

CHAPTER III

Experimental Procedures

3.1 Materials

Cotton Fabric : Unbleached and scoured, plain woven cotton fabric was used throughout this work.

Chemicals and dyes : All chemicals used throughout this work were laboratory reagent grade.

Table 3.1 List of chemicals used in this project

Chemicals	Company
Cyanuric chloride	Fluka
Glycidyltrimethylammonium chloride	Fluka
(3-chloro-2-hydroxypropyl)trimethylammonium chloride	Fluka
Ammonia solution 25%	Merck
Hydrogen peroxide	Carlo Erba
Sodium hydroxide	BHD Laboratory Supplies
Sodium carbonate	Merck
Sodium chloride	Carlo Erba
Non-ionic detergent	U.N.T. Chemical Co., LTD.
Reactive dyes: Procion Crimson CX-B	BASF (Red)
Modercion yellow HE4R	Modern Dyestuff & Pigments (Yellow)

3.2 Equipment

1. Laboratory dyeing machine, Fong's
2. UV-VIS spectrophotometer, Jenway 6405
3. Reflectance spectrophotometer, Macbeth 7000
4. Elemental Analyzer, Perkin Elmer PE2400 series II
5. Optical microscope, Olympus BH2-UMA
6. Xenon Weather Meter, Model X75, Suga Test Instruments Co., LTD. Japan
7. Standard lighting cabinet (Lighting box), VeriVide CAC 60
8. Nuclear magnetic resonance spectrometer, Jeol JNM-A500
9. Magnetic stirrer, Framo-Geratetechnik model M21/1
10. Magnetic bar
11. Ice bath
12. pH meter, Hanna model 400
13. pH paper 0-14, Merck
14. Filter paper, Whatman No. 40 and 42
15. Glasswares
 - Beakers 500, 250, 100 and 10 ml.
 - Volumetric flask 100 and 25 ml.
 - Three necked round bottom flask 250 ml.
 - Desiccator
 - Pipette 25, 10 and 1 ml.
 - Dropper

3.3 Synthesis of the modifying agent, 3-amino-2-hydroxyl-propyltrimethyl ammonium(3,5)-dichlorotriazine

3.3.1 Synthesis of intermediate I from (3-chloro-2-hydroxypropyl)trimethylammonium chloride

A 10 ml. (0.034 mole) of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (65% conc.) and 25 ml. ammonia solution (25% conc.) were added into a three necked round bottom flask. The mixture was heated under reflux for one hour on a heating mantle unit equipped with a magnetic stirrer. After that, the reaction mixture was cooled down to room temperature and left under covered overnight to allow excess ammonia to evaporate. The complete removal of ammonia could be determined using litmus paper.

The intermediate I was then precipitated in acetone. Identification of intermediate I was carried out using titration with standard hydrochloric acid solution to determine the concentration of the present primary amine. In addition ^1H NMR spectroscopy was employed to characterize the structure of the compound.

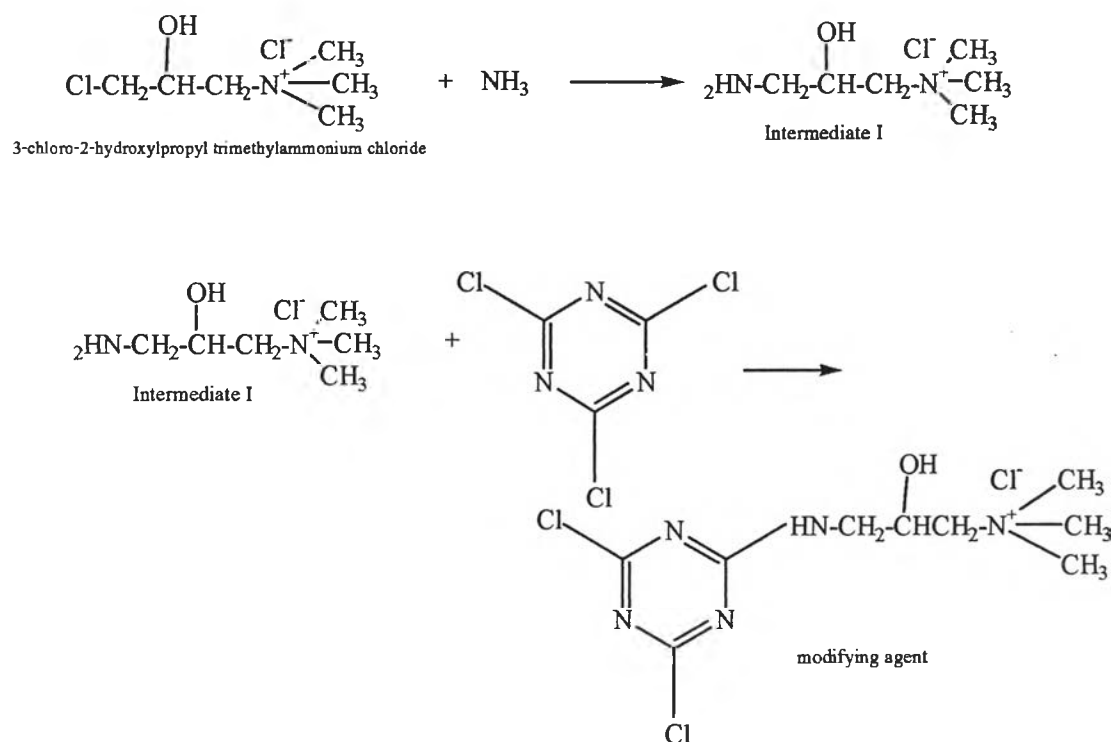
3.3.2 Synthesis of intermediate II from glycidyltrimethylammonium chloride

A 5 ml.(0.037 mole) of glycidyltrimethylammonium chloride (50wt%) and 20 ml. of ammonia solution 25%(excess) were added into a beaker which was placed on a magnetic stirrer. The mixture was then stirred at the room temperature over night. The reaction mixture was left over night to allow excess ammonia to evaporate. Intermediate II was identified by titration with standard hydrochloric acid solution to determine the concentration of the present primary amine. In addition ^1H NMR spectroscopy was employed to characterize the structure of the compound.

3.3.3 Synthesis consistency of the modifying agent, 3-amino-2-hydroxyl-propyltrimethylammonium(3.5)- dichlorotriazine from intermediate I

A 18.4 g. (0.1 mole) of cyanuric chloride, 100 ml. of acetone and 100 g. of ice were added into a beaker 250 ml. in ice bath which was placed in a magnetic stirrer at the temperature of 0-5°C. After that the intermediate I was added dropwise into the suspension over 10 min. The pH of reaction mixture was maintained between 4 to 6 by the addition of saturated Na₂CO₃ solution and the temperature being kept below 5°C throughout. The complete reaction would be obtained when the pH of reaction mixture was stable. Finally, the complete reaction was precipitated in acetone at the temperature of 5°C, washed with acetone and dried in a desiccator.

The reaction scheme may be written as follows:

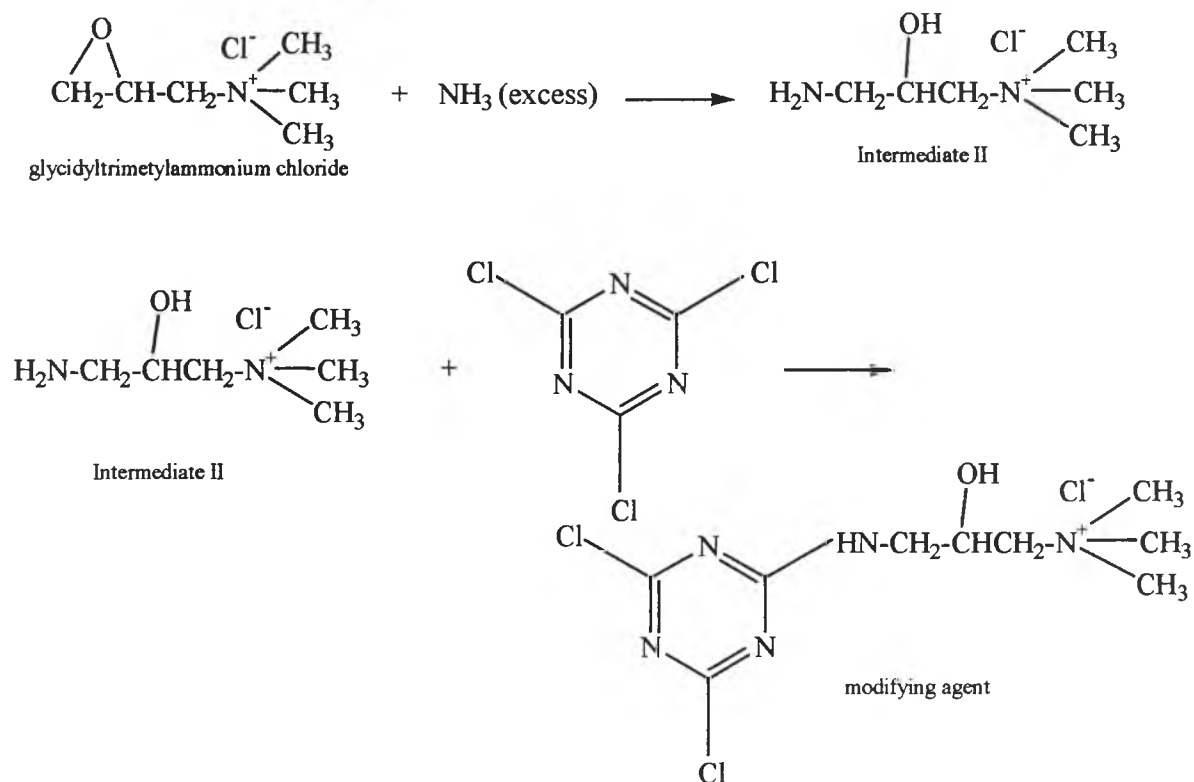


Scheme 3.1 The overall reaction scheme of the preparation of modifying agent from intermediate I

3.3.4 Synthesis consistency of the modifying agent, 3-amino-2-hydroxyl-propyltrimethylammonium(3.5)- dichlorotriazine from intermediate II

A 6 g.(0.033 mole) of cyanuric chloride, 25 ml. of acetone, 2.5 ml. of distilled water and 10 g. of ice were added into a beaker in ice bath which was placed in a magnetic stirrer at the temperature of 5°C. The intermediate II was added dropwise into the suspension over 10 min. The pH of reaction mixture was maintained between 4 to 6 by the addition of saturated Na₂CO₃ solution and the temperature being kept below 5°C throughout. The complete reaction would be obtained when the pH of reaction mixture was stable. Finally, the complete reaction was precipitated in acetone at the temperature of 5°C, washed with acetone and dried in a desiccator.

The reaction scheme may be written as follows:



Scheme 3.2 The overall reaction scheme of the preparation of modifying agent from intermediate II

3.4 Method of the modification and bleaching of cotton fabric in single-bath process

Application of the modifying agent was carried out using exhaustion method. Plain woven, scoured cotton fabric was cut into rectangles each weighed exactly 5.00 grams and was treated in solutions of different concentrations of modifying agent ranging from 0-40 g/l sealed stainless dye pots housed on the Fong's laboratory dyeing machine (Figure 3.1) at a liquor ratio of 1:10. Treatment was commenced at room temperature for 10 min. and then 20 g/l Na_2CO_3 was added to dye pots. The temperature was raised to 55°C for 30 min. and then 5 ml/l H_2O_2 and 2 g/l NaOH were added to dye pots, and the temperature was raised to 90°C . The temperature was maintained for 30 min. before the dye pots being taken out. Finally, the modified bleached cotton fabric was rinsed with water and dried in the open air.

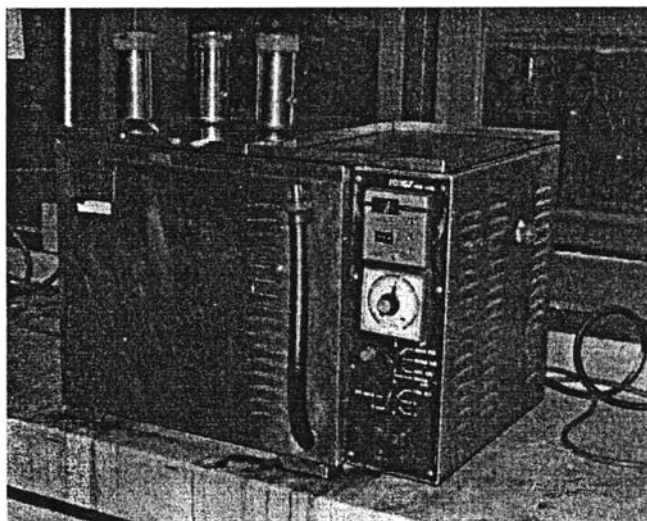


Figure 3.1 Fong's laboratory dyeing machine

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

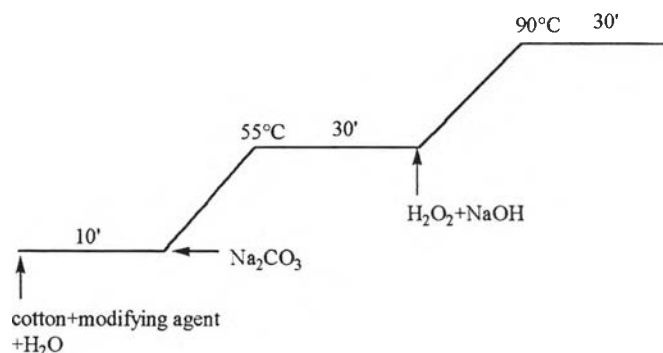


Diagram 3.1 Concurrent bleaching and modifying cotton in single bath

3.5 General Dyeing Procedure

3.5.1 Dyeing of modified fabric using exhaustion method

Modified cotton fabric was dyed in a solution of various concentrations of commercial Procion Crimson CX-B and 20 g/l Na₂CO₃. All dyeings were conducted in 100 ml. sealed stainless steel dye pots housed on the Fong's laboratory dyeing machine at the liquor ratio of 1:10. Dyeing of modified cotton fabric was commenced at 80°C for 40 min. The dyed cotton fabrics were taken out and rinsed thoroughly in tap water and cut into two equal portions. One of these portions was soaped in a boiling solution containing 2 g/l Na₂CO₃ and 5 g/l nonionic surfactant for 20 min. (liquor ratio 1:20). The dyeing profile of the exhaustion dyeing can be shown as follows:

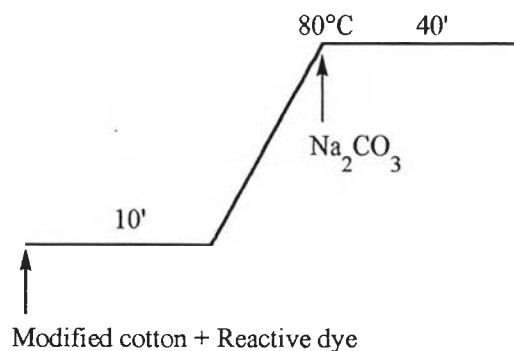


Diagram 3.2 The dyeing profile of modified fabric using exhaustion method

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

3.5.1.1 The effect of modifying agent concentrations on the degree of dye fixation

The modifying agent concentrations in modifying solutions were varied from 0-40 g/l. The dyeing of modified cotton fabric in the absence of salt was performed in a solution of 2% owf Procion Crimson CX-B at 80°C for 40 min. in the presence of 20 g/l Na₂CO₃. The dyeing procedure was followed according to the above method.

3.5.1.2 The effect of dye concentrations on the degree of dye fixation

The dyeing of modified cotton fabric in the absence of salt was investigated. Modified cotton fabrics with different concentrations of modifying agent were dyed in solutions containing various dye concentrations in the range of 1-4% owf in the presence of 20 g/l Na₂CO₃.

3.5.2 Dyeing of unmodified cotton fabric by conventional exhaustion method

Dyeings of unmodified cotton fabrics at four depths of shade, 1%, 2%, 3% and 4% owf of Procion Crimson CX-B were conducted in similar manner to the dyeing of modified fabrics and can be divided into two categories; dyeing with and without electrolyte, NaCl. As indicated in the dyeing diagram (Diagram 3.3), the varied amount of electrolyte (NaCl 0, 10, 20, 30 and 40 g/l) was added into the dye solution at the temperature of 50°C for 10 min. to promote dye exhaustion. Then the temperature was raised to 80°C and Na₂CO₃ was added to the dye pots. The dyeing was continued for 40 min. After that, the dyed cotton fabrics were taken out and then washed-off in the solution of 5 g/l nonionic surfactant and 2 g/l Na₂CO₃ at the boil for 20 min. to remove unfixed dyes. Finally, the washed-off fabric was dried and the degree of dye fixation was measured. The results obtained were used later in comparison with the modified cotton fabrics.

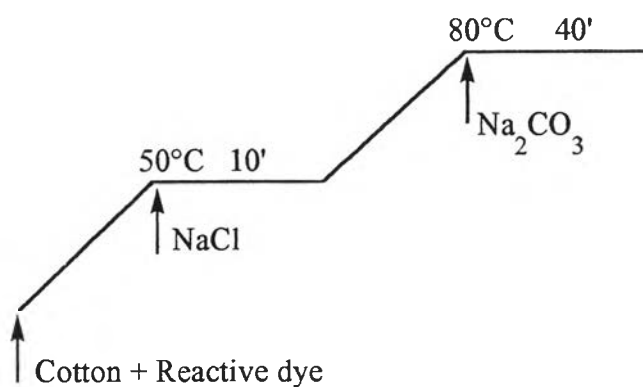


Diagram 3.3 Exhaust dyeing of unmodified fabric.

3.6 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 ^1H , ^{13}C , ^{14}N etc. The simplest NMR experiment consists of 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.

For identification of the chemical structure of modifying agent, the differences in frequency are measured with respect to some reference group of nuclei. For ^1H NMR technique, the sample was dissolved in D_2O , used as the internal reference and recorded on a JNM 500 MHz from Jeol, Japan.

3.7 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).

3.8 Evaluation of whiteness property of modified bleached cotton fabric

To measure the effect of the modifying agent on bleaching performance of modified and unmodified bleached cotton fabric obtained from single-bath treatment, the samples were subjected to whiteness index measurement using Macbeth spectrophotometer (Figure 3.2) to obtain the average whiteness value (front and back of fabrics). Measurement parameters were used as follows: UV (excluded or included): 10° observer.



Figure 3.2 Macbeth spectrophotometer

3.9 Measurement of dye exhaustion

The total amount of dye taken by both modified and unmodified cotton fabrics was measured by sampling the dye bath before and after the dyeing process. The absorbance of the equally diluted dye solutions was measured at the wavelength of maximum absorption of each dye using a UV/VIS spectrophotometer (Figure 3.3). The percentage of dye exhaustion (%E) was calculated with the following equation:

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

Where A_0 and A_1 are the absorbance of dye solution before and after dyeing process respectively.



Figure 3.3 UV/VIS spectrophotometer

3.10 Measurement of dye fixation

The degree of dye fixation was determined spectrophotometrically with an Instrumental Color System (I.C.S) spectrophotometer (Macbeth 700) which was used to measure the reflectance values of the coloured samples in the visible region of the spectrum (400-700 nm.), the reflectance values was measured at λ_{\max} 550 nm. for Procion Crimson CX-B and λ_{\max} 440 nm. for Modercion yellow HE4R.

The color strength of the fabrics before and after soaping were expressed as K/S values calculated by the Kubelka-Munk equation.

$$K/S = (1-R)^2/2R$$

Where K is the absorption coefficient

S is the scattering coefficient

R is the reflectance of the fabric at the wavelength of maximum absorption

(λ_{\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:

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

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

The apparent degree of dye fixation (%F) describes the amount of exhausted dye which is fixed covalently, thus giving an indication of the amount of unfixed dye which is removed during a washing-off process to achieve maximum wet fastness properties. And the total dye fixation (%T) describes the percentage of fixed dye compared to the overall dye applied at the beginning. Usually, %T value is less than %F value.

3.11 Image microscopic analysis (fiber cross sectional examination)

Although microscopic observations are extremely useful for determining numerous structural features and influences on fibers, careful sample preparation usually required is time-consuming and tedious. Thus, image analysis optically scanned with television camera was introduced as an alternative optical method to determine structural changes or staining in fibers.

Microscopic analysis of modifying agent, 3-amino-2-hydroxyl-propyltrimethyl ammonium(3,5)-dichlorotriazine,-treated dyed yarn was investigated using optical microscope (Figure 3.4). The fiber samples that sharply cut in perpendicular to the fiber axis were placed against transmitted light to be magnified by lenses and viewed on a screen to show the details of structural features, changes in fiber, and staining of dye.

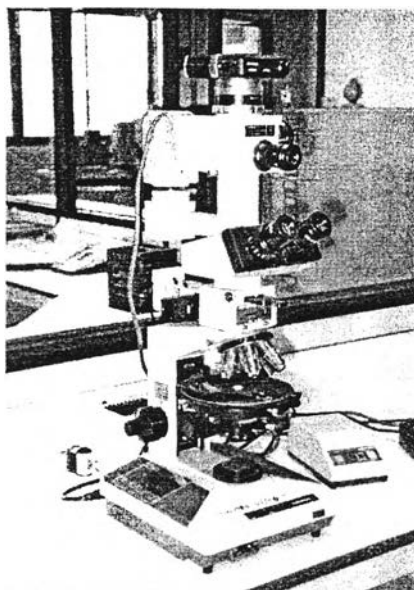


Figure 3.4 Optical microscope

3.12 Measurement of colorfastness

The ISO 105-BO2 : 1994 color fastness to artificial light was used to determine the resistance of the color of textile to the action of an artificial light source representative of natural daylight (D_{65}). In the test, a dyed fabric is exposed to Xenon arc fading cabinet under prescribed conditions along with eight dyed blue wool as references. These references are blue wool cloths dyed with the dyes listed in Table 3.2.

Table 3.2 Dyes for blue wool references 1 to 8

Reference	Dye-color index designation
1	C.I. Acid Blue 104
2	C.I. Acid Blue 109
3	C.I. Acid Blue 83
4	C.I. Acid Blue 121
5	C.I. Acid Blue 47
6	C.I. Acid Blue 23
7	C.I. Solubilized Vat Blue 5
8	C.I. Solubilized Vat Blue 8

The range from 1 (very low color fastness) to 8 (very high fastness) so that each higher numbered reference is approximately twice as fast as the preceding one. At intervals the dye is assessed visually to compare its fading rate with that of the references. The light fastness rating corresponds to the number of blue reference showing a contrast equal to that of the test dyed sample (visual contrast between exposed and unexposed parts of the specimen).

Fastness to light of modified and unmodified dyed cotton fabrics was conducted using Xenon Weather Meter (Figure 3.5), Model X75 (Suga Test Instruments Co., LTD, Japan) and following the ISO testing method. Blue wool fabrics were used as the standard of numerical ratings and were assigned to describe the colorfastness of the fabrics.

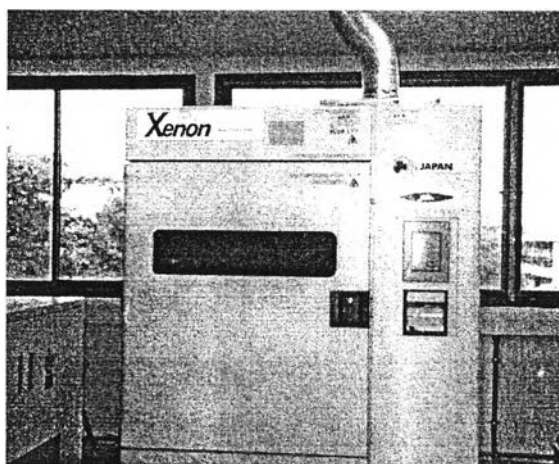


Figure 3.5 Xenon Weather Meter