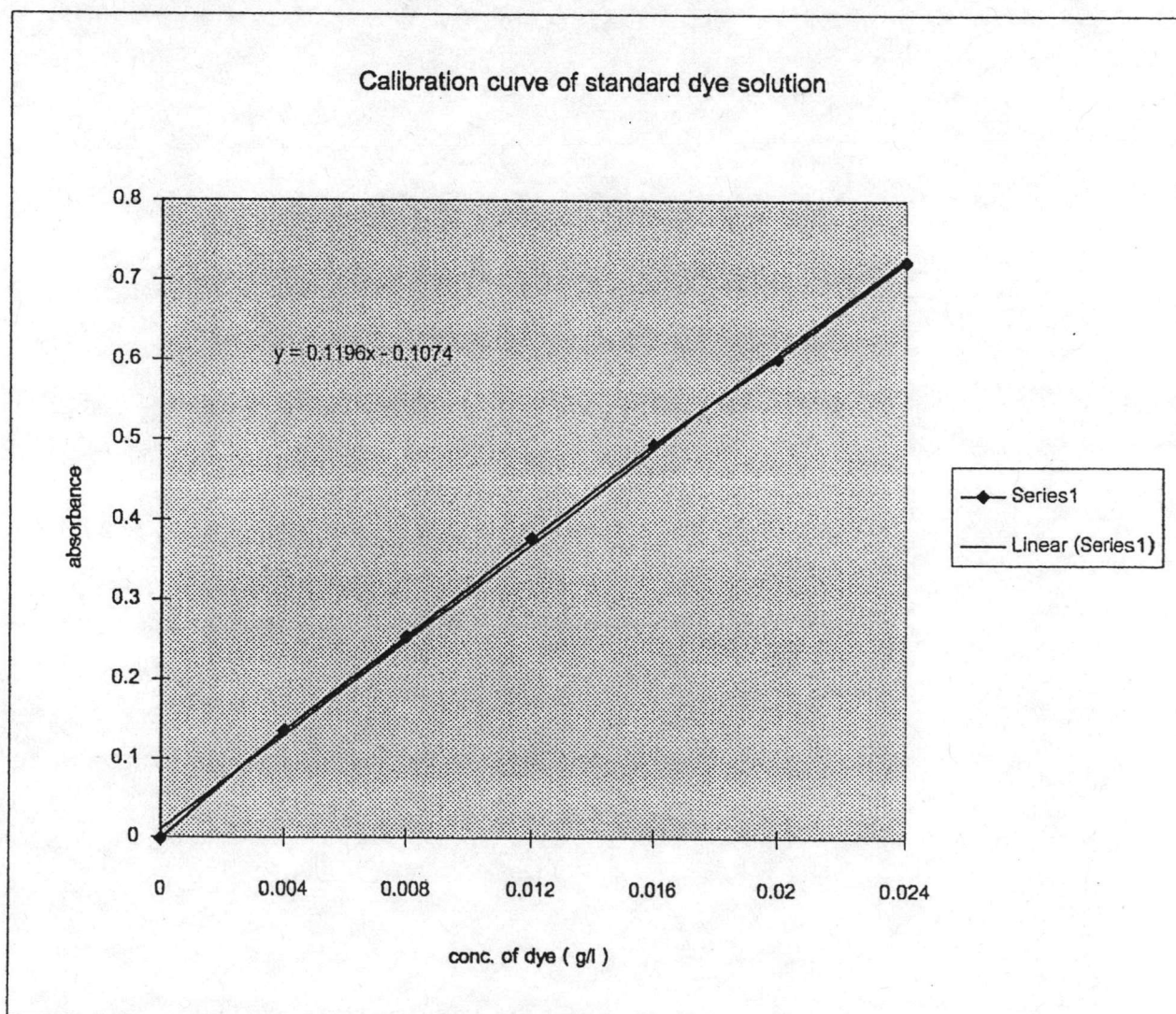


Figure 3.15 Calibration curve of standard dye solution.

### 3.10.2 Calculation of the total dye fixation

First of all, the amount of dyes on the fabric was calculated by using the following equation:

$$\text{The total weight of dye applied to cotton fabric} = \frac{C \times V}{1000}$$

where C = dye concentration

V = total volume of liquid taken by fabric after padding

The dyed cotton fabric after thermofixation was soaped in a solution containing 5 g/l of non-ionic detergent at the boil for 15 min. The volume of soaped-off solution was made-up to 250 ml. with distilled water. 10 ml. of diluted dye solution was taken and then re-diluted again by a factor of 25 in 250 ml. volumetric. After that, the final diluted dye solution was measured at the wavelength of maximum absorption ( $\lambda_{\text{max}}=540$  nm.) by using a UV-visible spectrophotometer. The absorbance of unknown dye solution was recorded. Finally, the concentration of unknown dye solution could be calculated and the percentage of dye fixation (%F) could be determined by using the following equation:

$$\%F = \frac{\text{the weight of fixed dye on cotton fabric after soaping (g)}}{\text{the total weight of dye applied to cotton fabric (g)}} \times 100$$

### 3.11 Total nitrogen content determination

The total nitrogen content of the treated cotton fiber was measured according to the rapid combustion method and quantitatively detected by thermal conductivity detector by using Elemental Analyser (Perkin Elmer PE2400 Series II : option CHN).