การสังเคราะห์สีรีแอกทีฟชนิดเอโซที่มีหมู่ควอเทอร์นารีแอมโมเนียม
เป็นหมู่ช่วยละลายน้ำแบบชั่วคราว
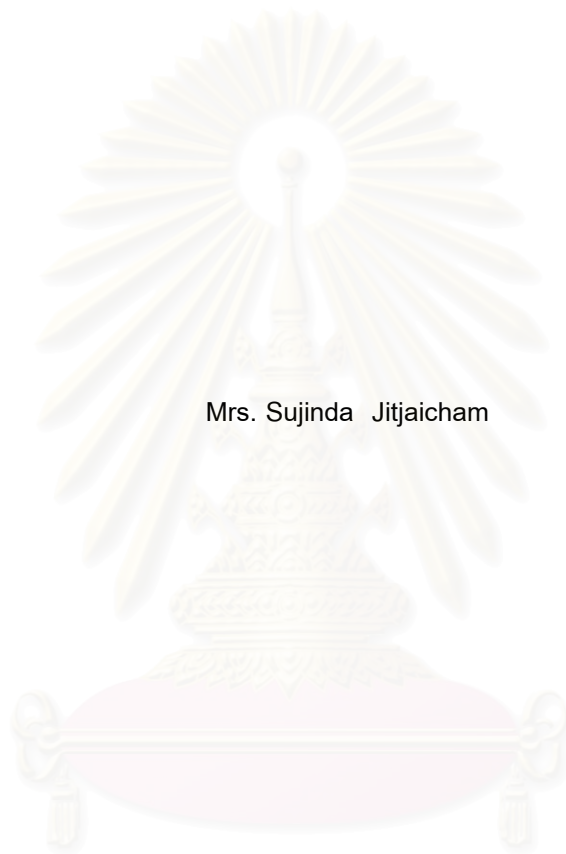
นางสุจินดา จิตต์ใจฉ่ำ

SYNTHESIS OF AZO REACTIVE DYES CONTAINING QUATERNARY AMMONIUM
GROUP AS TEMPORARILY SOLUBILIZING GROUP

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            งานวิจัยนี้ได้สังเคราะห์สีรีแอกทีฟชนิดเอโซที่มีหมู่ควอเทอร์นารีแอมโมเนียมเป็นหมู่ช่วย
ละลายน้ำแบบชั่วคราว โดยเริ่มจากการสังเคราะห์โครโมฟอร์ชนิดเอโซจาก 3-ไนโตรอะนิลีน และ
ฟาสต์บอร์โดซ์ซอล์ทจีพีซึ่งเป็นเกลือไดเอโซสำเร็จรูปกับอะนิลีน จากนั้นจึงทำปฏิกิริยากับไซยานูริก
คลอไรด์แล้วตามด้วยเอ็น–(2-อะมิโนเอทิล) ไพริดิเนียมคลอไรด์ไฮโดรคลอไรด์ การติดตามปฏิกิริยา
ได้อาศัยเทคนิคทินเลเยอร์โครมาโทกราฟี และหาลักษณะเฉพาะด้วยวิธีทางสเปกโทรสโกปีคืออยูวี-
วิสิเบิล เอฟทีไออาร์ และโปรตอนเอ็นเอ็มอาร์สเปกโทรสโกปี

            นำสีที่สังเคราะห์ได้ไปทดลองย้อมเส้นใยเซลลูโลสด้วยกระบวนการย้อมแบบดูดซึมโดยไม่ใช้
เกลือ พบว่าเปอร์เซ็นต์การดูดซึมและการผนึกสีต่ำ แต่อย่างไรก็ตามความคงทนต่อการซักอยู่ในระดับ
สูง และที่สำคัญคือความคงทนต่อแสงอยู่ในระดับที่ดีกว่าสีประจุบวกแบบทั่วไป   ทั้งนี้เนื่องจากหมู่
ควอเทอร์นารีแอมโมเนียมซึ่งเป็นหมู่ที่กระตุ้นแสงทำให้สีซีดเร็วนั้น ได้ถูกกำจัดออกจากโมเลกุลของสี
ในระหว่างกระบวนการซักล้าง

ภาควิชาวัสดุศาสตร์	**ลายมือชื่อนิสิต** ....
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ	**ลายมือชื่ออาจารย์ที่ปรึกษา** ....
ปีการศึกษา2543	**ลายมือชื่ออาจารย์ที่ปรึกษาร่วม** ....

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KEY WORD   CATIONIC AZO REACTIVE DYE / QUATERNARY AMMONIUM / TEMPORARILY SOLUBILIZING GROUP

SUJINDA JITJAICHAM : SYNTHESIS OF AZO REACTIVE DYES CONTAINING QUATERNARY AMMONIUM GROUP AS TEMPORARILY SOLUBILIZING GROUP, THESIS ADVISOR : ASSIS. PROF. KAWEE SRIKULKIT, Ph.D. 57pp. ISBN 974-346-566-9.

Cationic azo reactive dyes containing quaternary ammonium group as temporarily solubilizing group were synthesized from 3-nitroaniline and Fast Bordeaux Salt GP coupling with aniline. The obtained chromophores were reacted firstly with cyanuric chloride and then N-(2-aminoethyl)pyridiniumchloride hydrochloride. TLC technique was used to follow the chemical reaction. UV-Visible spectrophotometer, ^{1}H-NMR and FT-IR spectroscopy were employed to confirm the chemical structure of the dyes.

Dyeing of these synthesized dyes on cellulosic fiber was carried out in the absence of salt. The results showed that the exhaustion was quite low as well as the consequent fixation. However, the wash fastness and light fastness obtained were markedly improved compared to the conventional cationic dyes on cellulose. It was believed that quaternary ammonium group which could cause the photodegradation of dye chromophore was eliminated under alkaline soaping.

Department Materials Science   Student's signature ....

Field of study Applied Polymer Science and Textile Technology Advisor's signature ....

Academic year 2000   Co-advisor's signature ....

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CONTENTS

Contents (continued)   Page

Contents (continued)   Page

List of Tables

List of Tables (continued)

List of Figures

List of figure (continued)

List of Schemes

List of Diagrams

CHAPTER I

Introduction

Among synthesized dyes for dyeing cellulosic fiber, reactive dyes are the most important in textile industry since the introduction of Procion dye ranges in 1956. [1-4] The strong covalent bond, formed between the reactive group of dyes and the hydroxyl group of the fibre cannot be easily broken down during daily uses. With exception of the brightness and wide range of spectrum, they enable the high washing fastness for serving the high quality applications. [2,5-6]

However, there are some considerations regarding conventional reactive dyeing, i.e., a large amount of electrolytes, sometimes up to 100 g/l depending on the liquor ratio required, [4] is added to the dyebath in order to promote exhaustion, the unfixed and hydrolyzed dye in effluent, [2,6] energy consumption and labour overheads.

Several approaches were taken from both chemists and textile technologists in order to maximize the usage of reactive dyes with minimum disadvantages, i.e., dyestuff manufacturers have developed multifunctional reactive dyes by means of improving fixation efficiency and reducing salt consumption, [1,2,6-11] some researchers interest in the modification of cellulosic fibers to enhance dyeability, [12-14] and low liquor dyeing machines have been produced in order to minimize dyebath liquor as well.

The aim of this thesis is to develop a highly substantive reactive dye, by introducing the quaternary ammonium group into a dye chromogen. The quaternary ammonium group was expected to perform as a temporarily cationic solubilizing group, [15] as well as an attractive group towards negatively charged fiber surface. Thus dyeing in the absence of salt could be achieved.

Even though, the cationic dye ranges are currently available in the market but it is not suitable for coloring cellulosic fiber due to their tendency to self-photodegradation. [16] The new model of cationic reactive dye was prepared by Srikulkit *et al.* [17] This dye type was based on an anthraquinone chromophore containing a pyridinium cationic moiety which was eliminatable during washing off process. Hence, as a result of cationic group removed, the light fastness of dyed fabric should be improved.

In this experiment, further study on the synthesis of cationic reactive dyes based on azo chromophore will be investigated. The dyes used in this study will be prepared from several intermediates including commercial diazonium salts, 3-nitroaniline and aniline. The general structure of the dye is composed of an azo chromogen, a chlorotriazine reactive group and the *N*-(2-aminoethyl) pyridiniumchloride hydrochloride is used as a cationic solubilizing group. Characterizations will be carried out using fourier-transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and thin layer chromatography. After that, the synthesized dye will be applied onto bleached cotton fabric by exhaust dyeing method in the absence of electrolytes. The percentage of dye exhaustion and the degree of dye fixation will be determined spectrophotometrically. Finally, washing fastness and light fastness are investigated.

CHAPTER II

Literature Review

2.1 Cellulosic fibers

2.1.1 The molecular structure of cellulose

Cellulose, a naturally occurring fiber, is a linear polymer that can be represented as in Figure 2.1. [18] The high content of cellulose in cotton is the major determinant of fiber properties for textile industry whereas other cellulosic fibers i.e. flax, jute, ramie and some regenerated fibers contain a vary in proportion of cellulose. The cellulose content in some fibers are shown in Table 2.1. [19]

Table 2.1 The cellulose content of some typical fiber.

Typical fiber	Percentage of cellulose content
Cotton	94.0
Jute	71.3
Flax	80.1
Ramie	83.3
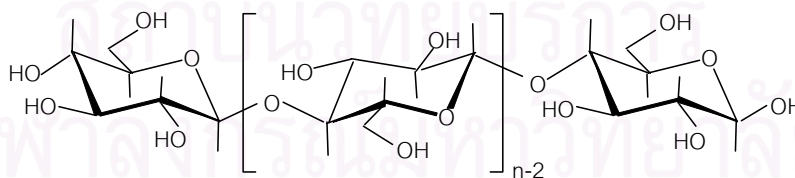
Figure 2.1 The structure of cellulose.

Cellobiose, the repeating unit of cellulose molecule, is the condensation product of two units of β-(D)–glucose linked together through 1,4 glycosidic bonds with the loss of a molecule of water as illustrated in Scheme 2.1. [15]
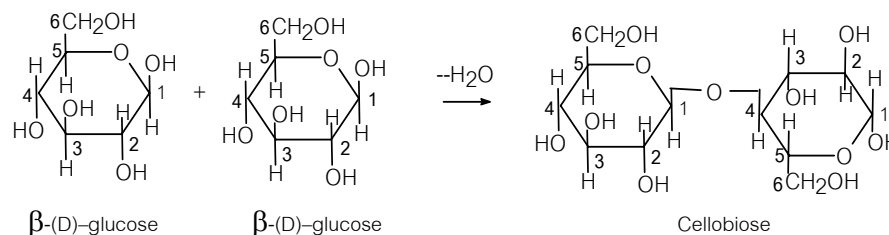
Scheme 2.1 Cellobiose unit.

The degree of polymerization (DP) of cellulose varies with its source[18] however, the number of subscript n in the Figure 2.1 indicates the average number of anhydroglucose units per chain molecule. The averages DP of native cellulose may be as high as 14,000 whereas those obtained from regenerated cellulose lie between 250 – 700. [15,18-19]

There are three hydroxyl groups in each glucose unit of the polymer chain which can readily form hydrogen bonds with water and other high electronegativity molecules, thus performing the hydrophilic properties. And the hydrogen bonds forming between the adjacent chain increase the degree of crystallinity in fiber. These intermolecular hydrogen bonds and the well – ordered structure of molecular chains enable cellulose to withstand normal textile treatments.

Since cellulose contains a large amount of ionizable hydroxyl groups, thus negative charge is developed on the fiber surface at the certain dyebath pH. [3] As a result, electrolyte is used to reduce electrical repulsion between dye and fiber when dyeing with anionic dyestuffs, hence promoting dyebath uptake. [4,19]

2.1.2 Cotton fiber : structure, morphology and chemical composition

Cotton, the most widely used of the natural cellulosic fibers, is obtained from the seed hairs of the plants of the genus *Gossypium*. [20-22] The mature fiber forms a convoluted flattened tubes with open at the base and tapering to a closed tip like a ribbon and a bean – shaped in cross section.[22] According to the source of the native cotton, a large variation in length, diameter, fineness, color, etc., can be founded. The easily recognized cotton under optical microscope is shown in Figure 2.2. [18]

Figure 2.2 Optical micrograph of raw cotton fiber X 184. [18]
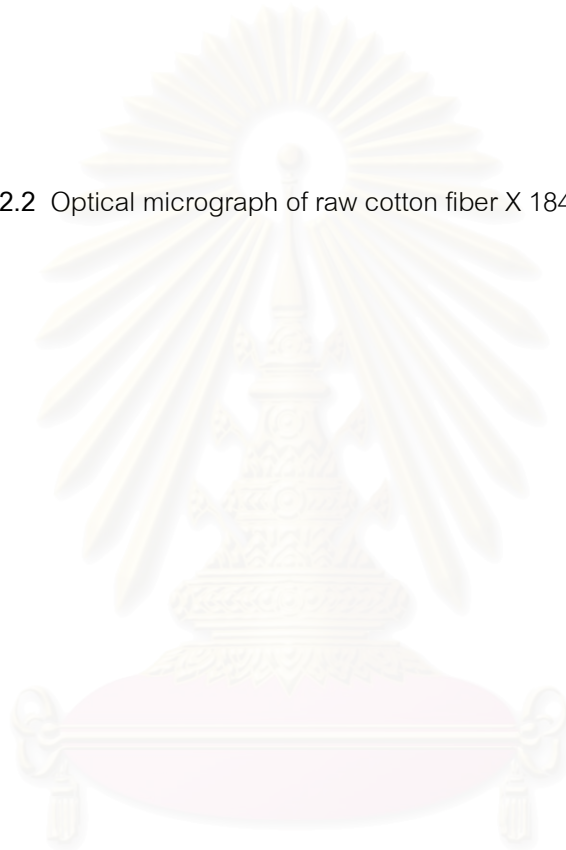
Figure 2.3 The idealized morphology of cotton. [18]

The morphology of cotton composes of three main parts as illustrated schematically in Figure 2.3. The primary wall, only 2.5 % of the fiber weight, is a network of cellulose fibrils covered with cuticle, which comprises of wax, protein, pectin and mineral matter. The secondary wall of 91.5 % of the fiber weight constitutes the bulk of a mature fiber, which arranges to a spiral feature around the fiber axis. This spiral fibril reverses its direction many times along the fiber length. Lumen, the remaining central core is composed of protoplasmic residues. The chemical composition of some cellulosic fibers are shown in Table 2.2. [18]

Table 2.2 The composition of some typical fibers.

Constituent	Percentage composition in fiber			
	cotton	jute	flax	ramie
Cellulose	94.0	71.3	80.1	83.3
Intercellular materials	2.5	27.1	10.5	7.5
Wax	0.6	0.4	2.6	0.2
Ash	1.2	0.8	1.5	2.1
Other substances	1.7	0.4	5.3	6.9

2.1.3 Cotton properties

The properties of cotton are shown in Table 2.3. [15,21]

Table 2.3 Properties of cotton.

Morphology	
- Microscopic features	Longitudinal view : ribbon like with convolutions at irregular intervals. Cross sectional view : bean or kidney shape.
- Fineness	1.28 to 5.23 micronaire
- Width	12 to 20 μm
- Length	Very short staple : less than 19.0 mm. Short staple : 20.6 to 23.8 mm. Medium staple : 23.8 to 28.5 mm. Long staple: 28.5 to 34.9 mm. Extra long staple: more than 34.9 mm.
- Color	Varies from white – light spotted – spotted – tinged – yellow stained - light grey
- Luster	Low unless mercerized
Physical properties	
- Density	1.54 to 1.62 g/cm^3
- Tensile strength	96,700 pound/inch^2

Table 2.3 (continued)

- Tenacity	Dry : 3.0 to 5.0 g/denier
	Wet : 3.6 to 6.0 g/denier
- Elongation	3 to 7% elongation at break
- Elastic recovery	75% recover at 2% extension
- Resilliency	low
- Moisture regain	Standard : 8.5%; Commercial : 7.0%
- Toughness and stiffness	High
- Abrasion resistance	Fair to good
- Thermal properties	Gradually decomposes under long exposure to dry heat above 150 $^{\circ}$C
Chemical properties	
- Acids	Strong mineral acids cause fiber damage whereas dilute organic acids do a little deterioration
- Alkalis	Highly resistant to alkalis
- Organic solvents	Highly resistant to most organic solvents
- Effect of bleaches	Can be bleached without fiber damage
- Dyeability	Good affinity for various types of dyes
	Dyeable with direct, vat, sulphur and reactive dyes
Biological properties	
- Effects of micro-organisms	Vulnerable to action by bacteria and mould
- Effects of insects	Starched cotton is attacked by silverfish
Optical properties	
- Axial refraction	1.596
- Transverse refraction	1.534
- Double refraction	0.062
Electrical and thermal con-ductivity	Good heat conductor
Flammability behavior	Burns readily with an odor similar to that of burning paper and leaves a small, fluffy gray ash.

2.2 <u>Reactive dyes</u>

Reactive dyes are those posses ions or groups which are capable of forming covalent bonds with other reactive groups presented in textile fibers, e.g. mercapto- and amino group of protein, hydroxyl group of cellulose and amino group of polyamide. [4,15,18,23] Such kind of chemical bonding is stronger than other types of dye – fiber interactions which depend on physical adsorption and mechanical retention. [2,4] As a result, reactive dyes owe the excellent wet fastness. [2,4-5]

The structural molecule of reactive dyes are illustrated in Figure 2.4. Fundamentally, they compose of four major parts: [4,15-16,20-21] a solubilizing group, a chromogen, a reactive system with leaving group and a bridging group which links the reactive system to the chromogen. However, it is found in some cases that the reactive group is attached directly to the chromogenic system.

| S |---| C |---| B |---| R-X |
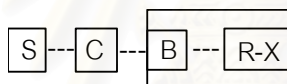
Where   S   =   solubilizing group

C   =   chromogen

B   =   bridging group

R-X =   reactive system with leaving group

Figure 2.4 The molecular structure of typical reactive dye.

2.2.1 <u>Chormogens</u>

Chromophoric group is responsible for color of a given dyestuff; for instance, metal-free monoazo dyes are yellow, orange and red; cupriferous mono- and disazo dyes are violet, ruby and navy; anthraquinone derivatives based on bromamine acid, phthalocyanine derivatives, formazan Cu-complexes and triphenodioxazines are bright blue. [20]

2.2.2 Solubilizing groups

Since cellulose is hydrophilic in nature, most involving process is carried out via water medium. In addition, dye molecules often carry one or more solubilizing group, i.e., sulphonated group. However, it is not easy for dyes with anionic charges to come closely to the fiber with same ionic charge like ionized cellulose. Amount of electrolyte, e.g., sodium chloride, sodium sulphate, depending on liquor ratio is added to the dyebath, in order to reduce ionic repulsion effect, hence promoting exhaustion and subsequent fixation.[4]

2.2.3 Reactive systems

According to the combination route with cellulose, which acts as an electrophile, reactive systems can be categorized into two main types: [18-19,24-25]   The first groups are those involving nucleophilic substitution as shown in Scheme 2.2,[19] which mostly are heterocyclic rings such as triazines, pyrimidines, pyrazines, quinoxalines and benzothiazoles, etc., containing one or more halogens as leaving groups.
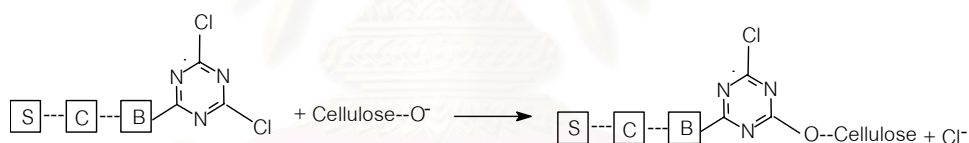
Scheme 2.2 The nucleophilic substitution mechanism of chlorotriazinyl dye.

Those involving nucleophilic additions belong to the second group. They contain β-sulphatoethylsulphone group or related species which readily form a vinylsulphone in alkali dyebath, leading to the formation of a dye-fiber covalent linkage. The nucleophilic addition mechanism is illustrated in Scheme 2.3[19]
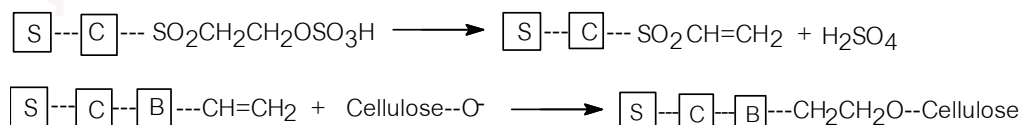
Scheme 2.3 The nucleophilic addition mechanism of vinylsulphone dye.

In most instances, however, hydroxyl anions, taking place from alkalis can also compete with cellulosate anions, subsequent to hydrolysis of reactive dyes.[2,6]

Though reactive dyes available in the market today may be viewed as the feature of reactive group present, i.e., monofunctional systems and heterofunctional systems as shown in Table 2.4. [18] However, their specific structural features can be divided into two main principal types: nitrogen containing heterocyclic ring and masked vinylsulphone.[15]

Table 2.4 Important reactive systems.

System	Typical brand name
Monofunctional	
Dichlorotriazine	Procion MX (BASF, formerly Zeneca)
Aminochlorotriazine	Procion H (BASF, formerly Zeneca)
Aminofluorotriazine	Cibacron F (CGY)
Trichloropyrimidine	Drimarene X (Clariant)
Chlorodifluoropyrimidine	Drimarene K (Clariant)
Dichloroquinoxaline	Levafix E (DyStar, formerly BAY)
Sulphatoethylsulphone	Remazol (DyStar, formerly HOE)
Sulphatoethylsulphonamide	Remazol D (DyStar, formerly HOE)
Bifunctional	
Bis(aminochlorotriazine)	Procion H-E (BASF, formerly Zeneca)
Bis(aminonicotinotriazine)	Kayacelon React (KYK)
Aminochlorotriazine-sulphatoethylsulphone	Sumifix Supra (NSK)
Aminofluorotriaizne-sulphatoethylsulphone	Cibacron C (CGY)

2.2.3.1 Nitrogen-containing heterocyclic ring

Nitrogen atoms present in heterocyclic rings cause a deficiency of electrons on the carbon atoms of those rings, thus contributing the electrophile characteristics to the molecules that can be easily attacked by the nucleophile i.e., cellulosate anions or hydroxyl ions as shown in Scheme 2.4. [3]
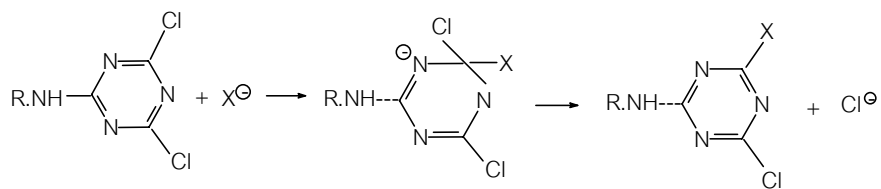
Where X   =   nucleophile

Scheme 2.4 Nucleophilic attacking the nitrogen-containing heterocyclic ring.

The reactivity of the system depends on the positional relationship between the hetero-nitrogen ring and the substituents. The various dye ranges characterized by differing reactivities are shown in Figure 2.5. [3, 24]
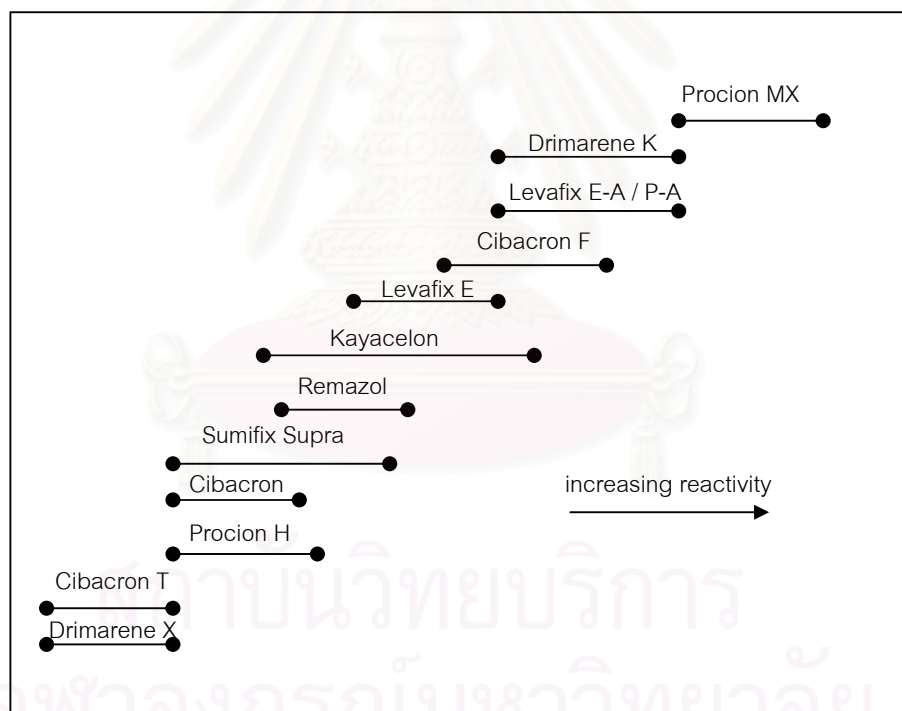
Figure 2.5 Relative reactivity of reactive dyes.

The leaving groups, attaching at carbon atom adjacent to the hetero ring are chlorine in common. Replacement of these leaving groups by other substituents affects

the reactivity of the remaining halogen atoms to a greater or lesser extent depending on the net electrical potential of the system.

The major reactive structure of this type is triazine ring, and cyanuric chloride or 2,4,6-trichloro-*s*-triazine is the most technically important of all. (Figure 2.6)
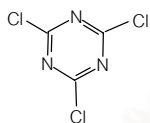
Figure 2.6 The structure of cyanuric chloride.

2.2.3.2 Vinylsulphone

Actually, reactive dyes of this group contains β- hydroxyethylsulphone which generates vinylsulphone, the more reactive form under alkali dyeing condition as shown in Scheme 2.3. The reactivity of these dyes are moderate when comparing to those containing mono- and dichlorotriazine group. (Figure 2.7) The dyeing temperature lies between 50 – 60 ^{O}C depending on pH.

(a)   (b)
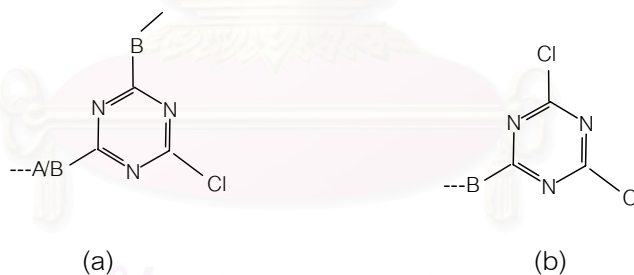
Figure 2.7 Chlorotriazine reactive group : a) monochlorotriazine and b) dichlorotriazine.

Where A   =   terminal group, alkoxy or substituted amino (not a chromophore)

B   =   bridging group, normally imino (-NH-), substituted imino, and amide linkage

2.3 Preparation of azo dye

Azo dyes, the largest group of all synthetic colorants, [25-29] are predominant because they are the most versatile of all the classes, such as acid, basic, direct, disperse and reactive dyes. They cover color gamut of fullest shade range, i.e., greenish yellow, red, orange, navy blue, violet to black with some green. [25,27,29] The chromophoric system consists essentially of the azo group, -N=N-, in associate with one or more aromatic systems. They can be subdivided into monoazo, disazo, trisazo and polyazo, depending on the number of azo group presented in the dye molecule.

Synthesis of azo dyes involve two basic reactions: the diazotization of a primary aromatic amine to give a diazo component or diazonium salt and the subsequent coupling reaction of a second substance, usually primary-, secondary-, tertiary aryl amine, phenolic compound, or an enolizable ketone.

2.3.1 The diazotization

The diazotization reaction proceeds according to the equation 2.1 [26,29-30]

$$Ar\text{-}NH_2 \; + \; NaNO_2 \; + \; 2\,HX \; \longrightarrow \; Ar\,N_2X \; + \; NaX \; + \; 2\,H_2O \qquad (2.1)$$

Where X   =   Cl, Br, NO_3, H_2SO_4, etc.

Normally, an aqueous solution of the amine is converted into the diazonium ion at a temperature of about 0-5 ^{O}C by the action of sodium nitrite in the presence of mineral acid. The use of at least two (usually 2.5-3.0) [25-26] equivalents of mineral acids in accordance with equation 2.1 is essential for smooth reaction.

A higher proportion of hydrogen ions is used in diazotizing weakly basic amines. In case of extremely weakly basic amines, diazotization can be performed in sulfuric acid (90-96 %). The diazotizing agent is nitrosyl sulfuric acid (HSO_4NO), which can be readily produced.

Excess nitrite in the reaction must be avoided, since it would exert an unfavorable influence on the stability of diazonium ions, apart from which it could form nitroso compounds with naphthols, secondary and tertiary amines, and diazo compounds in the subsequent coupling reaction with primary amines.

The following points are of great importance for diazotization. [29]

1. The starting material should be pure.

2. The quantities of materials should be measured accurately.

3. Vigorous and continuous stirring.

4. Diazo compounds should be protected from heat and light.

5. Hydrochloric acid is usually employed in diazotization in aqueous solutions because, it gives in general, the most soluble salts with aromatic amines.

6. It should be noted that concentrated hydrochloric acid reacts with nitrite to give chlorine, which of course leads to side reaction. For this reason, the diazotization mixture should never contain more than 20 % of free hydrochloric acid.

2.3.2 The azo coupling reaction

Since diazonium ion is a powerful electrophile, it can readily attack compounds having a nucleophilic center with the expulsion of a proton, or other entity, from the site of attack. This reaction leads to the formation of azo compound and the compound with the nucleophilic site being termed the coupling component which may be classified as follows : [29]

1. Aromatic hydroxy compounds, e.g. phenol, naphthols, etc.

2. Primary, secondary or tertiary amines in which the amino group is attached directly to an aromatic ring.

3. Pyrole, indole and similar ring systems.

The coupling position (attachment of an azo group to a carbon atom) in a coupling reaction is the site of high electron density, generally at carbon atom in aromatic system or heterocyclic system with aromatic in character. Coupling, therefore take place in the *o*- or *p*- position to the directing hydroxyl of amino group in the second component. It both of these positions are occupied, no coupling will take place, or one of the substituents will be displaced. Coupling never takes place in the *m*- position to the directing group. [31]

CHAPTER III

Experimental

3.1 Materials

Fabric : A 100 % cotton fabric of interlock knitted structure was scoured and bleached for this experiment.

Chemicals : The chemicals used throughout this experiment were laboratory reagent grade.

Table 3.1 List of chemicals used in this experiment.

Chemicals	Formula	Company
Acetic acid, Glacial	CH_3COOH	J.T. Baker Inc.
Acetone	$(CH_3)_2CO$	Merck
Aniline	C_6H_7N	Merck
2-Chloroethylaminehydrochloride, 98 %	$ClCH_2CH_2NH_2 \cdot HCl$	Fluka Chemie AG
Cyanuric chloride	C_3N_3Cl	Fluka Chemie AG
Hydrochloric acid, 37 %	HCl	Merck
3-Nitroaniline, 98 %	$C_6H_6N_2O_2$	Fluka Chemie AG
Nonionic detergent	-	U.T.N. Chemical Co.,ltd.
o-Phosphoric acid, 85 %	H_3PO_4	Merck
2-Propanol	$CH_3CH_2CH_2OH$	BDH Laboratory Supplies
Pyridine	$N(CH)_4CH$	Carlo-Erba
Sodium acetate	CH_3COONa	Carlo-Erba
Sodium bicarbonate	$NaHCO_3$	Ajax Chemicals
Sodium carbonate, anhydrous	Na_2CO_3	Fluka Chemie AG
Sodium hydroxide, pellet	$NaOH$	BDH Laboratory Supplies
Sodium nitrite, 99 %	$NaNO_2$	Carlo-Erba
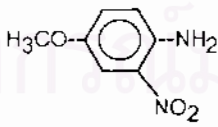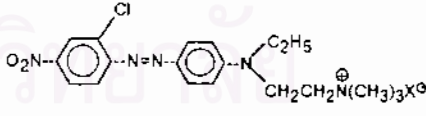
Table 3.1 (cont.)

Chemicals	Formula	Company
Sodium sulfate, anhydrous	Na_2SO_4	Fluka Chemie AG
Sulphuric acid, 98 %	H_2SO_4	BDH Laboratory Supplies
Tetrahydrofuran, 99.5 %	C_4H_8O	Fluka Chemie AG
Toluene	$C_6H_5CH_3$	Mallinckrodt

Azoic Coupling component : The azoic coupling component used in this experiment was Fast Bordeaux Salt GP. The general information is given in Table 3.2. [32-33]

Cationic dye : The commercial cationic dye selected for this experiment was Astrazon Red GTLN 200%. The general information is given in Table 3.2 [32,34]

Table 3.2 The general information of commercial dyes used in this experiment.

Commercial name	Fast Bordeaux Salt GP	Astrazon Red GTLN 200 %
Dye class	Azoic coupling component	Basic dye
Manufacturer	DyStar	DyStar
C.I. Generic name	C.I. Azoic Diazo Component 1	C.I. Basic Red 18 : 1
C.I. Constitution number	37135	11085
Structure		

3.2 Equipment

1. Filter paper: Whatman No. 40 and 42.
2. Fourier-transform infrared spectrophotometer: Shimadzu model 8201PC.

3. Hair dryer.

4. Heating mantle.

5. Laboratory dyeing machine: AHIBA Nuance.(Figure A-1)

6. Light fastness tester: Xenon weather meter model X 75, SUGA Test Instruments, Co., Ltd. (Figure A-2)

7. Magnetic bar.

8. Magnetic stirrer.

9. Nuclear magnetic resonance spectrometer: JEOL JNM-A500.

10. pH meter: Denver Instrument model 215.

11. pH paper: Merck.

12. Reflectance spectrophotometer: Gretag-Macbeth Color-Eye 7000 operated with Optiview software. (Figure A-3)

13. Rotary vacuum evaporator: Tokyo Eyela, Rikakikai co., ltd.

14. Thin layer chromatography sheets: Alltech Associates, Inc., TLC aluminium silica gel 60F254 pre-coated 500X20 cm layer thickness 0.2 mm.

15. UV/Visible spectrophotometer: Jenway 6405. (Figure A-4)

16. Washing fastness tester: Atlas. (Figure A-5)

17. Glasswares, i.e. three-necked round bottom flask, soxhlet extractor, suction flask, buschner funnel, condenser, beakers, pipettes, dropers, glass stirrer.

3.3 Preparation of azo chromophore

3.3.1 Azo chromophore from Fast Bordeaux Salt GP $\rightarrow$ aniline.

The Fast Bordeaux Salt GP (16.8 g, 0.1 mole) which was dissolved in cold water (the temperature not exceeding 20 $^\circ$C) 168 ml, was added to the solution containing aniline (9.3 ml, 0.1 mole) in acetic acid (60% v/v, 10 ml). The mixture was stirred continuously at 10-20 $^\circ$C for two hours and the pH value was maintained between 4-5 for the coupling reaction by the addition of saturated sodium bicarbonate solution. The precipitated dye was filtered off, and washed with excess water and oven dried at the temperature below 60 $^\circ$C for 15 minutes before keeping in a desiccator.

The reaction scheme may be written as shown in scheme 3.1.
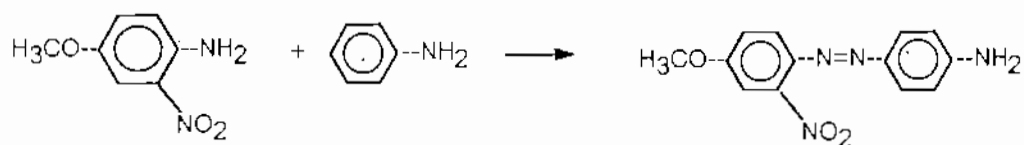
Scheme 3.1 The synthesis reaction of azo chromophore from Fast Bordeaux Salt GP $\rightarrow$ aniline.

3.3.2 Azo chromophore from 3-nitroaniline $\rightarrow$ aniline

The nitrosyl sulphuric solution, prepared by dissolving sodium nitrite (1.035 g, 0.015 mole) in 10 ml sulphuric acid , was added to the stirred mixture of 3-nitroaniline (1.38 g, 0.01 mole) in o-phosphoric acid (70% v/v, 5 ml) and sulphuric acid (10 ml). The temperature was kept constantly at 0-5 $^{\circ}$C for four hours.

The diazonium salt obtained was slowly added to the solution of aniline (0.94 ml, 0.01 mole) in 15 ml acetic acid . The mixture was then diluted by 200 ml water and ice and the dye was precipitated by adding sodium hydroxide solution (20 wt%) dropwise to pH 4-5.

Finally, the precipitated dye was filtered off and washed with excess water and oven dried at the temperature of below 50 $^{\circ}$C and then kept in a desiccator.

The reaction scheme may be written as shown in Scheme 3.2.
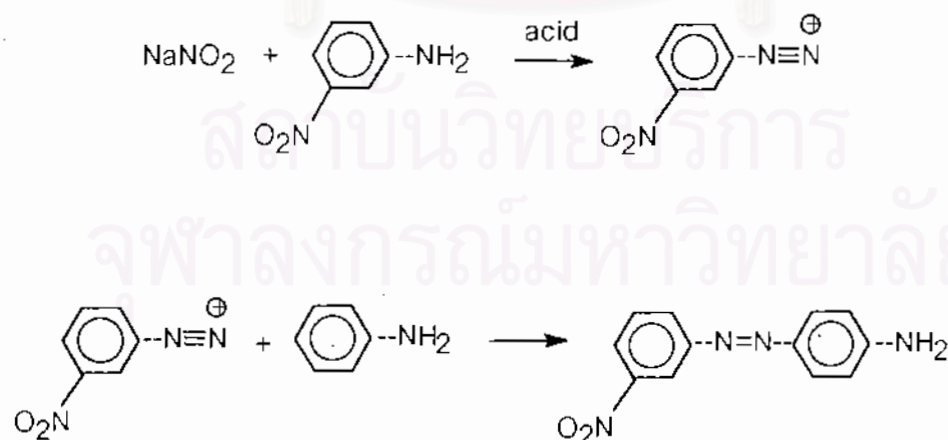
Scheme 3.2 The synthesis reaction of azo chromophore from 3-nitroaniline $\rightarrow$ aniline.

The azo chromophore obtained was recrystallized by dissolving in excess acetone and then gradually dropped into water. The precipitated dye was filtered off, washed with excess water and oven dried at the temperature of below 50 $^{\circ}$C and then kept in desiccator.

3.4 Reaction of the obtained chromophores with cyanuric chloride and N-(2-aminoethyl) pyridiniumchloride hydrochloride

3.4.1 Reaction of azo chromophore prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline

A solution of cyanuric chloride (1.83 g, 0.01 mole) in acetone 80 ml was added dropwise to the mixture of the obtained dye chromophore (1.36 g, 0.005 mole) in 200 ml acetone and continuously stirred for three hours at room temperature. The reaction was followed up using the TLC technique until the reaction was completed.

To follow the reaction by TLC technique, a starting chromophore and reaction mixture taken at various times of reaction were spotted on a TLC plate and using a blower to dry the sample. The developing solvent used were toluene/acetone mixture (20:1 by volume). The complete reaction would be observed when spot of dye chromophore on the TLC plate totally disappeared.

After that, A solution of N-(2-aminoethyl) pyridiniumchloride hydrochloride (see Appendix C) (1.93 g, 0.01 mole) and 50 ml of distilled water which was adjusted to pH 6.51 by sodium hydroxide solution (20 wt%), was added dropwise in the course of 30 minutes. The temperature was raised to 45-50 $^{\circ}$C and the pH value was maintained between 6.5-7.0 by the addition of sodium hydroxide solution. The reaction was followed up by TLC technique using toluene/acetone (20 : 1) as eluent and the complete reaction was determined by no change in pH value.

The mixture was left over night to allow acetone to evaporate, then filtered off the impurities from the reaction. The filtrate was dried in the air and washed out the unreacted dye by stirring in the mixture of THF / acetone (1 : 2) and acetone respectively before keeping in a desiccator.

The reaction scheme may be written as shown in scheme 3.3.

Scheme 3.3 The overall reaction scheme of azo reactive dye containing N-(2-aminoethyl) pyridiniumchloride hydrochloride, prepared from Fast Bordeaux Salt GP → aniline .

3.4.2 Reaction of azo chromophore prepared from 3-nitroaniline → aniline

A solution of cyanuric chloride (1.50 g, 0.0082 mole) in acetone 100 ml was added dropwise to the mixture of the resulted chromophore (1.02 g, 0.0041 mole) in 200 ml acetone and continuously stirred for four hours at room temperature. The reaction was followed up using the TLC technique until the reaction was completed.

After that, a solution of N-(2-aminoethyl) pyridiniumchloride hydrochloride (3.18 g, 0.016 mole) and 50 ml distilled water which was adjusted to pH 6.42 by sodium hydroxide solution (20 wt%), was added dropwise in the course of 30 minutes. The temperature was raised to 45-50 $^{\circ}$C and the pH value was maintained between 6.5-7.0 by the addition of sodium hydroxide solution. The reaction was followed up by TLC technique using toluene/acetone (20 : 1) as eluent and the complete reaction was determined by no change in pH value.

The mixture was left over night to allow acetone to evaporate, then filtered off the impurities from the reaction. The filtrate was dried in the air and washed out the unreacted dye by stirring in the mixture of THF/acetone (1 : 2) and acetone respectively before keeping in a desiccator.

The reaction scheme may be written as scheme 3.4.
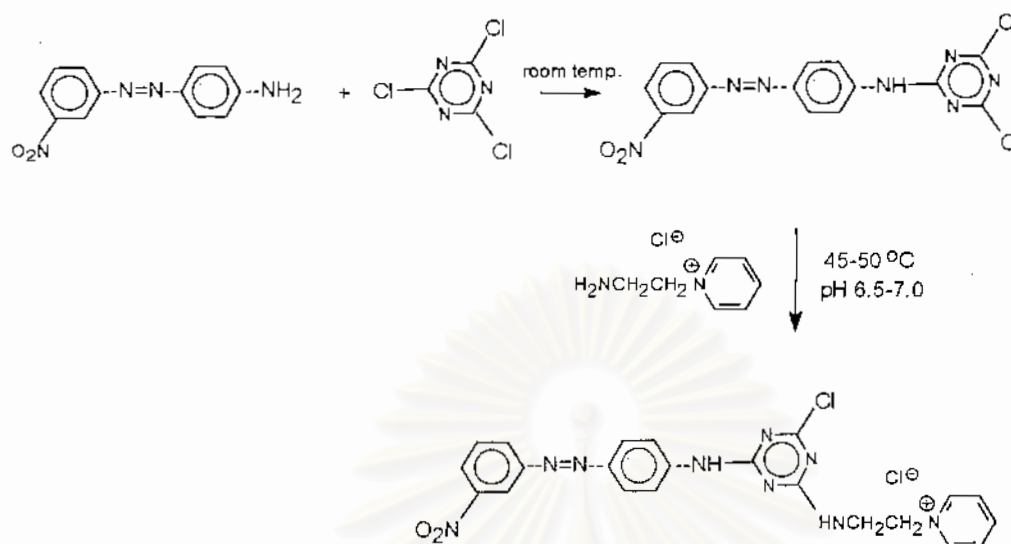
Scheme 3.4 The overall reaction scheme of azo reactive dye containing *N*-(2-amino ethyl) pyridiniumchloride hydrochloride, prepared from 3-nitroaniline $\rightarrow$ aniline .

An identification of the chemical structure of both synthesised dyes were carried out using FT-IR, ^{1}H-NMR techniques.

Infrared analysis of both dyes were measured using the Shimadzu spectrometer with diffuse reflectance attachment. Samples were mixed with KBr powder and pressed into clear pellet before taking IR spectra. All of the spectra were analysed using Shimadzu software.

The ^{1}H-NMR spectra was recorded by the Jeol JNM-A500 500 MHz spectrometer. Samples were dissolved in DMSO and the chemical shifts were expressed in δ ppm.

3.5 Application of synthesized cationic azo reactive dyes containing *N*-(2-aminoethyl) pyridiniumchloride hydrochloride to cotton fabric in the absence of electrolyte by exhaust dyeing method

The material used was bleached cotton fabric. The cationic azo reactive dyes were applied at a depth of shade of 2%, 4%, 6% and 8% o.w.g. (on weight of goods) in Ahiba Nuance, a laboratory dyeing machine at liquor ratio of 10 : 1. All dyeings were commenced at room temperature. The temperature was raised to 85 $^{\circ}$C over 25 minutes and continued at this temperature for 10 minutes. Then, 20 g / l of sodium carbonate powder was added to the dyebath. The temperature was kept constantly at 85 $^{\circ}$C for a further 45 minutes. The dyed fabrics were then taken out and rinsed thoroughly in running tap water. After that, rinsed fabrics were soaped– off (as required) in the boiling solution containing 5 g / l nonionic detergent and 2 g / l sodium carbonate for 15 minutes.

The dyeing process diagram of cationic azo reactive dye may be elucidated as diagram 3.1.
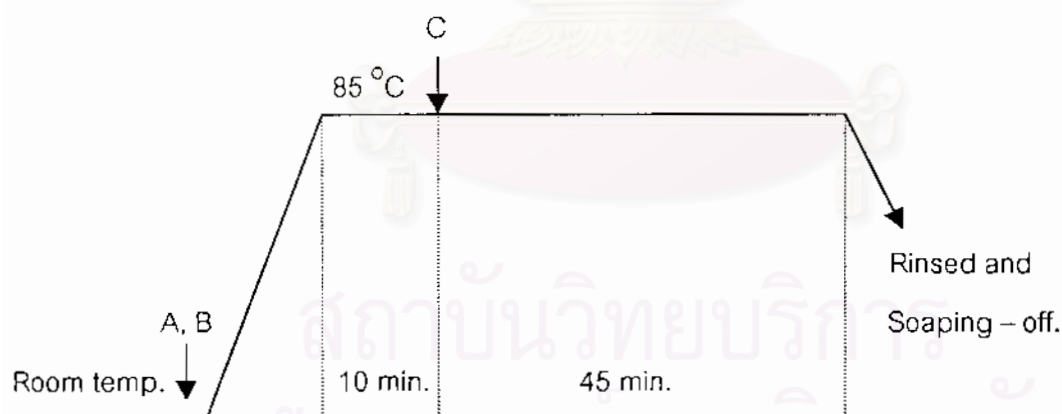
Where A = Cotton fabric

  B = Cationic monoazo reactive dye

  C = Sodium carbonate

Diagram 3.1 The dyeing process diagram of synthesized azo reactive dyes containing *N*-(2-aminoethyl) pyridiniumchloride hydrochloride.

3.6 Measurement of dye exhaustion

Dye exhaustion or amount of dye absorbed by the fiber is usually defined in terms of the difference between the initial and final dyebath concentrations. According to the Beer – Lambert law, the concentration of the dye in solution is determined from a measurement of absorbance at the wavelength of maximum absorption of the dye using UV / Visible spectrophotometer.

$$\text{Absorbance} = \log(I_0/I) = acl \tag{3.1}$$

Where I_0 = Intensity of light incident on the optical cell holding the dye solution

I = Intensity of light transmitted through the cell

a = absorptivity or extinction coefficient ($L\ g^{-1}\ cm^{-1}$) of the dye

c = concentration of the dye solution in the cell (g / l)

l = path length through the cell (cm)

The dye exhaustion of the cotton fabric was measured by sampling the dyebath before and after the dyeing process. All the solutions were diluted ten times and adjusted to the neutral condition of pH 7.0±0.5 using 0.1 M, 2 M hydrochloric acid and 0.1 M, 1.0 M sodium hydroxide with pH 7.0 buffer solution. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max}) of the dye using Jenway UV / Visible spectrophotometer model 6405. The percentage of dye exhaustion (%E) was calculated using the following equation [15] :

$$\%E = \frac{(Abs)_0 - (Abs)_1}{(Abs)_0} \times 100 \tag{3.2}$$

where $(Abs)_0$ and $(Abs)_1$ were absorbance of the initial dye solution and final dyebath solution respectively.

There were two stages dyebath exhaustion, the exhaustion taken place before adding sodium carbonate was called as primary exhaustion, and the further exhaustion after the addition of alkali was called as secondary exhaustion or final exhaustion.

3.7 Measurement of dye fixation

The degree of dye fixation was determined spectrophotometrically using reflectance spectrophotometer. The reflectance values of the dyed fabrics were measured in the visible region of the spectrum (400 – 700 nm.) and the color strength was expressed as K/S values, which was calculated using the Kubelka - Munk equation as follow [35] :

$$K/S = \frac{(1-R)^2}{2R} \qquad (3.3)$$

where K   is the absorption coefficient

S   is the scattering coefficient

and   R   is the reflectance of the dyed fabric at the wavelength of maximum

absorption (λ_{max})

The K/S value is directly proportional to the concentration of colorant in the substrate. The percentage of covalent fixation of the dye on the fiber was calculated by comparing the K/S values of the dyed samples before and after soaping.

Each dyed sample was divided into two portions. One portion was soaped in an aqueous solution containing 5 g / l nonionic detergent and 2 g / l sodium carbonate for 15 minutes in a 50 : 1 liquor ratio to remove any unfixed dye and then rinsed for 15 minutes in running water. After drying the soaped sample, K/S value was measured at λ_{max} using Gretag-Macbeth spectrophotometer model Color Eye 7000 and Optiview. The measurement parameter were as follows : 10 degree observer, illuminant D_{65}, specular reflectance included, UV included, large aperture, large area view, and average 5 times.

The apparent degree of dye fixation (%F) and degree of total dye fixation ($\%F_T$) were calculated from the following equation :

$$\%F = \frac{(K/S)_1 \times 100}{(K/S)_0} \qquad (3.4)$$

$$\%F_T \quad = \quad \frac{(K/S)_1 \times (\%E)}{(K/S)_0} \tag{3.5}$$

where $(K/S)_0$ and $(K/S)_1$ were the K/S values of the dyed samples before and after soaping respectively.

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 ($\%F_T$) describes the percentage of fixed dye compared to the overall dye applied at the beginning. Usually, $\%F_T$ value is less than %F value.

3.8 Color fastness comparison of synthesized cationic azo reactive dyes containing N-(2-aminoethyl) pyridiniumchloride hydrochloride with commercial cationic dye on cotton fabric

The light fastness properties of dyed cotton fabric between synthesized cationic azo reactive dyes and traditional cationic dye were evaluated to compare the photocatalytic effect of cationic dyes. Astrazon Red GTLN 200% was commercial cationic dyes in the market. They possess high substantive property towards cellulosic fiber, but not contain reactive groups that are capable of forming covalent bonds with cellulose, leading to poor wet fastness properties.

The color fastness properties were tested on the dyed fabrics at a depth of shade as 1 / 25 of standard depth. The sample of synthesized reactive dyes used were the dyed samples after washing – off process, whereas the conventional cationic dye dyed samples were those rinsed in tap water prior to testing. The fastness tests were carried out in accordance with ISO 105 – B02 : 1994 color fastness to artificial light : Xenon arc fading lamp test.[36]

3.8.1 Dyeing method of commercial cationic dye on cotton fabric

Cotton fabrics were dyed by varying the dye concentration in the range of 0.5 – 4% o.w.g. to give an appropriate depth of shade as 1/25 comparing to the Standard Depth Scales of AATCC Evaluation Procedure 4. Dyeing procedure of Astrazon Red GTLN 200% was carried out in similar manner to the dyeing of synthesized azo reactive dyes in section 3.5. The dyeing was started at room temperature and raised to the boil at rate of 2 $^{\circ}$C/minute and then held for a further 45 minutes. After that, the dyed fabrics were rinsed with clean water in three washing bath for 3 minutes, using liquor ratio 50 : 1 and then the fabrics were squeezed and dried. The process diagram of Astrazon Red GTLN 200% is shown in Diagram 3.2.

100 $^{\circ}$C

Rinsed

A,B

Room temp.

45 min.

Where   A   =   cotton fabric

B   =   Astrazon Red GTLN 200 %
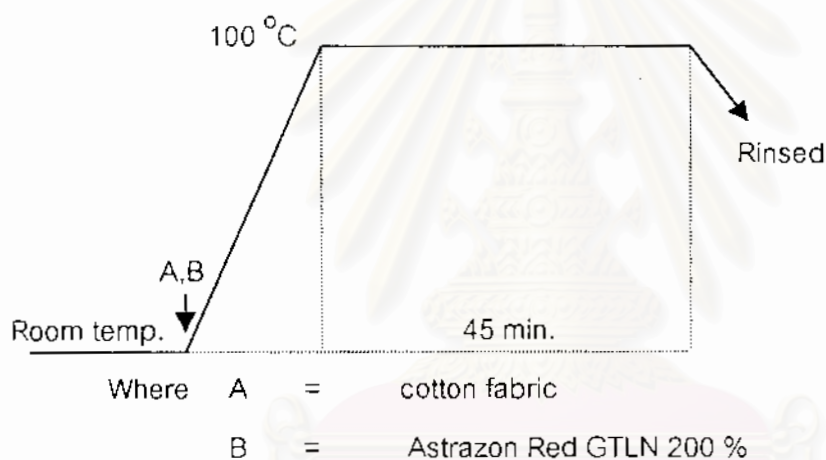
Diagram 3.2 The process diagram of Astrazon Red GTLN 200% used in this experiment.

3.8.2 Determination of light fastness

The ISO 105 – B02 : 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 3.3.

Table 3.3 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

They 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).

3.8.3 Determination of washing fastness

The ISO 105 – C03 : 1989 color fastness of washing : test 3 [37] is designed to determine the effect of washing only on the color fastness of the textile. In the principle, a dyed specimen in contact with specified adjacent fabric is mechanically agitated under specified conditions of time and temperature in a soaping solution, then rinsed and dried. The change in color of the specimen and the staining of the adjacent fabric are assessed with the grey scales.

Test procedure.

A specimen measuring 40 mm X 100 mm was attached to a piece of the multifiber adjacent fabric (DW type, which containing wool and acetate) also measuring 40 mm X 100 mm, by sewing along one of the shorter sides. The composite specimen was placed in the container and added the necessary amount of soap

solution, containing 5 g / l of standard soap and 2 g / l of anhydrous sodium carbonate in distilled water and previously heated to 60 $^\circ$C , to give a liquor ratio of 50 : 1. Then, treated the composite specimen at 60 $^\circ$C for 30 minutes. After the end of this stage, the composite specimen was removed, rinsed in cold water and running water for 10 minutes, and squeezed it. Opened out the composite specimen and dried in air at room temperature.

The change in color of the specimen and the staining of each type of fiber in the multifiber adjacent fabric were assessed with grey scales.

4.1 <u>Spectroscopy analysis of azo chromophore prepared from Fast Bordeaux Salt GP</u> → <u>aniline</u>.

    4.1.1 <u>FT-IR analysis of azo chromophore prepared from Fast Bordeaux Salt GP</u> → <u>aniline</u>

The azo chromophore prepared from Fast Bordeaux Salt GP → aniline by the method described in section 3.3.1 was characterized by using fourier transform infrared spectroscopy (FT-IR). The FT-IR spectrum is shown in Figure 4.1 and the result of functional group characteristic is summarized in Table 4.1.
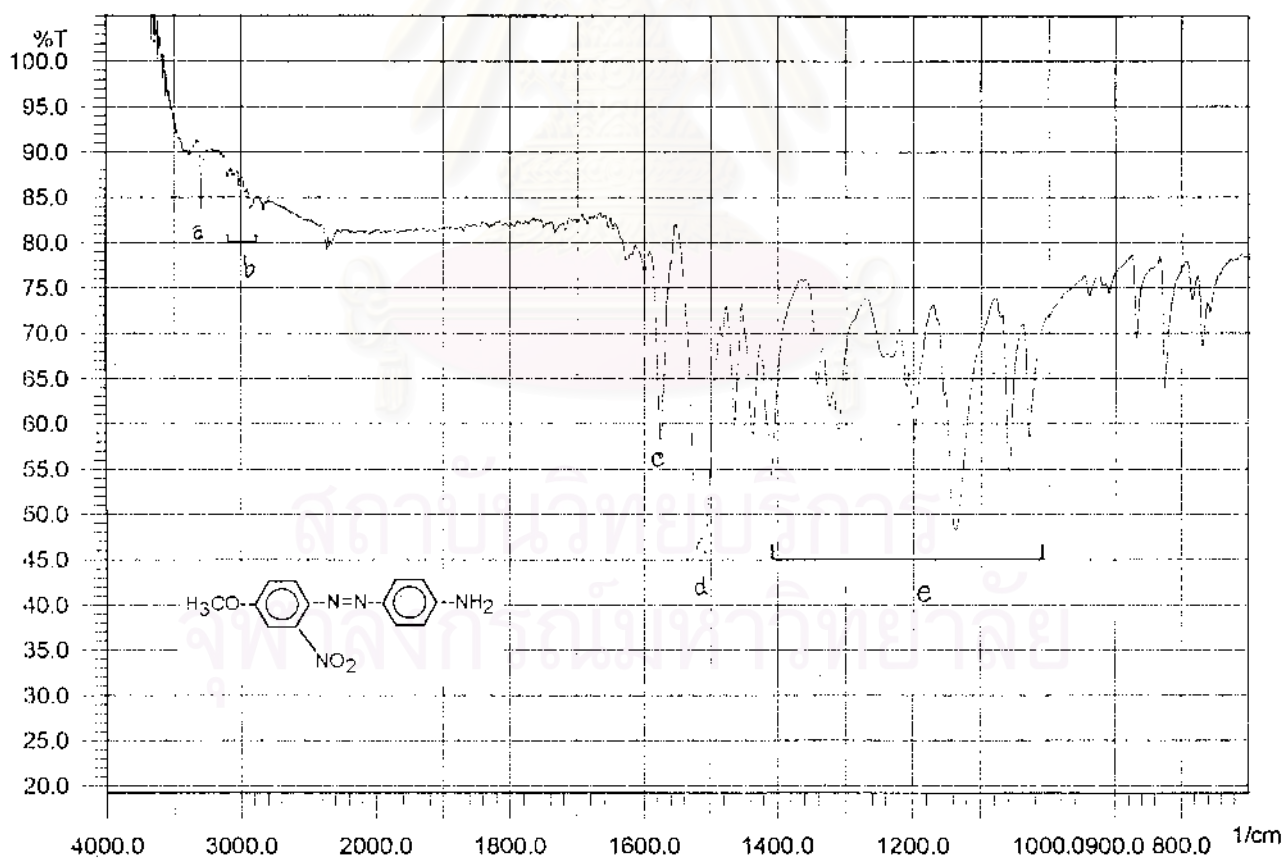
Figure 4.1 FT-IR spectrum of azo chromophore prepared from Fast Bordeaux Salt GP → aniline.

Table 4.1 FT-IR functional group analysis of azo chromophore prepared from Fast Bordeaux Salt GP → aniline.

IR absorption peaks	Wave number (cm^{-1})	Tentative assignment
a	3302	-N-H stretching
b	3100-2900	=C-H and –C-H stretching
c	1578	-C=C stretching
d	1508	-NO$_2$ stretching
e	1410-1030	-C-N and –C-O stretching

A signal at 3302 cm^{-1} of FT-IR spectrum revealed –N-H stretching overlapped with –OH stretching and –C-H stretching whereas =C-H and –C-H stretching appeared at 3100-2900 cm^{-1}, -C=C stretching of aromatic showing at 1578 cm^{-1} and –NH$_2$ stretching found at 1508 cm^{-1}, respectively. [38]

4.1.2 ^{1}H-NMR analysis of azo chromophore prepared from Fast Bordeaux Salt GP → aniline.

The ^{1}H-NMR spectroscopy was used to prove the chemical structure of azo chromophore prepared from Fast Bordeaux Salt GP → aniline. The ^{1}H-NMR spectrum of this azo chromophore in deuterated acetone is shown in Figure 4.2 and the chemical shifts of all protons are summarized in Table 4.2.

Table 4.2 Chemical shifts of azo chromophore prepared from Fast Bordeaux Salt GP → aniline.

Chemical shifts (δ)	Multiplicity	Assignments
~ 2.0	Singlet	Methyl proton
~ 7.0 – 7.5	Doublet	Aromatic protons
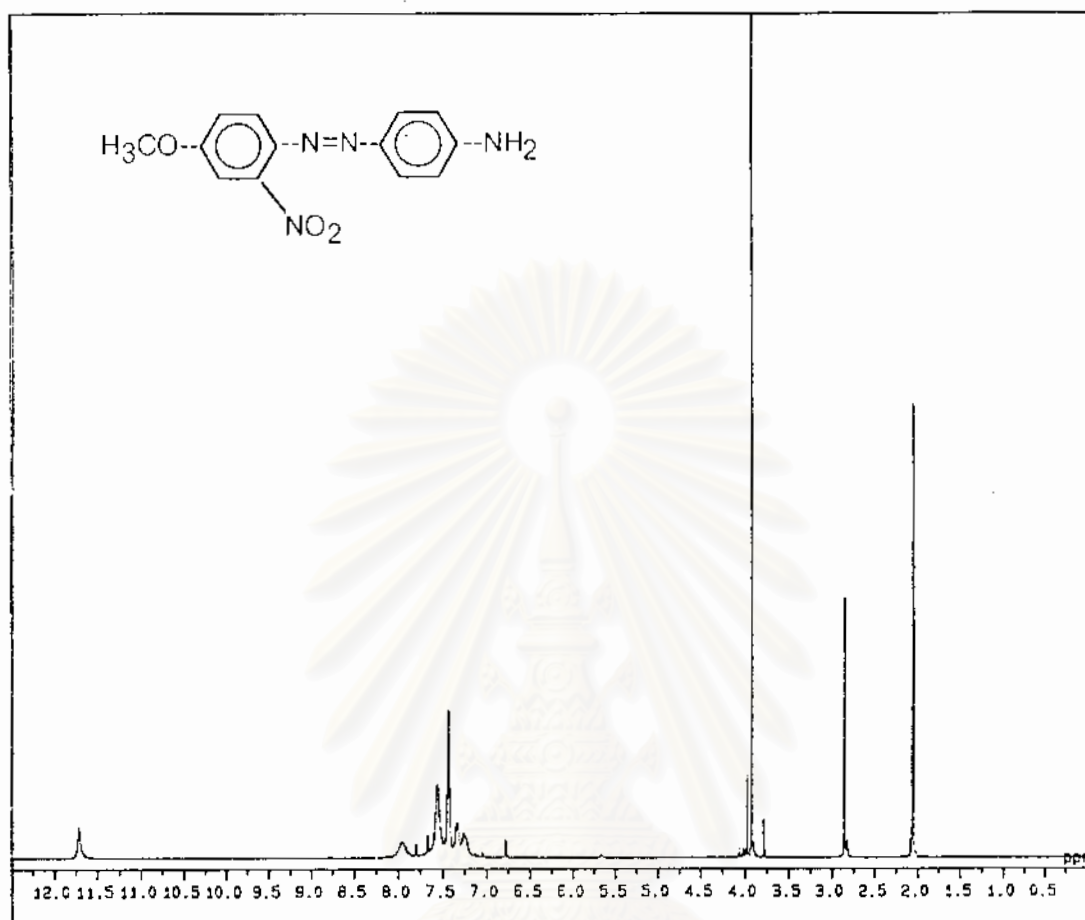
Figure 4.2 ^{1}H-NMR spectrum of azo chromophore prepared from Fast
Bordeaux Salt GP $\rightarrow$ aniline.

The ^{1}H-NMR spectrum (Figure 4.2) exhibited the proton signals at 2 ppm corresponding the presence of methyl proton. The ^{1}H-NMR signals around 7.0 – 7.5 ppm confirm the characteristic of aromatic protons which is the important part of the synthesized chromophore. The results proved that the designed chromophore was successfully produced.

4.2 <u>Following the synthesis reaction of azo chromophore prepared from Fast Bordeaux</u>
<u>Salt GP $\rightarrow$ aniline with cyanuric chloride and *N*-(2-aminoethyl) pyridiniumchloride</u>
<u>hydrochloride by TLC</u>

Thin layer chromotography (TLC) technique is used to follow the reaction of azo chromophore prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline with cyanuric chloride and *N*-(2-aminoethyl) pyridiniumchloride hydrochloride. The developing solvent was the mixture of toluene/acetone (20 : 1 by volume) and the stationary phase was silica gel TLC plates. The TLC chromatogram of reaction between azo chromophore prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline and cyanuric chloride at every hour is shown in Figure 4.3.

Figure 4.3 TLC chromatogram of azo chromophore prepared from Fast
Bordeaux Salt GP $\rightarrow$ aniline with cyanuric chloride :A=starting azo
chromophore; B,C,D=reaction mixture taken after 1,2 and 3 hour, respectively.

It can be assumed that the reaction between azo chromophore and cyanuric chloride was complete at the reaction time of three hours, as confirmed by the total disappearance of the main spot of azo chromophore. Reaction products are composed of two components at the retention times of hR_F values [39] of 41.176, and 55.882, respectively. It was seen that both products contain dichlorotriazinyl reactive groups, thus this group could be reacted further with *N*-(2-aminoethyl) pyridiniumchloride hydrochloride without purification. At this stage, it was aimed to introduce a solubilizing cationic group into the dye molecule. The TLC chromatogram of the reaction is illustrated in Figure 4.4.

Figure 4.4 TLC chromatogram of the reacted chromophore with *N*-(2-amino-
ethyl) pyridiniumchloride hydrochloride : A=product of reacted chromophore
and cyanuric chloride; B, C and D=reaction mixture after 1,2 and 3 hour,
respectively.

From the TLC chromatogram in Figure 4.4, it is found that the complete reaction time of introducing the cationic solubilizing group into dye molecule was three hours and the final product became water soluble, confirmed by the very little migration of the final product (B) in the organic developing solvent as shown in Figure 4.5.

Figure 4.5 TLC chromatogram of the reacted chromophore and cyanuric chloride (A) and the final cationic azo reactive dye (B).

4.3 FT-IR and ^{1}H NMR analysis of synthesized cationic azo reactive dyes containing *N*-(2-aminoethyl) pyridiniumchloride hydrochloride

4.3.1 Synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline

The FT-IR and ^{1}H NMR spectra of this synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline are shown in Figure 4.6 and 4.7 with the corresponding to the Table 4.3 and 4.4 respectively.

Figure 4.6 FT-IR spectrum of synthesized cationic azo reactive dye prepared
from Fast Bordeaux Salt GP → aniline.

Table 4.3 FT-IR functional group analysis of synthesized cationic azo reactive
dye prepared from Fast Bordeaux Salt GP → aniline.

IR absorption peak	Wave number (cm-1)	Tentative assignment
a	3256	-N-H stretching
b	3063-2978	-C-H stretching
c	1749	-C=O stretching
d	1624	-C=C stretching
e	1490	$-NO_2$ stretching
f	830-600	-C-Cl stretching

The FT-IR spectrum showed the important absorption band of $-C-Cl$ stretching at 830-600 cm^{-1}, confirming that the introduction of chlorotriazinyl group into the dye chromophore was successfully achieved. However, the strong absorption band at 1749 cm^{-1} suggested the presence of carbonyl group ($-C=O$) [38] which was not the part of dye structure. This might be due to the partial hydrolysis of chlorotriazenyl group to produce inactive carbonyl group. This undesired reaction could possibly affect the fixation capacity of prepared dye as a result of reactive group loss.
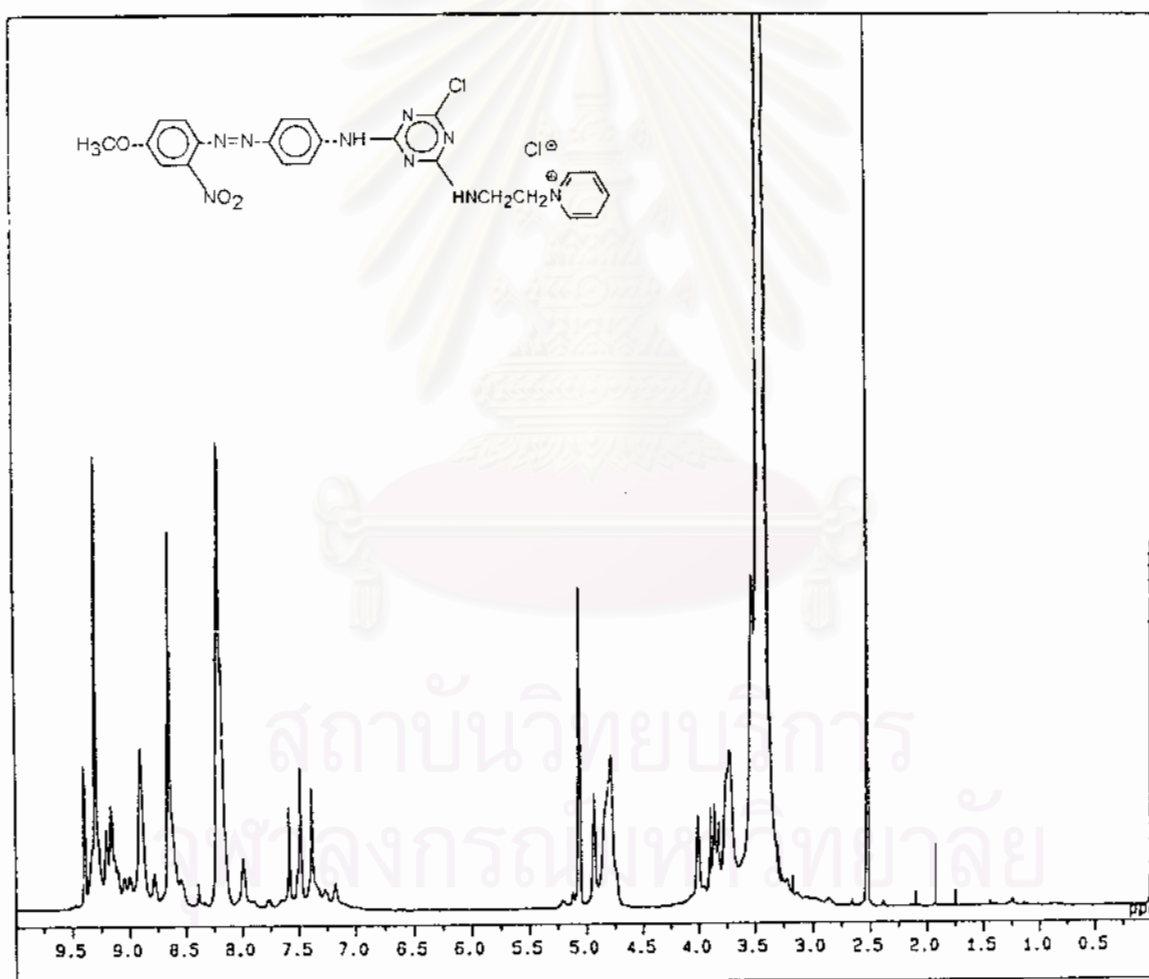
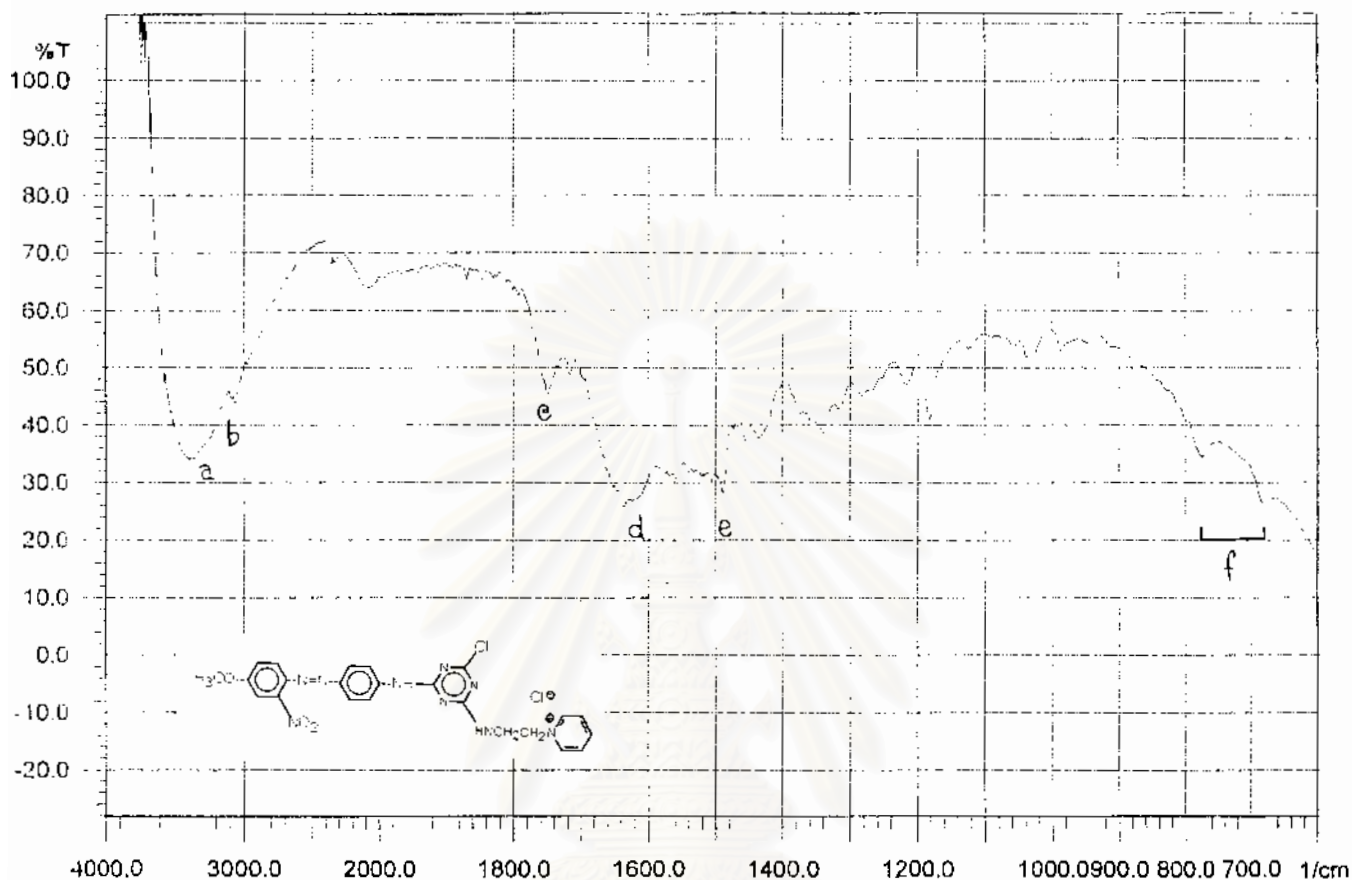
Figure 4.7 ^{1}H-NMR spectrum of synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline using DMSO as solvent.

Table 4.4 Proton chemical shifts of synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP → aniline.

Chemical shift (δ)	Multiplicity	Assignments
∼ 2.5	Singlet	Methyl protons
∼ 7.0 – 9.5	Multiplet	Aromatic protons on nitro-benzene and protons on pyridinium rings

Due to the introduction of quaternary pyridinium moiety into dye molecule, NMR analysis was one of convenient tool to prove the presence of this group. From Figure 4.7, the signals on the region of 7.0-9.5 ppm represented the absorption characteristic of aromatic protons on nitro benzene and pyridinium ring. However, protons on pyridine ring could be found further downfield of NMR spectrum due to the effect of heterocyclic system. Hence, the signals found in the region of 9.0-9.5 ppm could be assigned to the presence of quaternary pyridinium moiety.

4.3.2 <u>Synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline</u>

The FT-IR and ^{1}H NMR spectra of this synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline are shown in Figure 4.8 and 4.9 with the corresponding to the Table 4.5 and 4.6 respectively.

Table 4.5 FT-IR spectrum of synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline.

IR absorption peak	Wave number (cm-1)	Tentative assignment
a	3246	-N-H stretching
b	2870-2781	-C-H stretching
c	1734	-C=O stretching
d	768-687	-C-Cl stretching
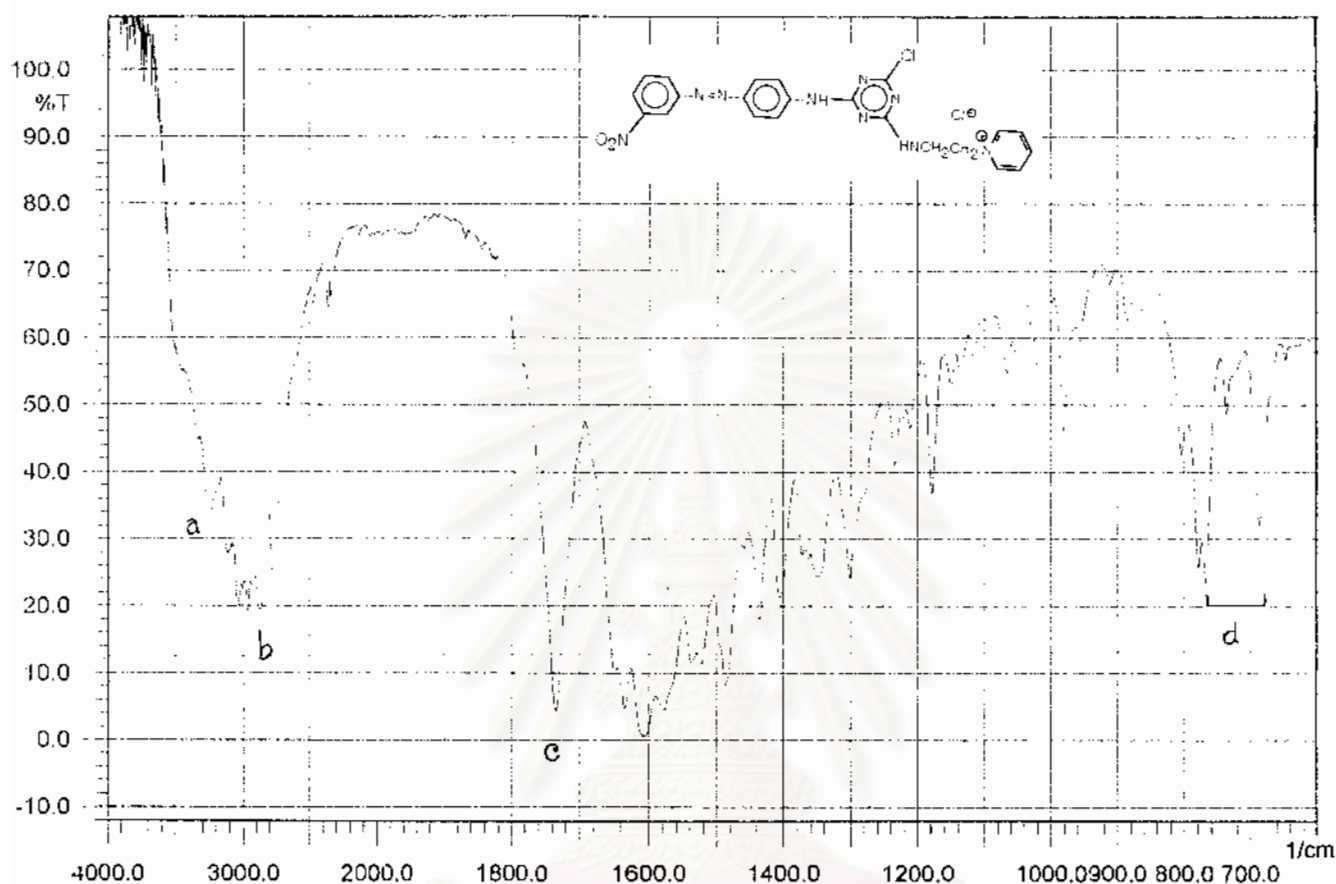
Figure 4.8 FT-IR spectrum of synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline.

The FT-IR spectrum revealed the important –C-H stretching of aliphatic compound and –C-Cl stretching of reactive group at 2870-2781 cm^{-1} and 768-687 cm^{-1} respectively.[38]

Table 4.6 Chemical shifts of synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline.

| Chemical shift (δ)	Multiplicity	Assignments
~ 7.5 – 9.5	Multiplet	Aromatic protons on nitro-benzene and protons on pyridinium rings.
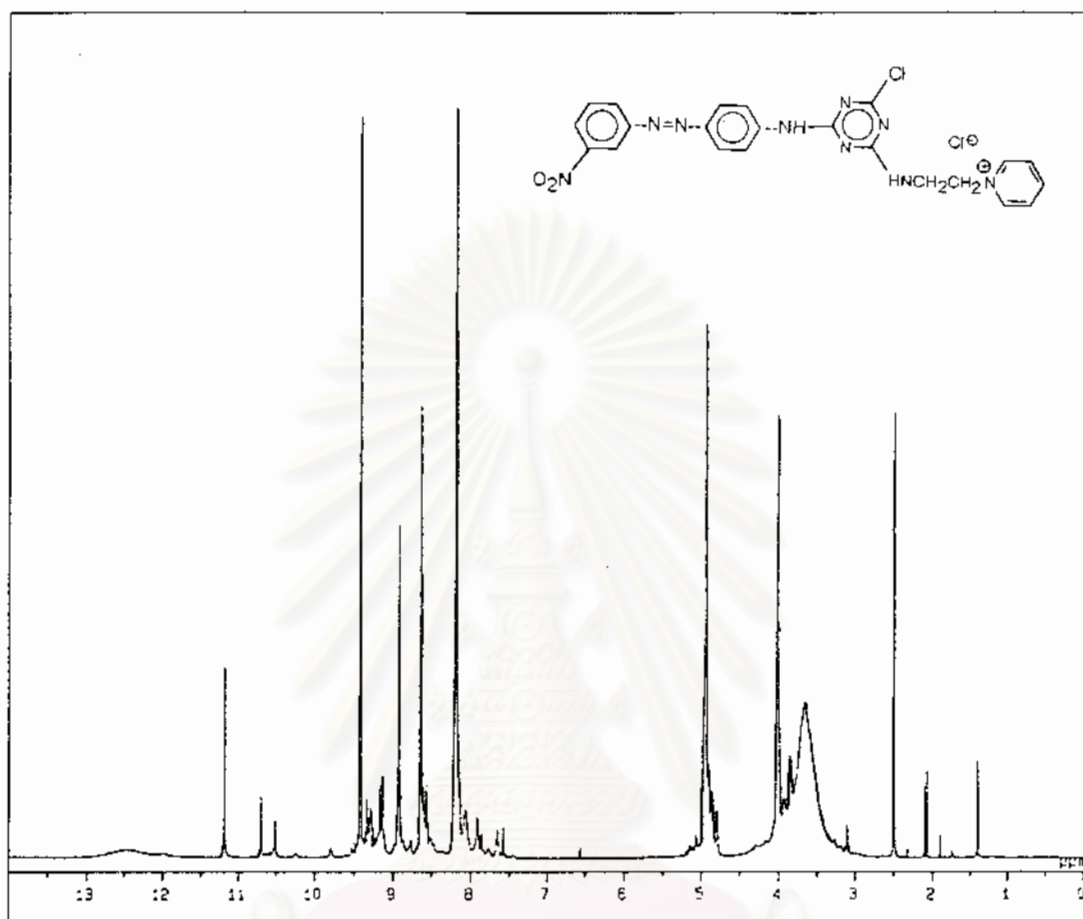
Figure 4.9 ^{1}H-NMR spectrum of synthesized cationic azo reactive dye
prepared from 3-nitroaniline $\rightarrow$ aniline using DMSO as solvent.

Similarily compared to the spectrum of synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP $\rightarrow$ aniline, the aromatic protons of benzene and pyridinium rings are observed at around 7.5 – 8.0 ppm, and 8.0 – 9.5 ppm, respectively.

As a result of the successful incorporation of cationic pyridinium moiety into the chromophore structure, the water-soluble reactive dyes containing highly substantive group to the cotton fiber were successfully prepared.

4.4 Dyeing properties of synthesized cationic azo reactive dyes on cotton fabric

4.4.1 Dyeing properties of synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP → aniline

The cotton fabrics were dyed with the synthesized cationic azo reactive using various dye concentrations ranging from 2 to 8 %o.w.f. in the absence of electrolyte by exhaust dyeing method as described in section 3.5. The results of the color yield,   % dye exhaustion and the degree of dye fixation were summarized in Table 4.7.

Table 4.7 Color yield, % dye exhaustion and the degree of fixation of the synthesized azo reactive dye from Fast Bordeaux salt GP → aniline at various concentrations of dye.

Dye concentration (%o.w.f.)	Color yield (K/S) [a]		% Exhaustion [a]		Fixation	
	Before soaping	After soaping	Primary	Secondary	%F	%F$_T$
2	0.637	0.514	20.796	24.022	80.691	19.384
4	1.080	0.823	17.381	22.678	76.204	17.282
6	1.526	1.053	8.631	28.827	69.004	19.892
8	1.785	1.228	7.353	31.013	68.796	21.336

[a] measured at 400 nm

4.4.2 Dyeing properties of synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline

The cotton fabrics were dyed with the synthesized cationic azo reactive using various dye concentrations ranging from 2 to 8 %o.w.f. in the absence of electrolyte by exhaustion dyeing method as described in section 3.5. The results of the color yield,   % dye exhaustion and the degree of dye fixation were summarized in Table 4.8.

Table 4.8 Color yield, % dye exhaustion and the degree of fixation of the

synthesized azo reactive dye prepared from 3-nitroaniline → aniline at various

concentrations of dye.

Dye concentration (%o.w.f.)	Color yield (K/S) [a]		% Exhaustion [a]		Fixation	
	Before soaping	After soaping	Primary	Secondary	%F	%F$_T$
2	0.690	0.445	34.815	31.818	64.493	20.520
4	1.199	0.695	29.630	43.541	57.965	25.239
6	1.650	0.896	17.079	48.955	54.303	26.584
8	2.074	1.023	11.932	52.258	49.325	25.776

[a] measured at 380 nm

The results show that the percentage of primary exhaustion decreases as the concentration of dye increases. The adsorption of dye was governed by the attractive interaction between cationic group of dye and negatively charged fiber surface. The adsorption was suited well with Langmuir isotherm in that adsorption of dye took place on specific sites in the fiber. No further adsorption occurred when the dye sites were fully occupied. The successive decrease in the percentage of dye exhaustion with an increase in the concentration in the dye bath is, therefore, due to the results of saturation effect. [40-41] After the addition of alkali, dye soluble in the dyebath were capable of further diffusing into the fiber. The capability of taking up more dyes in this stage was attributed to the presence of ionized cellulose generated by added alkali. [42-43] This kind of ionic interaction attracted cationic dyes to the interior of the fiber. As can be seen from the dyeing result, a significant increase in the percentage of dye exhaustion as high as 50 % in average was achieved without requirement of the addition of salt. The percent fixation after adding alkali suggested that the exhaustion dyes then underwent chemical reaction with cellulose hydroxyl groups under alkaline condition to produce dye-fiber covalent bond. However, the final fixation values was still unsatisfactory.

4.5 <u>Color fastness comparison of synthesized cationic azo reactive dyes with</u>
     <u>commercial cationic dye on the cotton fabric</u>

Both synthesized cationic azo dyes and selected commercial cationic dye, Aztrazon Red GTLN 200 % were dyed by the method described in the section 3.5 and 3.8.1 respectively to give the depth as 1 / 25 comparing to the Standard Depth Scales of AATCC Evaluation Procedure 4. The light and washing fastness properties of synthe- sized cationic azo reactive dyes and commercial cationic dye on the cotton fabric were evaluated.

4.5.1 <u>Light fastness evaluation</u>

The dyed fabrics were tested for the resistance of the color to the action of the artificial light source representative of natural daylight (D_{65}) according to ISO 105-B02 : 1994 (E) method. The degree of dye fading was assessed using standard blue wool scales.

Color fastness to artificial light of both synthesized cationic reactive dyes and selected commercial cationic dye are shown in Table 4.9.

Table 4.9 Light fastness (ISO 105-B02 : 1994 (E)) of both synthesized cationic
           azo reactive dyes containing *N-(*2-aminoethyl) pyridiniumchloride hydrochloride
           and selected commercial cationic dye at the depth of 1/25   comparing to the
           Standard Depth Scales of AATCC Evaluation Procedure 4.

Dyes	Light fastness	
	Before soaping	After soaping
Synthesized cationic azo reactive dye prepared from Fast Bordeaux Salt GP → aniline	3	3-4
Synthesized cationic azo reactive dye prepared from 3-nitroaniline → aniline	2-3	3
Astrazon Red GTLN 200 %	2	-

From the results in Table 4.9 showed that the light fastness of both synthesized cationic dyes on the cotton fiber were found to be better when compared to the commercial cationic dye. It is known that light fastness of cationic dye used in cellulosic dyeing is relatively low because of the existing positive charge causing the photo-catalytic fading on the cellulose. [15]   On the other hand, the cationic group of both synthesized dyes are believed to be temporarily attached to the chromophore and easily removed by alkali during washing-off. [15] In addition, the synthesized dyes containing monochlorotriazine reactive groups can readily form covalent bonds with the cotton fiber, enabling the transfer of energy from an excited state of the dye, due to light exposure, to the fiber, thus reducing the rate of photodegradation of the dye. [15]

4.5.2 Washing fastness evaluation

Washing fastness properties were evaluated by comparing the color change of dyed fabric and dye staining of each type of white multifiber adjacent fabric after washing test. The washing fastness was tested under ISO 105 : C03 condition and resultant values in this study were assessed with the grey scales. The washing fastness properties of both synthesized cationic azo reactive dyes using grey scales are shown in Table 4.10.

The higher the level number of standard grey scale (level 5) and lower value of Δ E means that there was little change in color of dyed fabric and no dye staining on white adjacent fabric after washing test.

Table 4.10 Washing fastness assessment of synthesized cationic azo
reactive dyes using grey scale.

Dye	Concentration of dye (%o.w.f.)	Color change	Color staining on multifiber adjacent fabric [a]					
			Ac	C	N	P	A	W
Synthesized cat-ionic azo reactive dye prepared from Fast Bordeaux Salt GP → aniline	2	5	5	5	5	5	5	5
	4	5	5	5	5	5	5	5
	6	5	5	5	5	5	5	5
	8	5	5	5	5	5	5	5
Synthesized cat-ionic azo reactive dye prepared from 3-nitroaniline → aniline	2	5	5	5	5	5	5	5
	4	5	5	5	5	5	5	5
	6	4-5	5	5	5	5	5	5
	8	5	5	5	5	5	5	5

[a] Ac = Acetate

C = Cotton

N = Nylon 6,6

P = Polyester

A = Acrylic

W = Wool

Good washing fastness of the synthesized dyes on cellulosic fiber was attributable to the covalent fixation of dyes onto cellulose. Overall, it can be possible that these reactive dye ranges could be developed, aiming at reducing the requirement of salts as well as simplicity of dyeing process. Hence, this new process would attract the interest of practical textile chemists in terms of environmental friendliness and simple dyeing process.

CHAPTER V
Conclusions

The results obtained from this thesis showed that azo reactive dyes containing a quaternary ammonium group as a temporarily solubilizing group can be prepared from several intermediates such as aniline, 3-nitroaniline and commercial diazonium salts reacting with cyanuric chloride and followed by N-(2-aminethyl) pyridiniumchloride hydrochloride.

TLC technique was particularly useful to follow the preparation of the designed dyes. Additional analytical techniques such as UV/Visible spectrophotometer, ^{1}H-NMR and FT-IR spectrometer provided further confirmation of the chemical structure of the dyes produced. However, purification of dyes was necessary in order to get clearly results.

The results of dyeing showed that the exhaustion in the absence of salt was quite low as well as the consequent fixation. However, the wash fastness and light fastness showed a marked improvement compared to the conventional basic dyes on cellulose.

The overall results revealed that these reactive dye ranges could be developed, aiming at reducing the requirement of salts as well as simplicity of dyeing process. Hence, this new process would attract the interest of practical textile chemists in terms of environmental friendliness and simple dyeing process.

CHAPTER VI

Recommendations

From this study, there leads to some recommendations for future work :

1. In the preparation of azo chromophore, the careful control of diazotization condition, i.e., temperature, pH, the diazo decomposition and side reactions are avoided, thus will lead to the high yield of diazonium salt.

2. The excess nitrite during diazotization may cause oxidation and decomposition of the resulted diazonium salt, thus the addition of sulfamic acid or urea is recommended.

3. Since there are many factors affecting dyeing properties, it is advisable to determine the appropriate condition for utilizing these dyes, such as the optimum temperature, liquor ratio, etc.

4. To cover the full range of shade, it is interesting to continue further research by choosing alternative coupling components.

REFERENCES

1. Mock, G.N. A Short History on Fiber Reactive Dyes. Textile Chemist and Colorist 28 No.11 (November 1996) : 10-11.

2. Renfrew, A.H.M. and Taylor, J.A. Cellulose Reactive Dyes : Recent Developments and Trends. JSDC, Review of Progress in Coloration 20 (1990) : 1-9.

3. Beech, W.F. Fibre-Reactive Dyes. London : Logos Press, 1970.

4. Aspland, J.R. Chapter 5 : Reactive Dyes and their Application. Textile Chemist and Colorist 24 No.5 (May 1992) : 31-36.

5. Hyde, R.F., Thompson, G. And Stanley, K.A. Commercial and Environmental Challenges in Continuous Dyeing with Fiber Reactive Dyes. Textile Chemist and Colorist 28 No. 10 (October 1996) : 25 – 29.

6. Carr, K. Reactive Dyes, Especially Bireactive Molecules : Structure and Synthesis. Edited by Peters, A.T. and Freeman, H.S., Modern Colorants : Synthesis and Structure, Advances in Color Chemistry Series - Volume 3, 87-122. London : Blackie Academic & Professional, 1995.

7. Aspland, J.R. Chapter 5 / Part 2 : Practical Application of Reactive Dyes. Textile Chemist and Colorist 24 No.6 (June 1992) : 35-40.

8. Lewis, D.M. New Possibilities to Improve Cellulosic Fibre Dyeing Process with Fibre-Reactive system. JSDC 27 (1997) : 5-17.

9. Zollinger, H. Some Thoughts on Innovation Impulses in Dyeing Research and Development. Textile Chemist and Colorist 23 No.12 (December 1991) : 19-24.

10 Uygur, A. and Hall, M. An Investigation into the Reaction of Bifunctional Reactive Dye at Various pH Levels. JSDC 112 (May/June 1996) : 167-169.

11. Stead, C.V. Chemistry of Reactive Dyes Edited by Shore, J., Colorants and Auxiliaries, Vol.1-Colorants West Yorkshire : Sxciety of Dyers and Colorists, 1990.

12. Lewis, D.M. and McIlroy, K.A. The Chemical Modification of Cellulosic Fibres to Enhance Dyeability. JSDC, Review of Progress in Coloration 27 (1997) : 5-17.

13. Seong, H.S. and Ko, S.W. Synthesis, Application and Evaluation of Cationising Agents for Cellulosic Fibres. JSDC 114 (April 1998) : 124-129.

14. Kamel, M., Kamel M.M., Youssef, B.M. and Shokry, G.M. Dyeing of Cationised Cotton with Acid Dyes. JSDC 114 (March 1998) : 101-104.

15. Suntifueangkul, P. Synthesis and Application of Highly Substantive Reactive Dyes. Master's Thesis Applied Polymer Science and Textile Technology, Faculty of Science, Chulalongkorn University, 1999.

16. Kuramoto, N. The Photodegradation of Synthetic Colorants. Edited by Peters, A.T. and Freeman, H.S., Physico-Chemical Principles of Color Chemistry, Advances in Color Chemistry Series - Volume 4, 196-204. London : Blackie Acadamic & Professional, 1996.

17. Srikulkit, K. and Suntifueangkul, P. Salt-free dyeing of cotton cellulose with model cationic reactive dye. JSDC accepted.

18. Nevell, T.P. Cellulose: Structure, Properties and Behaviour in the Dyeing Process. Edited by Shore, J., Cellulosic Dyeing, 1-15. West Yorkshire : Society of Dyers and Colourists, 1995.

19. Nevell, T.P Cellulose-Its Structure and Properties. Edited by Preston, C., The Dyeing of Cellulosic Fibres, 4-5. West Yorkshire : Dyers' Company Publication Trust, 1986.

20. Chankatlieat, M. Introductory Textile Science, Bangkok : Horattanachai, 1998.

21. Hudson, P.B., Clapp, A.C. and Kness, D. Joseph's Introductory Textile Science, 6th Edition, Fort Worth Philadelphia : Harcourt Brace Jovanovich College Publishers, 1993.

22. The Textile Institute, Identification of Textile Materials, 7th Edition, Manchester : 1985.

23. Zollinger, H. Color Chemistry. Weinheim : VCH, 1987.

24. Rys, P. and Zollinger, H. Reactive Dye-Fiber Systems Edited by Johnson, A., The Theory of Coloration of Textiles. 2nd Edition, West Yorkshire : Society of Dyers and Colorists, 1989.

25. Abrahart, E.N. Dyes and Their Intermediates. 2nd Edition, London : Edward Arnold (Publishers), 1977.

26. Stead, C.V. Chemistry of Azo Colorants Edited by Shore, J., Colorants and Auxiliaries, Vol.1-Colorants. West Yorkshire : Society of Dyers and Colorists, 1990.

27. Booth, G. The Manufacture of Organic Colorants and Intermediates. Bradford : Society of Dyers and Colorists, 1988.

28. Rangnekar, D.W. and Singh, P.P. An Introduction to Synthetic Dyes. Bombay : Himalaya
      Publishing House, 1980.

29. Shah, K.M. Handbook of Synthetic Dyes and Pigments Volume 1-Synthetic dyes.
      Bombay : Multi-Tech Publishing, 1994.

30. Morrison, R.T. and Boyd, R.N. Organic Chemistry. 2nd Edition. Boston : Allyn and Bacon
      Inc., 1971.

31. Chumanee, S. Study of Some 2,7-Bis(2-hydroxynitrophenylazo) Derivatives of
      Chromotropic Acid as Spectrometric Reagents for Bismuth (III). Master's Thesis
      Department of Chemistry, Faculty of Science, Chulalongkorn University,

32. Color Index. Volume 1,4,5. 3rd Edition. Bradford : Society of Dyers and Colourists &
      American Association of Textile Chemists and Colorists, 1987.

33. Naphthol AS. Technical Information. DyStar Textilfarben GmbH & Co.

34. Astrazon. Technical Information. DyStar Textilfarben GmbH & Co.

35. Berger-Schunn, A. Practical Color Measurement. New York : John Wiley & Sons, Inc.,
      1994.

36. International Standard ISO 105-B02:1994 Color Fastness to Artificial Light : Xenon Arc
      Fading Lamp Test.

37. International Standard ISO 105-C03:1989 Color Fastness to Washing : Test 3.

38. Biemann, K., Tables of Spectral Data for Structure Determination of Organic
      Compounds. 2nd Edition. Berllin : Springer-verlag, 1989.

39. Venkataraman, K. The Analytical Chemistry of Synthetic Dyes. New York : John Wiley &
      Sons, 1977.

40. Bae, S.H. et al. Adsorption Behavior of Reactive Dyes on Cellulose. Dyes and Pigments.
      34 No.1(1997) : 37-55.

41. Bae, S.H. et al. Diffusion / Adsorption Behavior of Reactive Dyes in Cellulose. Dyes and
      Pigments. 34 No.4(1997) : 321-340.

42. Motomura, H. et al. Dissociation of Hydroxyl Groups of Cellulose at Low Ionic Strengths.
      Dyes and Pigments 39 No.4 (1998) : 243-258.

43. Bae, S.H. et al. Effect of Anionic Groups in Cellulose on the Adsorption of Reactive
      Dyes on Cellulose. Dyes and Pigments 36 No.1 (1998) : 61-77.

Appendices

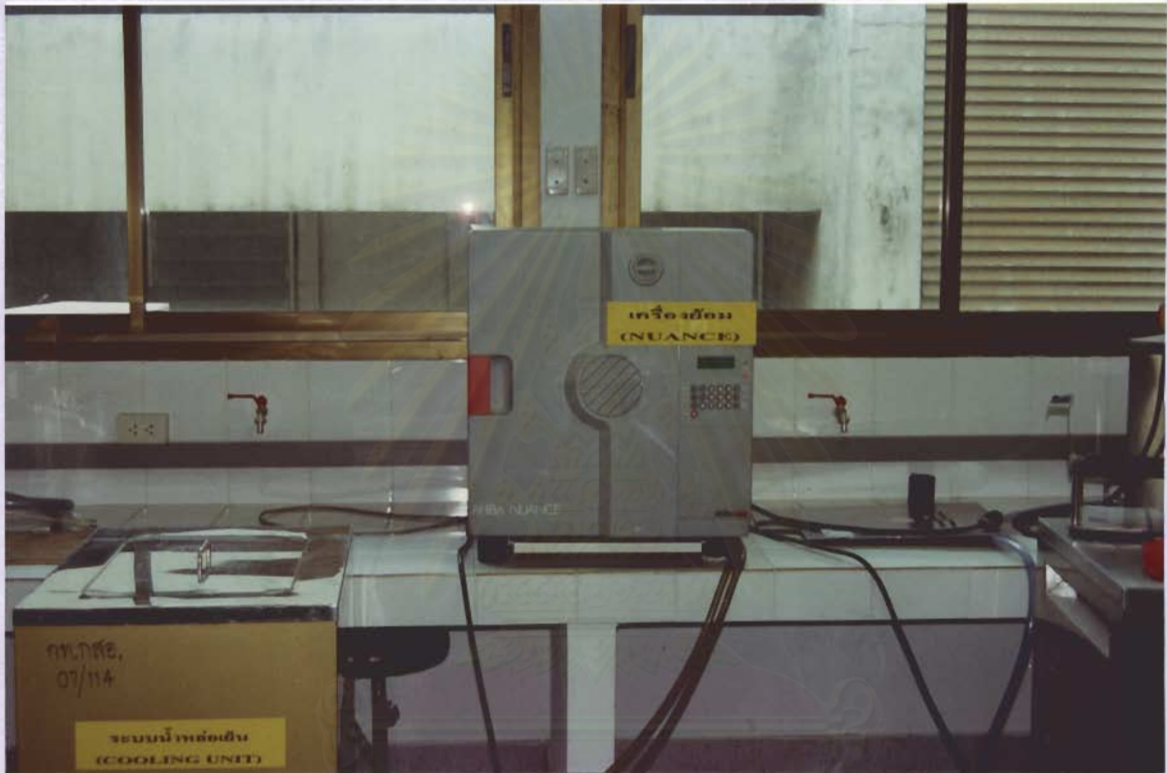# Appendix A

Photographs of instrument used in this experiment.

Figure A-1 Laboratory dyeing machine: Ahiba Nuance.

Figure A-2 Light fastness tester: SUGA Xenon weather meter.

Figure A-3 Reflectance spectrophotometer: Gretag-Macbeth Color Eye 7000 and Optiview software.

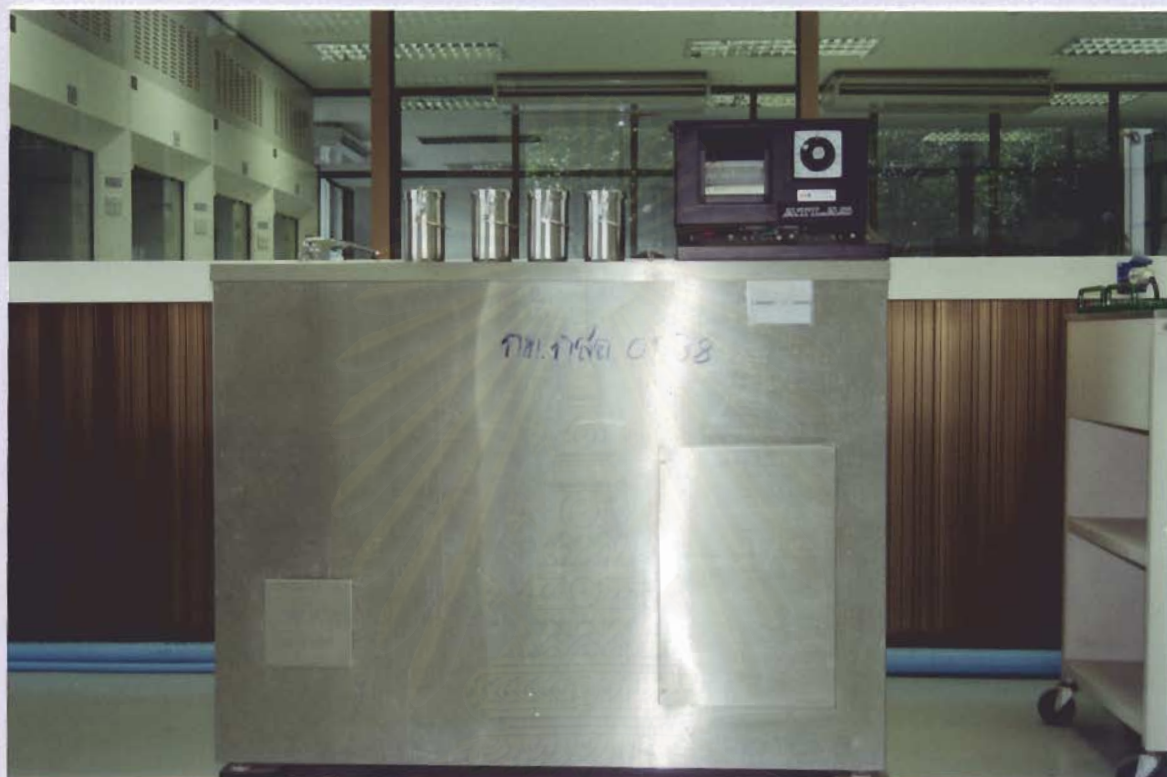Figure A-4 UV/Visible spectrometer: Jenway 6405.

Figure A-5 Washing fastness tester : Atlas.

Appendix B

Example of dyed cotton fabric

% o.w.g.	Synthesized cationic azo reactive dye (I) containing *N*-(2-aminoethyl) pyridiniumchloride hydrochloride [Fast Bordeaux Salt GP → aniline]	Synthesized cationic azo reactive dye (II) containing *N*-(2-aminoethyl) pyridiniumchloride hydrochloride [3-nitroaniline → aniline]
2		
4		
6		
8		

Appendix C

Preparation of *N*-(2-aminoethyl) pyridiniumchloride hydrochloride. [15]

An aqueous solution containing 23.5 g. (0.2 mole) of 2-chloroethylamine hydrochloride, 55 ml. (0.7 mole) of pyridine and 75 ml. of distilled water were added into a 250 ml. three necked round bottom flask. The mixture was heated under reflux for three fours on a heating mantle unit equipped with a magnetic stirrer. After that, the reaction mixture was cooled down to room temperature and extracted with toluene   (three portions, 150 ml. each), the aqueous layer was then acidified to pH 2 with concentrated hydrochloric acid and evaporated to concentrated syrupy liquid under vacuum. An isolation of *N*-(2-aminoethyl) pyridiniumchloride hydrochloride was made by dropping syrupy liquid into 2-propanol. The solidified product was filtered off and washed with acetone and dried to give yield of 85 %.

BIOGRAPHY

Mrs. Sujinda Auancharoenkul Jitjaicham was born in Bangkok, Thailand, on July 8th, 1965. She graduated with a Bachelor of Engineering degree with a major in Textile Chemical Engineering from Rajamangala Institute of Technology, formerly the Institute of Technology and Vocational Education, Bangkok in 1989. After ten years working in textile dyeing, she started as a graduate student in the Department of Materials Science with a major in Applied Polymer Science and Textile Technology, Chulalongkorn University in June 1998, and completed the program in October 2000. She has been working at the Department of Home Economics, Faculty of Science, Srinakharinwirot University since 1996 to present.