CHAPTER 3

EXPERIMENT

3.1 MATERIALS

3.1.1 Yarn

The yarn used was tape yarn made of 100 % polypropylene. It was hot-stretched after polypropylene pellets had been extruded into film and slit into narrower tape-like yarn. Its final appearance was transparent and colorless, about 3.1 mm. in width and about 54 μ in thickness. It had been recieved from Pacific Polysack Industry Co.,Ltd.

3.1.2 Fabric

White 100 % polyester fabric which was already scoured and heat-set was used.

3.2 DYES, AUXILIARIES AND CHEMICALS

3.2.1 Dyes

All dyes used were disperse dyes of both azo and anthraquinone types.

36

3.2.1.1   C.I. Disperse Orange 3 (Kayalon Fast Orange GR)from Metro Company Limited.

3.2.1.2   C.I. Disperse Red 1 (Kayalon Fast Scarlet B)from Metro Company Limited.

3.2.1.3   C.I. Disperse Orange 5 (Kayalon Fast Brown R) from Metro Company Limited.

3.2.1.4   C.I. Disperse Brown 1 (Kayalon Polyester Brown GR-SE) from Metro Company Limited.

3.2.1.5   C.I. Disperse Violet 8 (Palanil Violet 3 B) from BASF.

3.2.1.6   C.I. Disperse Violet 28 (Resolin Violet RL 200%) from Bayer Co.,Ltd.

3.2.1.7   C.I. Disperse Red 60 (Palanil Red BFY 200%) from BASF.

3.2.2 Auxiliaries

3.2.2.1 Dispersing agent (EGANAL PS). Its appearance was viscous clear liquid with colorless. It was supplied by Hoechst.

3.2.2.2 Carrier (Matexil CA-MN).It composed of methyl naphthalene as major constituent, with anionic and non-ionic emulsifying agents. Its appearance was clear yellow liquid. It was supplied by ICI.

3.2.3   Chemicals

3.2.3.1   Chlorobenzene (Technical grade,Carlo
Erba, Italy)

3.2.3.2   Sodium hydrosulphite
(Commercial grade)

3.2.3.3   Sodium hydroxide (Commercial grade)

3.2.3.4   Non-ionic soap (Luxnon 9 N)
(Commercial grade)

3.2.3.5   Acetone (Commercial grade)

3.3   INSTRUMENT AND APPARATUS

3.3.1   Dyeing Machine

3.3.1.1   Colourpet 12 Type 12 LMP-E, Nippon
Dyeing   Machine Mfg. Co., Ltd. in Japan. It contained 12
stainless pots (cylinder-like shape) served as dyebaths of
250-350 ml.

3.3.1.2   The Jet Dyeing Apparatus Type JF,
Werner Mathis AG (Textile Machines-Laboratory Equipment),
Switzerland

3.3.2   Double Beam Spectrophotometer Model UVIDEC-
650,JASCO, Japan

3.3.3   Quartz Rectangular Cuvette, 10 mm., Starna

3.3.4 Ultrasonic Cleaner Model BRANSONIC 12, Branson
Cleaning Equipment Company, U.S.A.

3.3.5 A Balance which can weigh exactly to 0.0001 gm.

3.3.6 Griffin Oil Bath 100 Series, Griffin & George
Ltd., London

3.3.7   A Stopclock

3.3.8   Fade   O-Meter: Xenon   Arc Lamps Model 25 WR, Atlas Electric Devices Company, U.S.A.

3.4   PRELIMINARY STUDY OF DYEING OF POLYPROPYLENE TAPE YARN WITH DISPERSE DYES

Polypropylene tape yarn was dyed with seven available disperse dyes at three representative temperatures, i.e., 90, 110 and 130 °C, in the presence of three representative concentrations of carrier (Matexil CA-MN), i.e., no carrier, 2 and 5 g/l, in this section. Dyeing of tape yarn with each disperse dye was performed as followed:

3.4.1   Prepare   three   samples   of   tape yarn of one gram each.

3.4.2   Prepare dye solution by dissolving 0.0300 gm. of dye   in   270   ml of distilled water at about 60 °C with 0.27 gm. of dispersing agent (EGANAL PS) and then divided it   into   3   dyebaths of 90 ml each. The composition of each dyebath just prepared was:

Initial Dyebath Concentration - 1 % owf. (on weight
                                         of fibre/fabric)
Liquor Ratio   - 90:1 (Tape yarn 1
                                         gm. per 90 ml. of
                                         water)
Dispersing Agent Concentration - 1 g/l

3.4.3   Add   emulsion   of   carrier,   prepared   by stirring 1 part (0.18 ml) of carrier in 3 parts (0.54 ml) of water, into the dyebath (in 3.4.2) requiring the

carrier concentration of 2 g/l.

3.4.4 Add emulsion of carrier, prepared by stirring 1 part (0.45 ml) of carrier in 3 parts (1.35 ml) of water, into the dyebath (in 3.4.2) requiring the carrier concentration of 5 g/l.

3.4.5 Immerse the three samples of tape yarn prepared in 3.4.1 into each dyebath and dyed them soon after by Jet Dyeing Machine at 90 °C for 60 minutes with rate of increasing temperature about 4 °C/min (Figure 3.1) and speed of rotation of dyebath holder through dyeing period at 50 RPM.
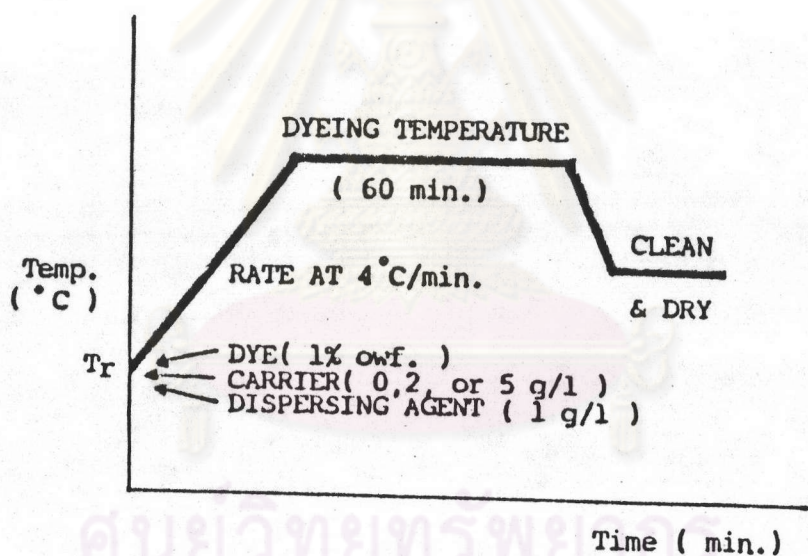
Figure 3.1 Temperature increasing diagram

3.4.6 Rinse all the tape yarns after dyeing and allowed them to dry.

3.4.7 Repeat all the above steps (from 3.4.1 to 3.4.6) with the same dye at 110 °C, and 130 °C respectively.

3.4.8 Repeat all the above steps (from 3.4.1 to 3.4.7) with the other six dyes.

3.5 DYEING POLYESTER FABRIC WITH SELECTED DISPERSE DYES

From section 3.4 above, it was apparent that not all the dyes could color the tape yarn under the test conditions. Two dyes in particular were considered not capable of dyeing tape yarn on the basis of comparatively inadequate depth of shade. The two dyes are C.I. Disperse Brown 1 and C.I. Violet 8. Thus these two dyes were neglected for all subsequent experiments.

Polyester fabrics, which were dyed with five selected disperse dyes of various shade, were primarily prepared for the subsequent calibration curve preparing experiment. The procedure of dyeing were described as in the following:

3.5.1 Preparing the Fabric Sample

Five pieces of white 100 % polyester fabric were prepared using a pattern in cutting to get all samples of nearly about the same size. Each piece of fabric had its width about 8-8.5 cm. which did not exceed the height of the stainless sample holder (about 9 cm.) used for dyeing with the Colourpet 12 Machine, and had its length about 60-65 cm. providing the weight of about 10 gm. for each sample.

3.5.2 Preparing Dye Solution

Each of the five selected dyes of required weight (weighed accurately for 0.3000 ± 0.0005 gm.) was separately dissolved in 250 ml. of distilled water at the temperature of 60 °C with dispersing agent 0.25 gm. of weight. While maintaining at this temperature for about 10 minutes, stirred the solution for sometime to get well dispersed dye solution.

3.5.3 Dyeing Procedure

All five dye solutions already prepared above (in 3.5.2) were poured separately into five stainless pots used for dyeing in the Colourpet 12 Machine The pots were all assembled in the machine the water-bath temperature (tank temperature) of which was controlled at 90 °C. Then after a few minutes, each piece of fabric prepared in 3.5.1 was immersed in each pot which acted as its dyebath when dyeing. The composition of each dyebath (or pot) was:

Initial Dyebath Concentration – 3 % owf.(on weight of fibre/fabric)

Liquor Ratio – 25:1(Fabric 10 gm. per 250 ml. of water)

Dispersing Agent Concentration– 1 g/l

The temperature was then gradually raised up to 130 °C, which was the dyeing temperature, with the

rate of increasing at 1 °C/min. (Figure3.2). The length of dyeing was 60 minutes. After dyeing, the dyebath was cooled to below 60 °C before all the dyed fabric samples were rinsed with water.
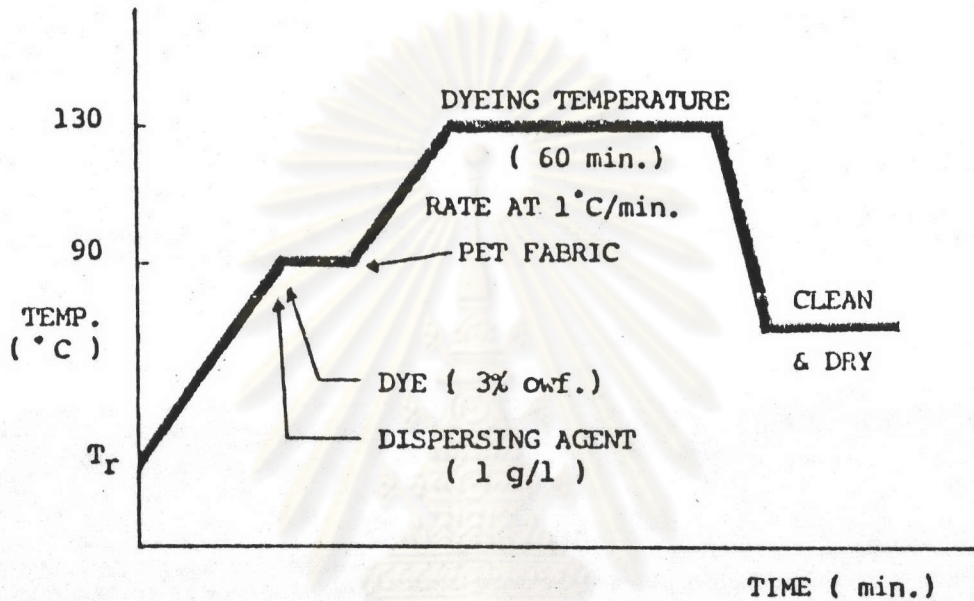

Figure 3.2 Temperature increasing diagram

3.5.4 Reduction Clearing

Since disperse dye was substantially water-soluble, so after dyeing there would be some dye particles loosely attached onto the fabric and could be removed by reduction clearing treatment. The dyed fabric samples which were rinsed from the above dyeing procedure were separately immersed in the solution bath whose composition was:

Sodium hydrosulphite ($Na_2S_2O_4$)   1 g/l

Sodium hydroxide (NaOH)   1 g/l

Non-ionic soap (Luxnon 9 N)   1 g/l

The treatments were carried out at 50 $^\circ$C for 15 minutes before the five fabric samples were rinsed againwith water and allowed to dry.

3.6 CALIBRATION CURVE PREPARATION

Calibration curve was a curve plotted between various concentrations of a kind of solution, i.e., dye solution, against the absorbance measured spectrophotometrically corresponding to each concentration. Calibration curve of each disperse dye used in this study was important for the purpose of determining the amount of dye uptake per 1 gm. weight of polyester fabric or polypropylene tape yarn (mg. of dye/ 1 gm. of fabric or tape yarn) and the purity of each disperse dye in percent in the subsequent experiment. The steps in preparing the calibration curves were as followed:

1. Preparation of the stock solution of each purified disperse dye.

2. Determination of the wavelength at which each disperse dye absorb maximum light in the visible region (λ_{max}- in nanometer).

3. Determination of the concentration of each stock solution prepared above in step 1.

4. Preparation of a series of standard solution with various concentrations for each stock dye solution and measure their absorbance.

5. Plotting calibration curve.

The detail of each step was as described in the following:

3.6.1 Preparation of the Stock Solution of Each Purified Disperse Dye

Since the commercial disperse dyes (in powder form) used for this study were not pure. They were manufactured by mixing, with dispersing agent and some diluents or some additives. So it was necessary to purify them before subsequent experiment was done. The purification that could be done was easily classified into 2 ways, namely,

3.6.1.1 Crystallization from organic solvents repeatedly to remove all impurities combined with the dye till the pure dye was left. This method was time consuming and difficult because to find proper solvents for dissolving all many kinds of impurities was not so easy sometime. So an alternative method was presented below.

3.6.1.2 Solvent extraction of pure dye from dyed fabric, e.g. polyester fabric. In the case of dyeing polyester fabric using disperse dye and without any carrier, only the dye was adsorbed onto the fabric. So when the dyed

fabric was extracted by a suitable solvent, the pure disperse dye on the fabric would come out and after the removal of solvent, pure dye sample would be obtained. This method was chosen in this study.

The polyester fabrics, already dyed with disperse dyes of each color as described in section 3.5, were used for this experiment. Dyed fabric of each color of about 3 gm. (see Table 3.1) was weighed and placed in a 250 ml round-bottom flask equipped with an water condenser on the top. Fill the flask with 120 ml of chlorobenzene and extraction of dye proceeded during heating up to the boiling point of the solvent used and maintained for 15 minutes. Then collect the dye solution, after cooling for sometime, in a 250 ml volumetric flask through filter paper. Extract again with 120 ml of chlorobenzene and collect this second dye solution, in the same volumetric flask and then filled upto the mark by the same solvent. Shake the flask gently to mix the solvent. By doing the same in all the above steps for the remaining dyed fabrics, five stock solutions of each purified disperse dyes were ultimately obtained.

Table 3.1   The weight of fabrics, dyed with various
             dyestuffs, used for preparing stock solutions

DYESTUFF	WEIGHT (gm.)
C.I. Disperse Orange 3	3.2610
C.I. Disperse Red 1	3.2082
C.I. Disperse Orange 5	3.1341
C.I. Disperse Violet 28	3.1333
C.I. Disperse Red 60	3.2003

3.6.2   Determination of λ_{max} for Disperse Dyes

Dye solutions suitable for spectrophotometric measurement were prepared by taking out a small volume of dye solution from each stock solution in section 3.6.1 and diluted with chlorobenzene until optimum concentration was obtained. Then the absorption spectra corresponding to each dye were measured separately by UVIDEC-650 spectrophotometer using chlorobenzene as blank. The wavelength determined was in the region of 300-700 nm which was visible light region and the chlorobenzene solvent caused no interference on the absorbance of all measurements (determined prior to desired measurements, Figure 3.3). The conditions of operating were as followed:

scale	=	40	nm/cm.
scan speed	=	100	nm/cm.
% T ABS scale	=	0.000 - 0.600	ABS.

The absorption spectra of each disperse dye solution were shown in Figure 3.4 - Figure 3.8 and the wavelengths corresponding to peak of maximum absorption of each dye were listed in Table 3.2.
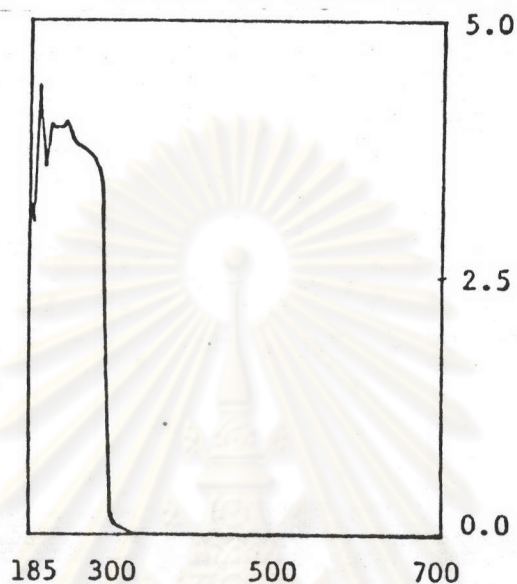

Figure 3.3   Absorption spectrum of Chlorobenzene with Air as blank
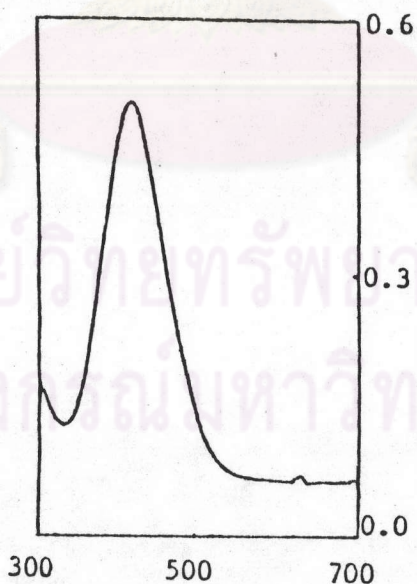

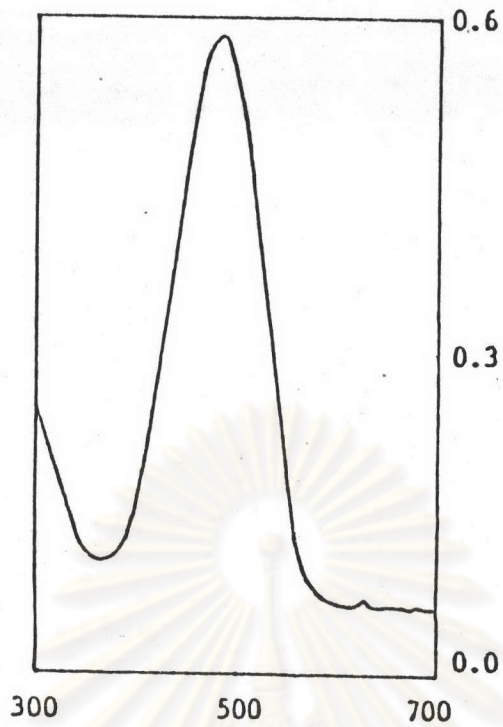Figure 3.4   Absorption spectrum of C.I. Disperse Orange 3

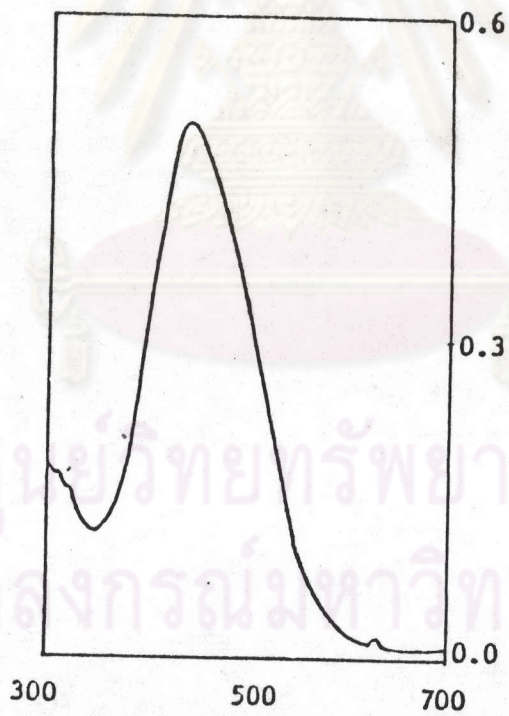Figure 3.5   Absorption spectrum of C.I. Disperse Red 1

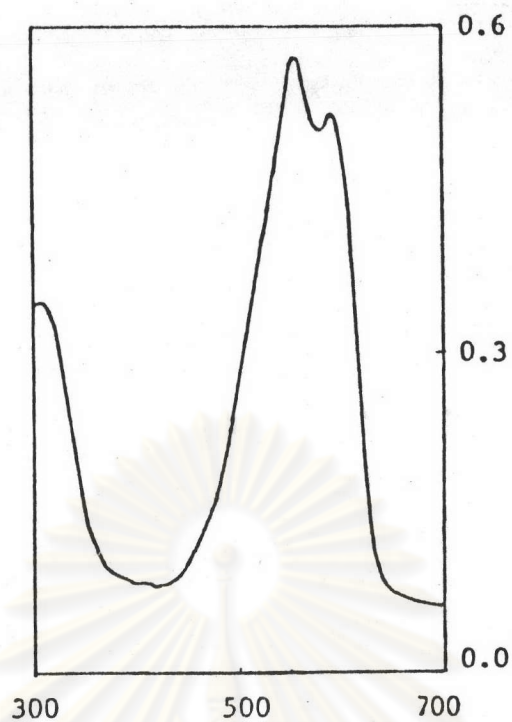Figure 3.6   Absorption spectrum of   C.I. Disperse Orange 5

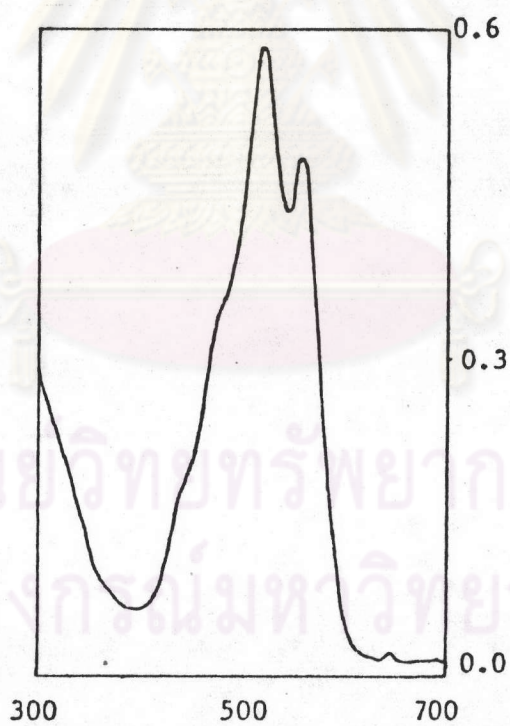Figure 3.7   Absorption spectrum of C.I. Disperse Violet 28

Figure 3.8   Absorption spectrum of C.I. Disperse Red 60

Table 3.2   The wavelengths of maximum absorption for various
disperse dyes in chlorobenzene solvent

DYESTUFF	λ_{max} (nm.)
C.I. Disperse Orange 3	417.2
C.I. Disperse Red 1	482.8
C.I. Disperse Orange 5	436.0
C.I. Disperse Violet 28	553.2
C.I. Disperse Red 60	516.8

3.6.3   <u>Determination   of the Concentrations of Stock
Solutions</u>

Before   a   series   of   standard   solutions of
each   disperse   dye   could   be   prepared   in next section of
experiment,   the   concentration of each stock solution taken
out   for   preparing   should   be   already   determined.   By
evaporating   chlorobenzene   solvent   out   of   each   stock
solution   (in   the   section 3.6.1 above) of exact volume and
determining the weight of the dye left, the concentration
of   each   stock   solution   then   could   be   obtained.   The
procedure for each stock solution was:

3.6.3.1   Determine   the   constant weights   of
two   50 ml   beaker   after   2-3 times of drying in an oven at
above 100 °C and kept cool in a desiccator.

3.6.3.2 Pipet 100 ml of stock solution into two 250 ml beaker individually and heat the beakers until a small amount of stock solution was left in each beaker.

3.6.3.3 Transfer stock solution of each beaker from above into two 50 ml beakers of known exact weights in 3.6.3.1 and continued evaporating in anovenat 130 °C until their constant weights were obtained.

3.6.3.4 Determine the dye weight of the pipetted 100 ml. of each stock solution and calculated their concentrations in mg/l

The average concentration of stock solutions of various disperse dyes were shown below in Table 3.3.

Table 3.3 The concentrations of stock solutions of various disperse dyes

DYESTUFF	CONCENTRATION (mg./l)
C.I. Disperse Orange 3	214
C.I. Disperse Red 1	255
C.I. Disperse Orange 5	234
C.I. Disperse Violet 28	171
C.I. Disperse Red 60	328

3.6.4 Preparation of Standard Solutions and Their Absorbance Measurements

A series of standard solutions for each dye were prepared by pipetting stock solution (in section 3.6.1) in various volumes to yield, after diluting them with chlorobenzene into equal volume of 10 ml, an absorbance in the range of 0.1-1.0. This is the range which Beer's law can be effectively applied in subsequent calibration curve plotting. The absorbance measurements for each series of standard solutions were performed at its corresponding λ_{max} (Table 3.2) by using UVIDEC-650 Double Beam Spectrophotometer.

3.6.5 Calibration Curve Plotting

The calibration curve for each dye was plotted between its series of various concentrations of standard solutions against their corresponding absorbances. By applying the least square method, a linear straight line representing the relation between the concentration and the absorbance for each dye was obtained and the general expression of their relationship was in the form CONC = K(ABS) + C where CONC was concentration, ABS was absorbance, K was a constant or the slope of the curve, and C was the intercept on concentration axis. The data of preparing each calibration curve were summarized in Table 3.4, the calibration curves were shown in Figure 3.9(A) - 3.9(E) and the expressions for each curve were presented in Table 3.5 consecutively.

Table 3.4   The data for calibration curves preparation

(A)   C.I. Disperse Orange 3

Conc.(mg/l)	4.280	6.420	8.560	12.84	17.12	21.40
ABS	0.195	0.292	0.390	0.587	0.787	0.987

(B)   C.I. Disperse Red 1

Conc.(mg/l)	2.550	5.100	7.650	10.20	15.30	20.40
ABS	0.113	0.227	0.342	0.458	0.683	0.902

(C)   C.I. Disperse Orange 5

Conc.(mg/l)	4.680	7.020	9.360	14.04	18.72	23.40	28.08	35.10
ABS	0.130	0.183	0.246	0.364	0.484	0.604	0.718	0.882

(D)   C.I. Disperse Violet 28

Conc. (mg/l)	5.130	6.840	10.26	13.68	17.10	20.52	25.65	34.20	41.04
ABS	0.110	0.150	0.224	0.298	0.368	0.442	0.555	0.754	0.890

(E)   C.I. Disperse Red 60

Conc.(mg/l)	6.560	9.840	13.12	19.68	26.24	32.80	39.36
ABS	0.130	0.207	0.281	0.401	0.531	0.684	0.809

Figure 3.9 (A)   Calibration curve of C.I. Disperse Orange 3

Absorbance

Figure 3.9 (B)   Calibration curve of C.I. Disperse Red 1
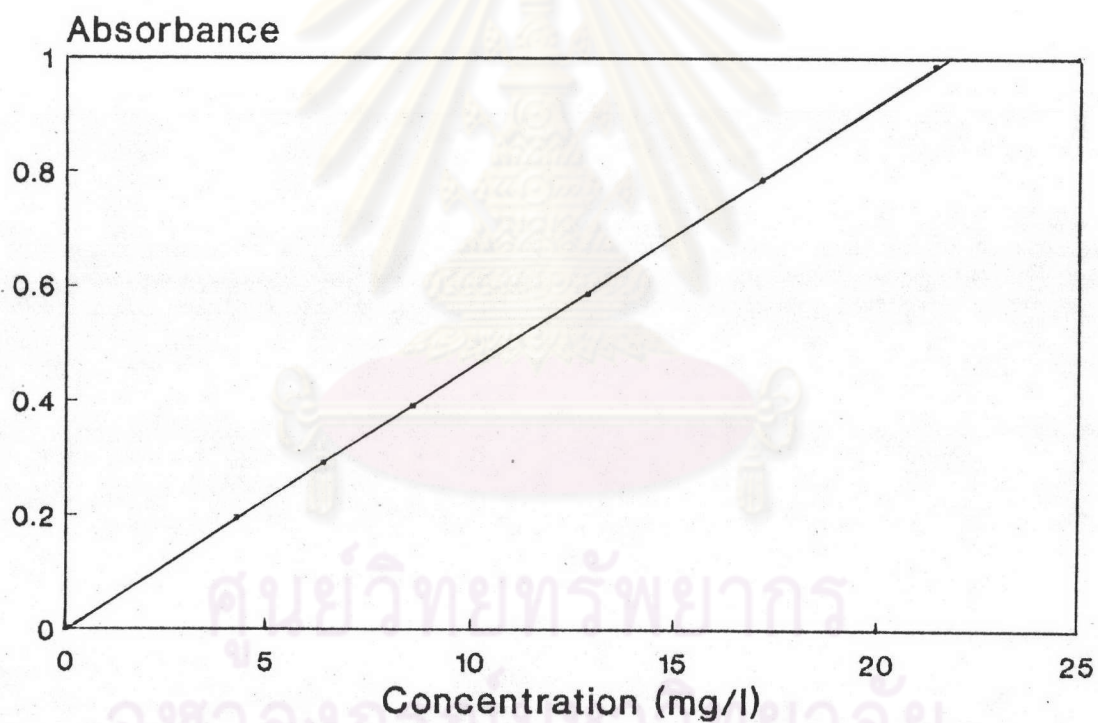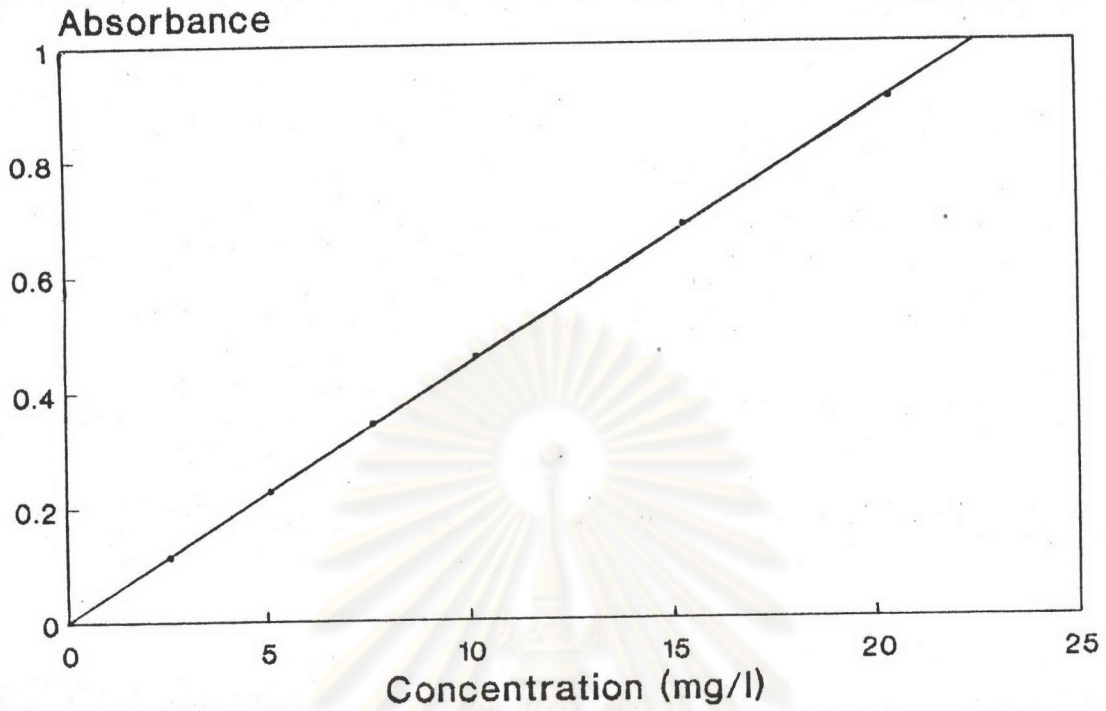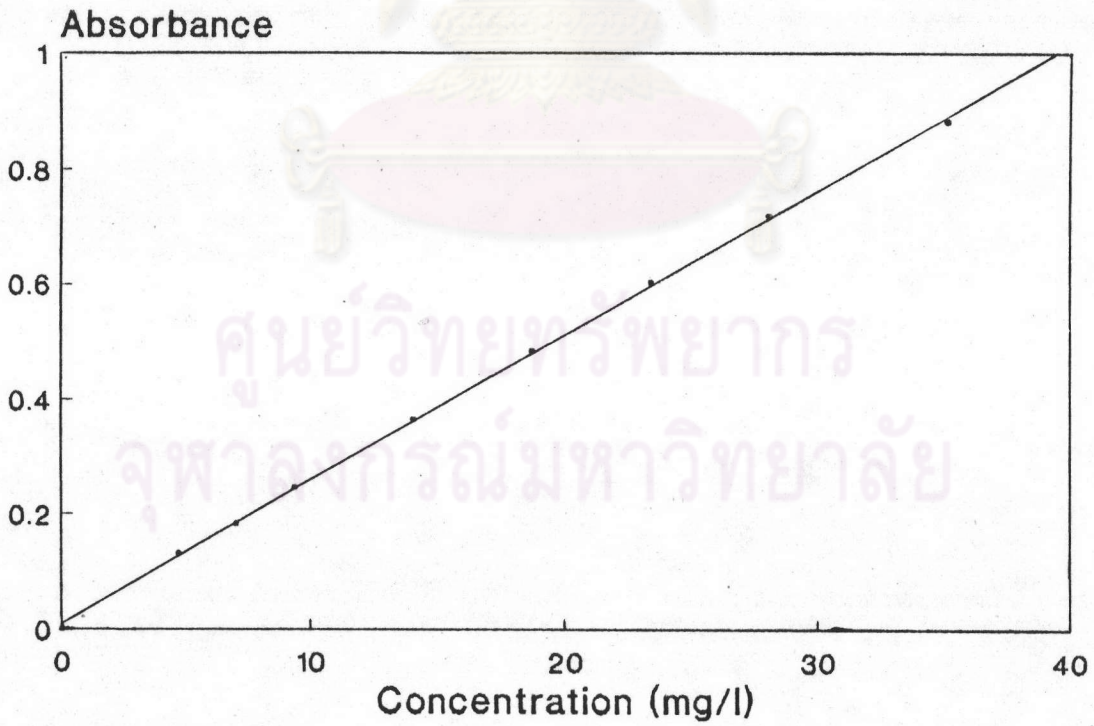
Absorbance

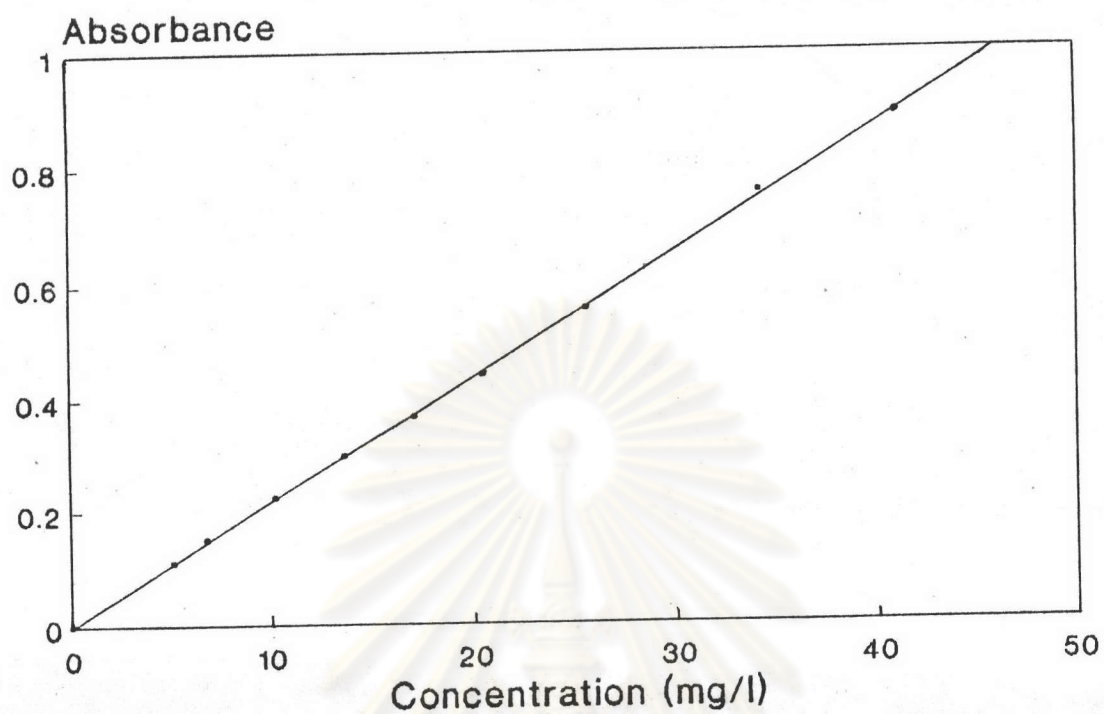Figure 3.9 (C)   Calibration curve of C.I. Disperse Orange 5
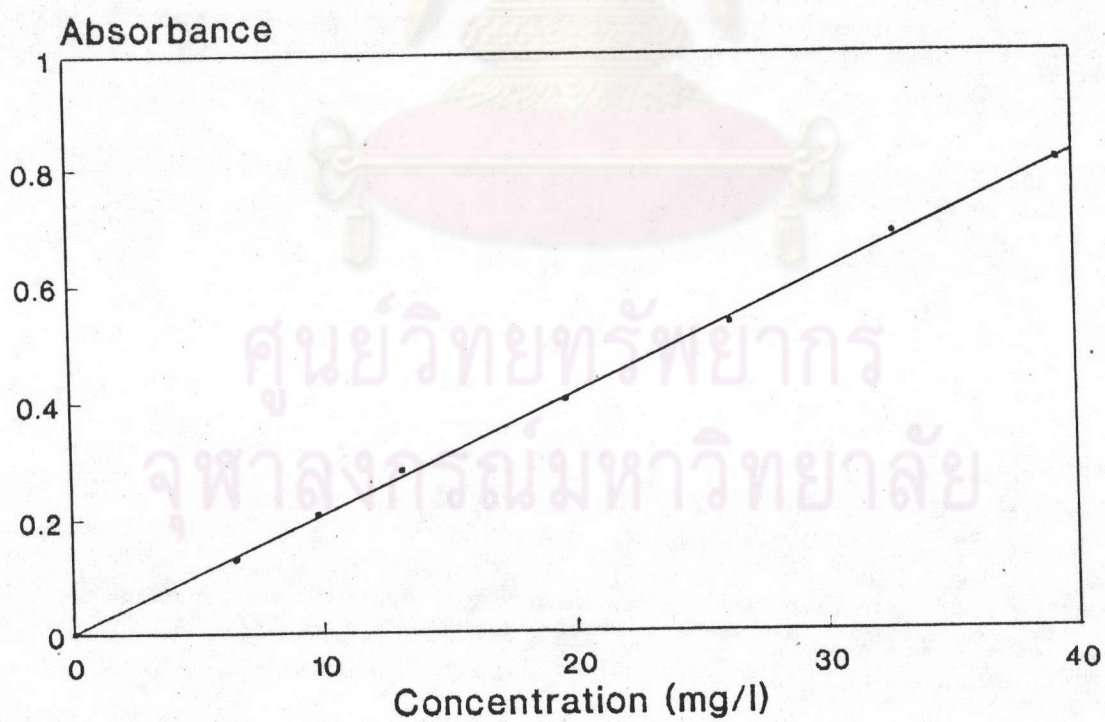
Figure 3.9 (D)   Calibration curve of C.I. Disperse Violet 28

Figure 3.9 (E)   Calibration curve of C.I. Disperse Red 60

Table 3.5   The expressions for various dyes

DYE	EXPRESSION
C.I. Disperse Orange 3	CONC = 21.60 ABS + 0.115
C.I. Disperse Red 1	CONC = 22.58 ABS - 0.054
C.I. Disperse Orange 5	CONC = 40.03 ABS - 0.516
C.I. Disperse Violet 28	CONC = 45.84 ABS + 0.072
C.I. Disperse Red 60	CONC = 48.64 ABS - 0.058

3.7   DETERMINATION OF DYE PURITY

Each dye of 0.0100 gm of weight was dissolved in 50 ml of chlorobenzene in the water bath at 60 °C. From each dye solution prepared, an amount was pipetted to yield, after diluting to equal volume of 10 ml, an absorbance in the range of 0.4-0.6 at its λ_{max}. The purity of each dye in percent was then calculated, utilizing the expression in Table 3.5, by equation (3.1)

$$\text{Dye Purity (\%)} = \frac{CONC \times V_1 \times V_2 \times 10^{-4}}{V_3 \times W} \qquad (3.1)$$

where CONC is the concentration (in mg/l) of diluted dye solution; V_1 is the volume of pre-diluted dye solution; V_2 is the volume of diluted dye solution; V_3 is the volume of pre-diluted dye solution pipetted; and W is the

dye weight dissolved. The % purity of each dye obtained was shown in Table 3.6

Table 3.6 Each dye purity

DYE	PURITY (%)
C.I. Disperse Orange 3	57.40
C.I. Disperse Red 1	73.23
C.I. Disperse Orange 5	51.05
C.I. Disperse Violet 28	90.83
C.I. Disperse Red 60	85.11

3.8 DETERMINATION OF % DYE UPTAKE ON POLYPROPYLENE TAPE YARN FOR VARIOUS DYES

The amount of each dye adsorbed on polypropylene tape yarns, which were dyed under various conditions with five selected dyes excluding C.I. Disperse Brown 1 and C.I. Violet 8 in section 3.4, were determined by solvent extraction technique. Dye adsorbed on each dyed sample of about 0.15 gm was extracted three times, each using 6 ml of chlorobenzene solvent in an Griffin Oil Bath kept nearly constant at 100 °C by a thermostat. The extracting period in each time was 5 minutes. The three dye solutions extracted from each sample were combined and diluted to 25 ml. Its absorbances was then measured at λ_{max}. The amount of dye adsorbed per tape weight ratio

then could be evaluated, utilizing the expression in Table 3.5, by equation (3.2)

Amount of dye adsorbed/tape weight ratio = $\dfrac{CONC}{40W_T}$ (3.2)

where the ratio has the unit of mg dye /1 g tape (or mg/g), CONC is the concentration in mg/l of dye solution and W_T is the weight of dyed tape yarn used for extraction.

Since the amount of dye adsorbed per tape weight ratio was not yet a suitable indicator of dyeability for each final dyeing because initial amount of dye used per weight of tape to be dyed ratio was not taken into consideration. The dyeability then should be expressed in the relative form, % dye uptake, which was a new ratio between two above ratio, i.e. the former divided by the latter and determined in percent form.

3.9 STUDY OF EFFECTS OF TEMPERATURE AND CARRIER CONCENTRATION ON THE DYEING

3.9.1 Dyeing with the Most Suitable Dye Under Various Conditions

Polypropylene tape yarn was dyed with the dye determined as the most suitable on the basis of highest dye adsorption per tape weight ratio or highest % dye uptake from section 3.8 above. The conditions of dyeing were carried out at the temperature of 10 degrees

interval in the range of 70-130 °C, and in the presence of sixdifferent concentrations of carrier (Matexil CA-MN), i.e., no carrier, 1, 2, 3, 4, and 5 g/l. The preparation steps, the composition of dyebath and the dyeing procedure by Jet Dyeing Machine were performed in the same manner as in section 3.4.

3.9.2 Determination of % Dye Uptake

The % dye uptake of the most suitable dye on polypropylene tape yarn, dyed under various conditions in section 3.9.1, was determined in the same manner as in section 3.8. The determination of % dye uptake was duplicated for each tape yarn specimen.

In order to determine that all the dyes uptaken on the tape yarns were completely extracted by the procedure mentioned above, the extracted tape yarns were re-examined through re-extraction in a soxhlet for 2 hours. This procedure was performed to see how much amount of residual dye still left on the tape yarn after the prior extraction. The tape yarn samples chosen for this purpose were the ones dyed with C.I. Disperse Red 60 under various conditions, i.e. at 110 °C with 1 g/l of carrier (S.1), at 120 °C without carrier (S.2), and at 130 °C without carrier (S.3). The residual dye uptakes, determined after re-extraction, for these samples relative to their corresponding % dye uptakes determined before were shown in Table 3.7 below.

Table 3.7   % Residual dye uptakes for extracted tape yarn
            samples

SAMPLE	RESIDUAL DYE UPTAKES AFTER RE-EXTRACTION (1)	% DYE UPTAKES (2)	% RESIDUAL DYE UPTAKES (3)
S.1	0.000	41.552	0.000
S.2	0.003	49.982	0.006
S.3	0.001	47.209	0.002

Note : (3) = (1) x 100/ (2)

        The % residual dye uptakes shown in Table
3.7 were found to be small and hence the residual dye
uptakes after re-extraction for each sample could be
neglected. This result indicated that the extraction
procedure performed above were efficient and could be
applied for this study.

3.10   FASTNESS TO LIGHT EXPERIMENT (24,29,30)

        The dyed tape yarn specimen with highest % dye
uptake, determined in section 3.9.2 above, was examined for
its fastness to light under specified conditions according
to the standard method of ISO 105-B03-1978(E) (29). The
tape yarn specimen with the area of 1.5 x 6 cm, wound
parallel close together on a card, was exposed to sunlight
along with outdoor weather condition for 120 hours (only 6

hours during 9 A.M. - 3 P.M. per day for 20 days period of experiment were accounted). A master set of the standards, made of eight blue color dyed wool fabrics with different level of light fastness from 1-8 and each with the same area as the specimen, was exposed to sunlight under prescribed conditions together with the specimen.