การสังเคราะห์และประยุกต์สีรีแอคทีฟประเภทติดทนสูง

นายพรชัย สันติเฟื่องกุล

SYNTHESIS AND APPLICATION OF HIGHLY SUBSTANTIVE REACTIVE DYES

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Applied Polymer Science and Textile Technology

Department of Materials Science

Graduate School

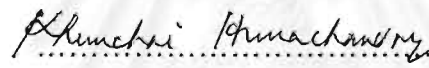Chulalongkorn University

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Thesis Title   Synthesis and Application of Highly Substantive Reactive Dyes

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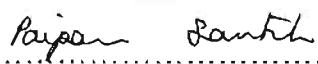Thesis Advisor   Kawee Srikulkit, Ph.D.

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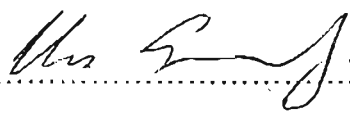
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พรชัย สันติเฟื่องกูล : การสังเคราะห์และประยุกต์สีรีแอคทีฟประเภทติดทนสูง
(SYNTHESIS AND APPLICATION OF HIGHLY SUBSTANTIVE REACTIVE DYES)
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งานวิจัยนี้ได้สังเคราะห์สีย้อมรีแอคทีฟที่มีสมบัติการดูดซึมสูง ซึ่งจะนำไปสู่กระบวน
การย้อมสีแบบใหม่ที่ไม่จำเป็นต้องอาศัยอิเล็กโทรไลต์เป็นสารช่วยย้อม การสังเคราะห์สีทำได้
โดยการดัดแปรโครโมฟอร์ชนิดแอนทราควิโนนที่มีหมู่อะมิโนอิสระเป็นองค์ประกอบ โดยเริ่ม
จากการทำปฏิกิริยากับไซยานูริกคลอไรด์แล้วตามด้วยเอ็น-2-(อะมิโนเอทิล)พิริดิเนียมคลอไรด์
ไฮโดรคลอไรด์ การติดตามปฏิกิริยาได้อาศัยเทคนิคทินเลเยอร์โครมาโตกราฟี

นำสีที่เตรียมได้ไปทดลองย้อมเส้นใยเซลลูโลสโดยอาศัยกระบวนการย้อมแบบย้อม
แช่ การย้อมได้กระทำในสภาวะไร้อิเล็กโทรไลต์เพื่อศึกษาความสามารถในการดูดซึมของสี
ปรากฏว่าได้เปอร์เซ็นต์การดูดซึมสีที่สูงแม้ว่าจะไม่ได้เติมสารอิเล็กโทรไลต์ลงไปในน้ำย้อมก็
ตาม การที่สีมีความสามารถในการดูดซึมสูงนั้นได้อาศัยแรงดึงดูดระหว่างประจุบวกบน
โมเลกุลสีกับศักย์ประจุลบที่เกิดขึ้นรอบๆผิวของเส้นใย การวัดเปอร์เซ็นต์การผนึกของสีทั้ง
หมดบนเส้นใยสูงเทียบได้กับสีรีแอคทีฟประเภทที่ย้อมแบบจำเป็นต้องเติมเกลือที่มีอยู่ในตลาด
ความคงทนของสีต่อการซักล้างก็อยู่ในระดับสูง และสมบัติที่สำคัญอันหนึ่งคือ ยังพบว่าสีย้อม
รีแอคทีฟที่มีประจุบวกประเภทนี้ให้สมบัติความคงทนต่อแสงบนเส้นใยเซลลูโลสที่ดีต่างจาก
กรณีของสีย้อมประจุบวกแบบเก่า เป็นเพราะว่าหมู่ประจุบวกบนสีรีแอคทีฟประเภทนี้ได้ถูก
ทำลายออกจากโครโมฟอร์และถูกกำจัดออกไปในกระบวนการซักล้าง.

ภาควิชา วัสดุศาสตร์
สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ
ปีการศึกษา 2542
ลายมือชื่อนิสิต พรชัย สันติเฟื่องกูล
ลายมือชื่ออาจารย์ที่ปรึกษา กาวี ศรีกูลกิจ
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

A novel highly substantive reactive dye based on anthraquinone chromophore was prepared. The synthesis of this dye was achieved by the modification of free amino group containing anthraquinone by, firstly, reacting with cyanuric chloride and followed by N-(2-aminoethyl)pyridiniumchloride hydrochloride. TLC technique was employed to follow the chemical reactions.

The application of the prepared dye into cellulosic fabric was carried out using exhaustion dyeing process in the absence of electrolytes. The results showed that, despite no electrolyte present in the dyebath, high percentage of dye exhaustion could be obtainable. The high percentage of dye exhaustion was attributed to the attractive force between positive charge on the dye molecule and negatively charged fiber surface. The high degree of total dye fixation comparable to the low salt reactive dye available in the market was also achievable. The wash fastness of dyeing was excellent. Surprisingly, it was found that this type of cationic group containing reactive dye showed markedly improved light fastness properties which could not be achieved in the case of traditional cationic dyes. It was believed that the cationic group was loosely attached to the chormophore which was later eliminated during washing-off process.

ภาควิชา................วัสดุศาสตร์................................. ลายมือชื่อนิสิต..

สาขาวิชา.วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา........................

ปีการศึกษา..........2542.. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม....................

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CHAPTER I

Introduction

The world's demand for textile continues to grow. The annual consumption of textile fibers rose by 2% in 1995 and that rate of growth is expected to continue[1]. Cellulose fibers (such as cotton, linen, jute and also of regenerated cellulosic fiber) consumption still represents the largest market share at 45%; it is estimated that this figure will have remained constant during 1996 and 1997. The dyes currently employed for dyeing cellulosic fibers, reactive dye shows the greatest growth potential. The reason for the popularity of this dye class can be attributed to their brilliant shades, good to excellent wet fastness, wide shade range and versatile, fairly simple application method. Today some 21% of the dyes used around the world for dyeing cellulosic fibers are reactive dyes[2].

There are however certain environmental problems which may arise from the use of reactive dyes and associated chemicals. The problems occur from using high salt concentration (40-100 g/l)[3,4], usually sodium chloride or sodium sulfate, to achieve adequate dye substantivity for the fibers. It is well known that when fibers are immersed in water they develop a negative charge on the fiber surface. Since the sign of this charge is the same as that on the anionic dye, the fiber repels the dye, hindering or even preventing its close approach. With most water-soluble anionic dyes (such as direct, reactive dyes etc.), the addition of an electrolyte enhances the attractions by masking the negative charges of the fiber, and the dye uptake is therefore increased. However, high electrolyte concentration of both sodium chloride and sodium sulfate in dyebath discharges are undesirable, as increase salinity in rivers upsets the delicate balance of aquatic flora and fauna[1]. Sulfate discharge may be even more suspect since it attacks

concrete pipes and also has been associated with an increase in total acidity of streams, lakes and rivers[1,3]. Furthermore, when dyeing polyester/cotton blends by the one-bath/one-step method, the high salt concentrations needed for the reactive dye can cause particles of disperse dye, used for the polyester component, to aggregate.

These problems have attracted the research and development activities of both universities and dye manufacturing laboratories[4]. Recently, dye manufacturers have developed several dye ranges including multifunctional reactive dyes as a means of improving fixation efficiency of reactive dyes and also reducing salt consumption. For example, Ciba has launched the Cibacron LS high conc dyes (where LS stands for Low Salt) and the Remazol EF (Environmentally Friendly) range (DyStar company). An alternative approach for improving the dyeability of cellulosic fiber was reported by an incorporation of amino cationic groups into the cellulosic fiber before dyeing process[1,3,5]. The presence of cationic group has a marked effect on the uptake of anionic reactive dyes. Such modified fibers could be dyed with most reactive dyes in the absence of salt. However, the major disadvantage of modification of cellulosic fibers to enhance their dyeability is that this process requires severe treatment condition which leads to fiber degradation and discoloration. So, these procedures are not widely used in industrial practice.

The purpose of this thesis is to develop the novel reactive dye which has a highly substantive property towards cellulosic substrates, hence eliminating of electrolyte addition during dyeing process as possible. The principle idea on how to prepare such a dye is derived from the modification of structure of cationic dyes. Eventhough, cationic dyes have been well-known to have high substantivity towards cellulosic fibers but, because of their self-degradative disadvantage when exposing to sunlight dye chemists in the past were discouraged to continue carrying out researches on the application of cationic dyes onto cellulosic substrates. Yet the author still believes that dyeing of cellulosic substrates with cationic dyes without compromising on light fastness

properties could be possible. In this experiment, the novel cationic reactive dye will be prepared and its application and also its dyeing properties, especially light fastness properties will be investigated. The general structure of the dye is composed of a chromogen, a reactive group and a cationic group. It is intended that the cationic group of the dye will act as the solubilizing group and play an important role in promoting dye absorption into the fiber. Once being absorbed inside the fiber, the dye molecule could undergo the chemical reaction and then be covalently fixed onto the fiber. After that the cationic group must be removed from the dye molecule by soaping-off at the boiling temperature. Finally the cationic group is expected to be no longer present on the dyed fabric, hence producing no effect on light fastness properties of dyed fabric. The scope of this experiment will comprise three parts. Firstly, the novel reactive dye will be synthesized. Characterizations of the synthesized dye will be carried out using fourier-transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, thin layer chromatography and elemental analysis techniques. Secondly, the synthesized dye will be applied onto bleached cotton fabric by exhaustion dyeing method in the absence of electrolytes. The percentage of dye exhaustion and the degree of dye fixation will be determined spectrophotometrically. Finally, fastness properties including wash fastness and light fastness properties are evaluated.

CHAPTER II

Literature Review

2.1 Cellulosic fiber

2.1.1 The molecular structure of cellulose

Cellulose is the most abundant of all organic polymer, natural or otherwise. Cotton fiber, the most important cellulosic fiber and widely used in textile industry, is almost pure cellulose (up to 95%)[6]. Other fibers which have been embodied as cellulosic are linen, jute, hemp, viscose rayon and cuprammonium rayon and these contains a vary in proportion of cellulose.

The structural formula of cellulose can be written as in Figure 2.1[7]. It is a linear polymer which is composed of glucose unit linking together by 1,4-β-(D)-glycosidic bond. The repeating unit is the cellubiose which is two glucose units joined together at the terminal hydroxyl groups attached to carbon atoms position 1 and 4 with the loss to a molecule of water (Scheme 2.1)[8].
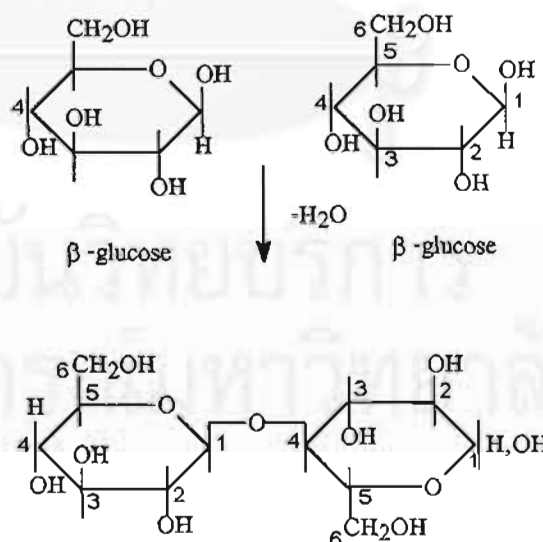
Scheme 2.1 Cellubiose unit
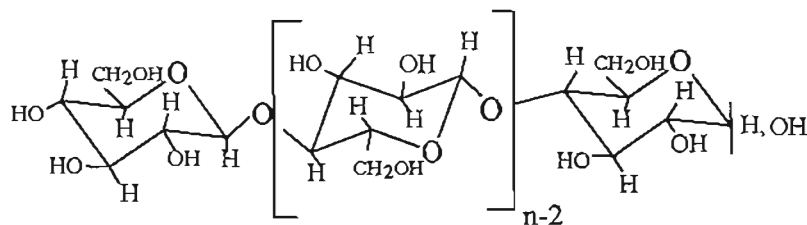
Figure 2.1 Structure of cellulose.

The average degree of polymerization (DP) or the number of subscript n indicates the average number of glucose molecules of a given cellulosic fiber. With native cellulose it may be as high as 14,000 but alkali purified cellulose usually reduces this to about 1,000-2,000, whereas with regenerated fibers it lies between 250 and 700[9].

Since each glucose unit in the polymer chain contains 3 hydroxyl groups (two secondary and one primary alcohol) at carbons in position 2, 3 and 6. The large number of hydroxyl groups readily form hydrogen bonds with water and are therefore responsible for the hydrophilic nature of cellulosic fibers. The formation of hydrogen bonds between adjacent cellulose chains has a particularly important effect. Cellulose will not dissolve in water , and in fact is insoluble in all but a few organic solvents. Furthermore, the interaction between the polymer chains is so strong that cellulose dose not melt on heating.

Cellulose contains no groups which will ionize readily in neutral solutions[7,8]. But all polymers develop a negative charge on the fiber surface when immersed in water and the possibility of the formation of some few carboxylic groups (-COOH), during bleaching or other degradation processes. Since the pK_a of these carboxylic groups is approximately 3.2, the cellulose fibers consequently carry a negative charge in aqueous conditions[10]. As the dyebath pH rises above 7.0 the fiber becomes more negatively charged due to the ionization of the hydroxyl groups[3,10].

Since the major classes of dye used for dyeing cellulosic fibers are applied as anions, exhaustion dyeing of such fibers is carried out in the presence of electrolyte which reduces dye-fiber repulsion and thereby promotes dye uptake.

2.1.2 Cotton fiber : structure, morphology and chemical composition.

Cotton is obtained from the seed hair of plants of the genus Gossypium[9]. The mature staple fiber takes the form of flat, convoluted ribbon, varying in length, fineness, color, etc., according to source. With a cross section that looks a bit like a bean-shaped. These characteristics make cotton easy to recognize under optical microscope as Figure 2.2

The cotton fiber consists of four main parts[10,11]. Their morphology, illustrated schematically in Figure 2.3. The layers in the cell structure are from the outside of the fiber to the inside, cuticle, primary wall, secondary wall and lumen. The cuticle comprises a very thin outer layer of wax, protein, pectin and mineral matter, is 2.5% of the fiber weight and is amorphous. The primary wall is 2.5% of the fiber weight, has a crystallinity index of 30%, and is composed of cellulose. The secondary wall constitutes the bulk of the mature fiber and comprises cellulose fibrils arranged spirally around the longitudinal fiber axis laid down in successive layers, the direction of spiral reversing at intervals along the fiber length. The secondary wall is 91.5% of the fiber weight, has a crystallinity index of 70% . The lumen or cavity is composed of protoplasmic residues. The general state of knowledge of the chemical composition of a mature cotton fiber is presented in Table 2.1[11].
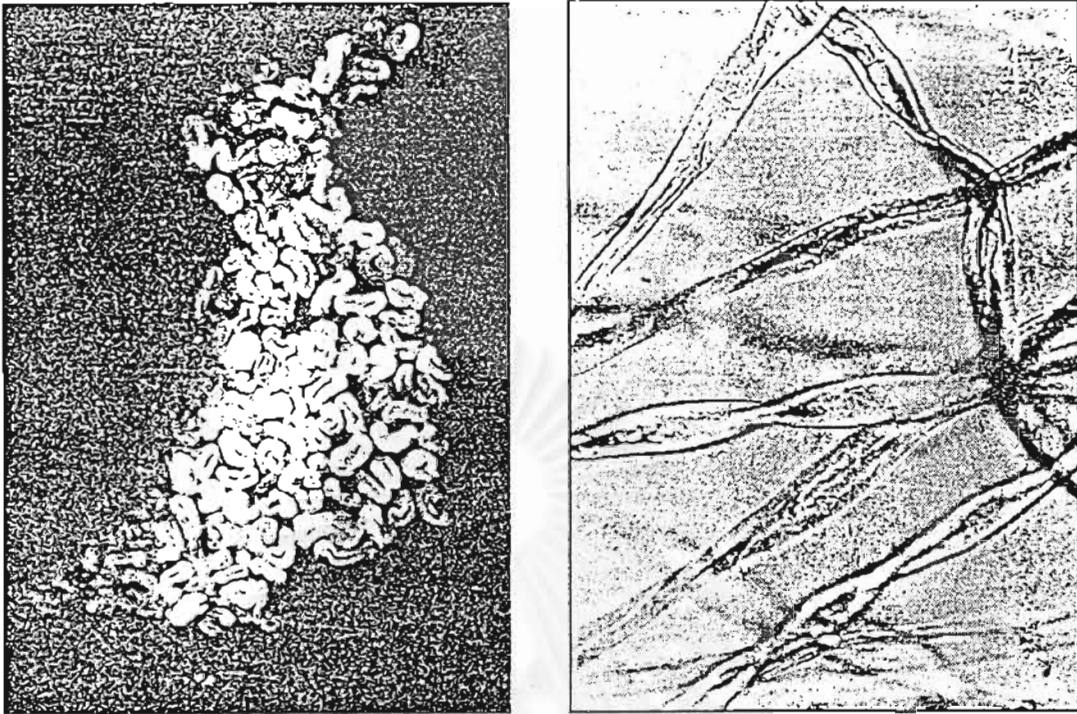
Figure 2.2 Optical micrographs of raw cotton fibers x 184[9].
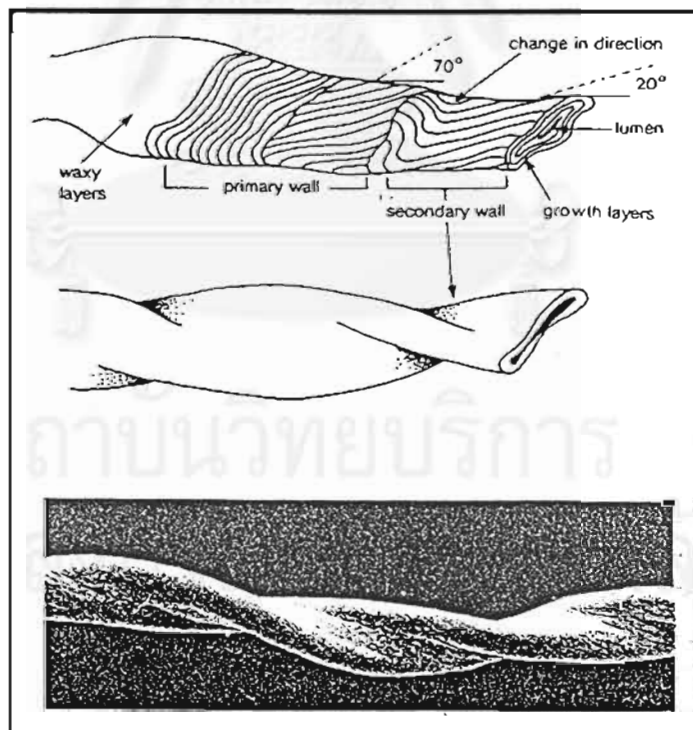
Figure 2.3 The structure of a cotton fiber[8].

Table 2.1 Typical values for the composition of a mature dry cotton fiber[11].

| Constituent | Composition of a fiber | | |
	Typical%	Low%	High%
Cellulose	94.0	88.0	96.0
Protein	1.3	1.1	1.9
Pectin substances	0.9	0.7	1.2
Wax	0.6	0.4	1.0
Mineral matters	1.2	0.7	1.6
Maleic, citric, and			
other organic acids	0.8	0.5	1.0
Total sugars	0.3		

2.1.3 Cotton properties

The properties of cotton are shown in Table 2.2.

Table 2.2 Properties of cotton[12].

Molecular Structure	Long chain of cellulose
Microscopic Features	
Length:	25 to 60 nm.
Width:	12 to 20 μm.
Cross-section:	Bean-shaped
Color:	Usually a creamy off white color
Light reflection:	Low luster, dull appearance

Table 2.2(continued)

Physical Properties	
Tensile strength:	96,700 pound/inch^2
Elongation:	4 to 13% elongation at break
Tenacity (g/den.):	3 to 5 (dry), 3.6 to 6 (wet)
Density (g/cm^3):	1.54 to 1.62
Moisture content:	8.5%
Resiliency:	Low
Toughness and stiffness:	High
Abrasion resistance:	Fair to good
Chemical Properties	
Sunlight and heat:	May be heated in the dry state to a temperature of 150°C without undergoing decomposition but can be damaged by excessive light.
Organic solvents:	Resistant to most organic solvents.
Effect of bleaches:	Can be bleached without fiber damage.
Acids and alkalis:	Highly resistant to alkali. Strong mineral acid causes fiber damage readily and organic acids do a little damage.
Dyeability:	Good affinity for various types of dyes. Dyeable with direct, vat, sulphur and reactive dyes.
Biological Properties	
Effects of microorganisms:	Vulnerable to action by bacteria and mould.

Table 2.2(continued)

Effects of insects:	Starched cotton are attacked by silverfish.
Optical Properties	
Axial refraction:	1.596
Transverse refraction:	1.534
Double refraction:	0.062
Electrical and thermal conductivity	Good heat conductor.
Flamability behavior	Burns very readily and once ignited, a fabric will carry flame.

2.2 Dyes for cellulosic fibers

Cellulose fiber are dyed using various classes of dyes such as direct, sulphur, vat, azoic, basic and reactive dyes. Each type of dyes differentiates from another by differences in dyeing methods and their abilities to adhere to the fiber.

Dyers and dye chemists have known for a long time that three ways in which dyes can be retained by fibers[10,13]. In the case of azoic, vat and sulphur dyes, water soluble precursors are applied to the fiber and then, after generation of the dye, are caused to aggregate to form water insoluble molecules which are, essentially, trapped within the fiber pores. Direct dyes rely upon van der Waals forces and the formation of hydrogen bonds between a long planar dye molecule with substrate. The wet fastness of direct dyes on cellulose is distinctly limited. Reactive dyes ,which usually have excellent wash fastness, achieve fixation by the formation of covalent bonds between the reactive groups on the dye and the hydroxyl groups on the cellulose.

Of all cellulosic dyes, reactive dye are increasingly applied to cellulosic fibers. Table 2.3 shows dye consumption for cellulosic fibers in the world market and in

Japan[14]. The rapid acceptance and widespread use of reactive dyes have been due to their useful properties, the growing consumption of cellulosic fiber and the rising proportion of cotton in end-uses for which the fastness properties of reactive dyes are appropriate.

Table 2.3 Market share of dyes for cellulosic fibers by dye class (1988)

Dye class	Market share (%)	
	World	Japan
Reactive	21	47
Direct	25	28
Vat	13	5
Sulphur	32	11
Azoic	9	9

2.2.1 Direct Dyes

Direct dyes are defined as water - soluble anionic dyes with good substantivity for cellulosic fiber, which are usually applied from an aqueous dyebath containing an electrolyte and not requiring the use of a mordant[15]. Most direct dyes have azo structures, particularly in the diazo and polyazo types. Other chemical classes derived from non-azo chromogens such as stilbene, thiazole, dioxazine and phthalocyanine have also been synthesized. Figure 2.4 to 2.8 are examples of direct dye that have been used in commercial ranges[10].
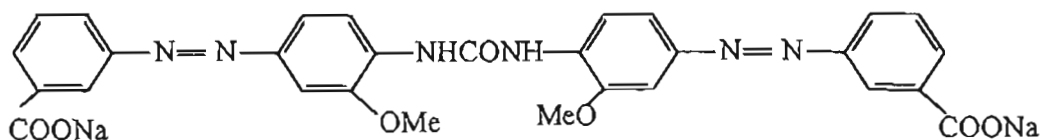
Figure 2.4 Sirius Yellow G, C.I. Direct Yellow 49 (Diazo class).
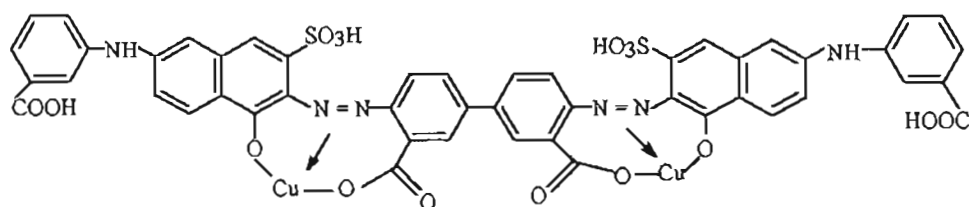
Figure 2.5 Sirius Supra Blue 3RL, C.I. Direct Blue 93 (Copper – complex azo).
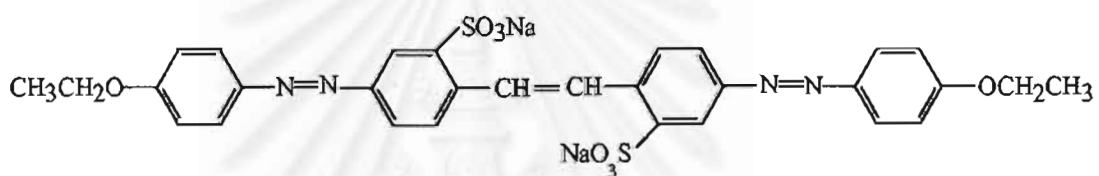
Figure 2.6 C.I. Direct Yellow 12 (Stilbene- azo dye).
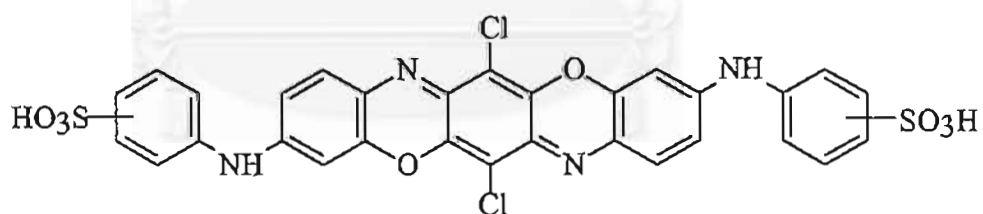
Figure 2.7 C.I. Direct Blue 106 (Triphenodioxazine).
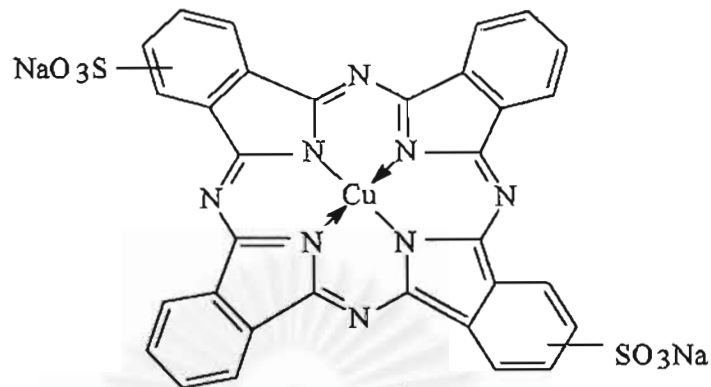
Figure 2.8 C.I. Direct Blue 86 (Phthalocyanine dye).

The forces of interaction operating between this class of dye and celluloses are predominantly van der Waals, arising from the highly conjugated nature of the large, linear, and coplanar dye molecules. Furthermore, hydrogen bonding between the cellulosic hydroxyl groups and appropriate groups in the dye may also contribute to dye–fiber attachment in the dye, dyed state[10]. This relatively weak dye–fiber bonds, coupled with the fairly high water solubility of the dyes and the hydrophilic nature of the cellulosic fibers, are responsible for the generally poor to moderate wet fastness properties as compared with other classes of dye for cellulosic fiber. In the application method, the adsorption of direct dyes from the dyebath is promoted by the presence of salt. Added electrolytes neutralize the negative charge of the cellulosic fiber that would repel a direct dye anion, and thus promote dye exhaustion, binding of the dye onto the fiber surface and facilitate diffusion of it into the fiber pores. The differences in dyeing behavior of direct dyes are subclassified in accordance with their relative needs for salt in the dyebath and the regulation of dyebath temperature. The subdivisions of this dye are covered by the following S.D.C. classification.

Class A (self – levelling dye) : These dyes have little salt sensitivity and are self–levelling or good migration properties. The dye can be applied easily and require high concentration of salt

Class B (Salt controllable dye) : These are not self–levelling but dye uptake is controlled by careful salt addition.

Class C (Temperature controllable dye) : There are not self–levelling and highly sensitive to salt. The exhaustion cannot be adequately controlled solely by salt addition and additional control of temperature is required for level dyeing. Dyes in the this class all possess very high substantivity, even in the presence of only small amounts of salt.

The merits of direct dyes are their simplicity of application, the wide range of shades they can provide, and relatively inexpensive. However, the wet fastness properties of dyeing on cellulosic fibers generally leaves much to be desired. But variety of methods after dyeing (so–called "aftertreatment") are used to improve wash fastness (cationic fixing agent, formaldehyde–containing resin, and diazotization and coupling) and light fastness (copper or chromium salt) properties of the dyes on substrates.

2.2.2 Vat dyes

Vat dyes are insoluble in water and are applied to cellulosic fibers, usually with sodium dithionite under alkaline conditions, by a vatting process involving reduction to produce a water–soluble leuco form which possesses affinity for the substrate. Air or chemical oxidation then results in regeneration of the insoluble form of the dye (pigment) trapped within the fiber pore. This can be represented simply as follows:
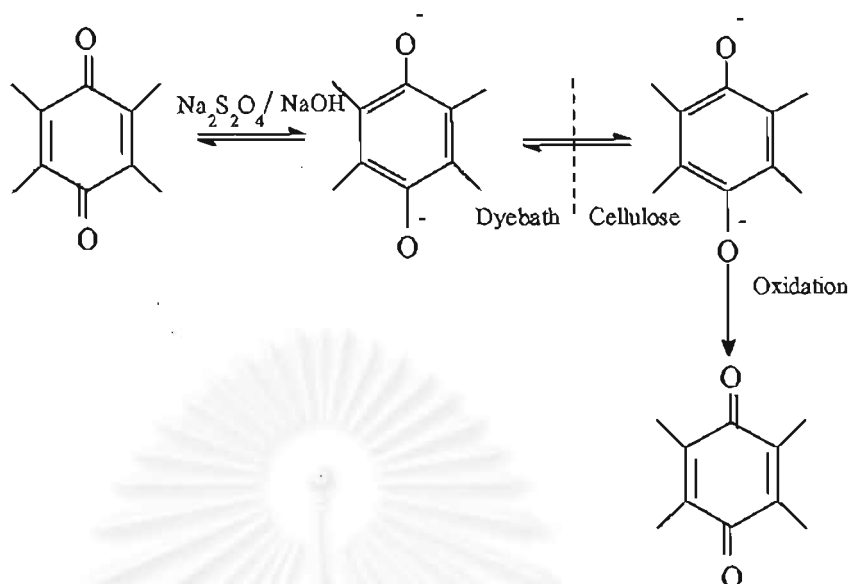
The large majority of vat dyes are based on the anthraquinonoid and indigo (or thioindigo) chromophores[8,16]. Important subclasses of vat dyes include: indanthrones, flavanthrones, pyranthrones, benzanthrones, acridones, anthraquinone carbazoles and anthraquinone oxazoles[17]. All these dyes contain two or more keto (C=O groups), separated by a conjugated system of double bonds. This molecular arrangement is responsible for the easily reversible redox reaction on which the application of vat dyes depends. The chemical structure example of vat dyes are shown in Figure 2.9 to 2.10.
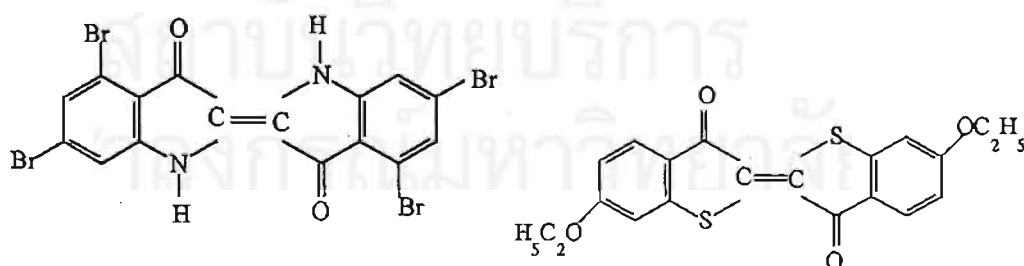
C.I. Vat Blue 5 (Indigo)   C.I. Vat Orange 5 (Thioindigo)

Figure 2.9 Structural of indigo and thioindigo vat dyes.
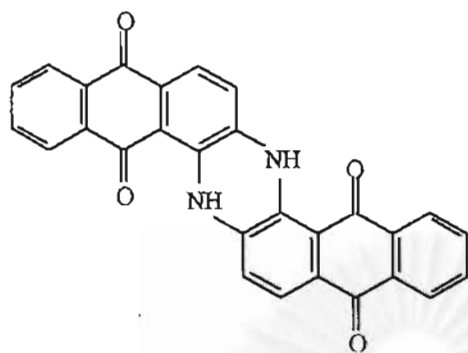
C.I. Vat Blue 4 (Indanthrone)
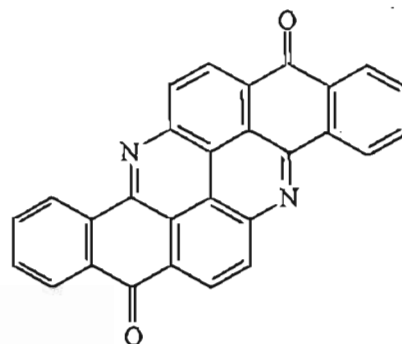
C.I. Vat Yellow 1 (Flavanthrone)
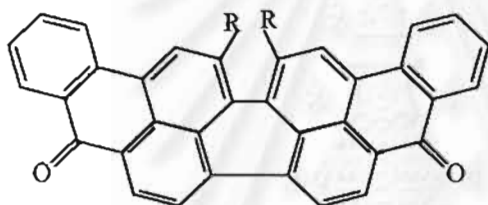
C.I. Vat Green 1 (Dibenzanthrone)

R = OCH$_3$
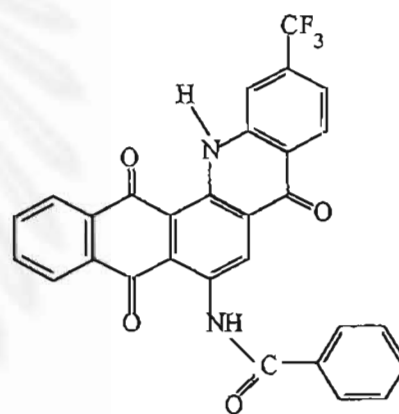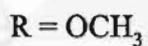
C.I. Vat Blue 21 (Acridone)
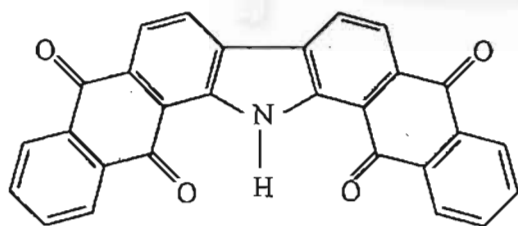
C.I. Vat Yellow 28 (Carbazole)
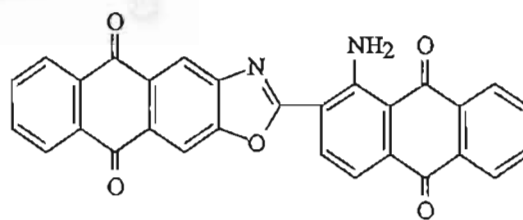
C.I. Vat Red 10 (oxazole)

Figure 2.10 Anthraquinone derivative of some vat dyes.

The vat dyes section of the Colour Index incorporates a subgroup called solubilized vat dyes. These are sodium salts of sulphuric acid esters of the parent leuco vat dyes. In contrast to the leuco compounds, the vat leuco esters dissolve readily in water at neutral pH. They have relatively low substantivity for cellulose and thus have been used mainly in continuous dyeing and printing.

Vat dyes are widely used in the manufacture of high–quality, high fastness properties fabrics. The disadvantages of this dyes are associated with the high price and the relative difficulty of application.

2.2.3 Sulphur dyes

Like the vat dyes, the sulphur dyes (D–S–S–D in Scheme 2.2) comprise water–insoluble colored compounds that are solubilized by reduction. In leuco (alkaline–reduced) form (D–S⁻) from a sodium sulphide bath they are used to dye cellulosic fabrics, and after the dyeing stage is complete they are oxidized once again to the insoluble pigment form in the fiber (see Scheme 2.2).

$$D-S-S-D \overset{\substack{\text{reduction} \\ \text{withNa}_2\text{S}}}{\rightleftharpoons} D-S^- \rightleftharpoons D-S^- \overset{\text{oxidation}}{\rightleftharpoons} D-S-S-D$$

(Insoluble)   (Soluble)   (Insoluble)

Dyebath   Cellulose
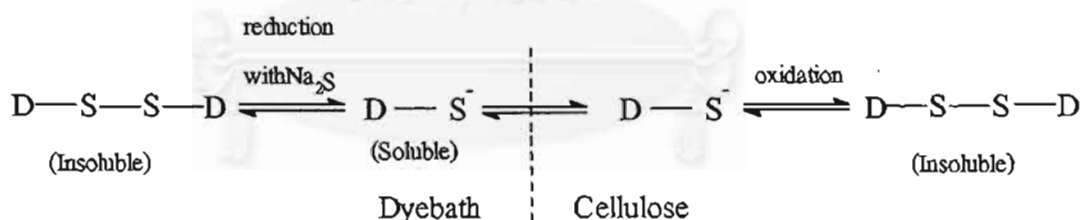
Scheme 2.2 The simplified dyeing mechanism of sulphur dye.

The structure of the chromophore of sulphur dyes are complex and unknown, for the main part , the majority of which are prepared by thionation of various aromatic intermediates[10]. So, the dyes are composed of disulphide linkages in the dye molecules and are readily reduced by sodium sulphide to give alkali–soluble thio groups. Sulphur

dyes differ from the vat dyes in being easier to reduce, but more difficult to reoxidize, different oxidants producing variations in hue and fastness properties.

Sulphur dyes are widely used for the dyeing of cellulosic fibers and their blends in medium to heavy shades of generally dull brown, black, olive, blue, green, maroon and khaki hues. Although the wet fastness in general is good, but the fastness to chlorine of sulphur dye is poor (presumably due to the instability of the disulphide groups), and in some instances cause the fabric to tender or degrade at high temperatures and humidities[17].

2.2.4 Azoic dyes

The azoic dyes are actually azo pigment synthesized inside textile substrates in the course of the dyeing process rather than readly–formed coloring matters[18]. They are principally used for dyeing cellulosic, polyamide, polyester, and cellulose di– and triacetate fibers , but are now obsolescent because of environmental hazards and the time–consuming application procedure.

In dyeing with azoic dye, an insoluble azo–pigment compound is produced within the interstices of the fibers by the coupling of an azoic diazo component (a diazotized of arylamine or stabilized diazonium compounds, often called fast bases and salt, respectively) with an azoic coupling component (usually nowadays an arylide of 3–hydroxy–2 naphthoic acid or a related member of the Naphtol AS (HOE) series)[16]. The two types of azoic component form separate generic series in the Colour Index. There is also a third series, designated C.I. Azoic composition. These are mechanical mixture of azoic coupling component and stabilized diazo component. The example of azoic dye can be shown as follows.
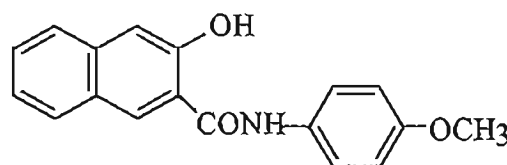
C.I. Azoic Coupling Component 11   C.I. Diazo Component 4 (Fast base)
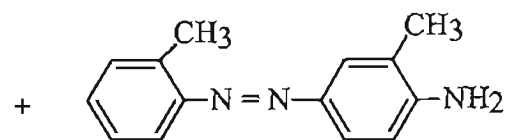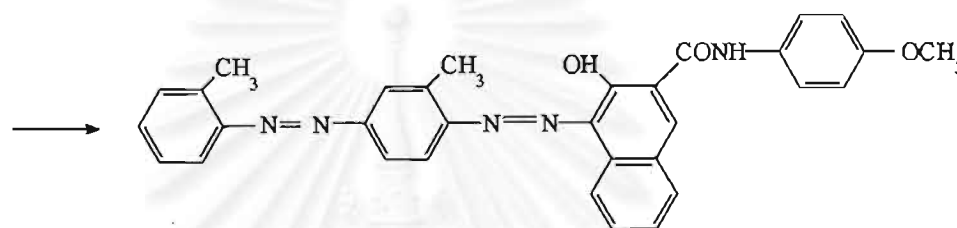
The normal procedure for azoic dyeing includes application of the napthol in alkaline solution, removal of excess liquor, development in a solution of the diazonium compound, which is prepared by diazotization of a base or simply by dissolving a stabilized diazonium salt, and soaping aftertreatment to achieve satisfactory fastness. Azoic dyes provide only relatively dull violets and navy blues, costly greens, and browns or blacks of limited versatility, but are tinctorially strong, bright and economical in the orange–scarlet–red sectors. Fastness to wet treatment and light of this dyes in general are good to excellent but fastness to crocking is poor[17].

2.2.5 Basic dyes

An alternative name for this dye class is the cationic dyes. This indicates clearly that they dissociate in water to yield colored cations and are characterized by their brilliance and very high tinctorial strength. In the term 'basic dyes', The Society of Dyers and Colourists defines a basic dye as 'characterized by its substantivity for the acidic types of acrylic fibers and for tannin–mordanted cotton'[16]. The earliest basic dyes

was originally used for dyeing wool, silk, and mordanted cotton, but the generally poor light fastness of the dyeing suppressed their use until the introduction of acrylic fibers on which the dyes exhibited higher light fastness and very good fastness to wet treatments. Currently, these dyes are used for dyeing acrylic, acid–modified polyamide and polyester fibers[10].

Because of the small number of carboxyl groups in cotton and due to the surface negative potential associated with the immersion of cellulosic fiber in water and sometime referred to as the zeta potential (see Figure 2.11), basic dye cations are weakly adsorbed onto cellulosic fiber with low wet fastness properties and when first introduced were applied to mordanted material. For cotton they involved the application of tannin (tannic acid) which could be fixed using a suitable metal salt (tartar emetic, $2(K(SbO)C_4H_4O_6)H_2O)$ followed by application of the dye. Treatment of the mordanted cotton with basic dyes results in the formation of water insoluble ionic complexes on the fiber by interaction of the tannic acid anions and the basic dye cations.
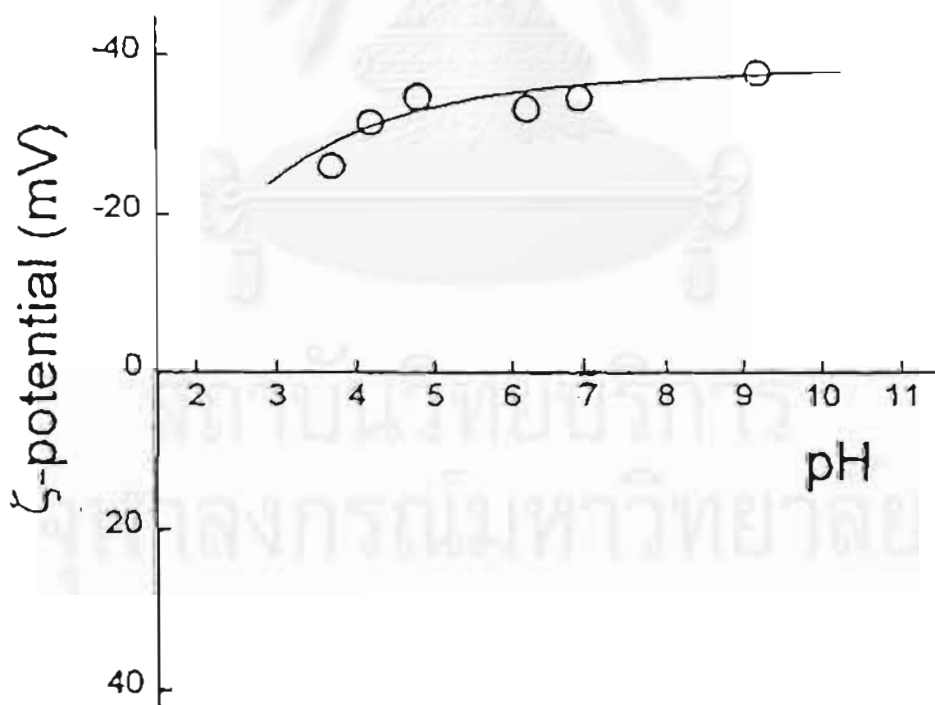
Figure 2.11 Zeta potential of cotton fabric at variety of pH[19].

The most interesting chemical feature of basic dyes is the variety of their chromophores, some of which are shown in Figure 2.12 to 2.14. They include anthraquinoid, azo, triphenylmethane, oxazine, thiazine, xanthene and a variety of products collectively known as polymethines (Figure 2.14)[20].
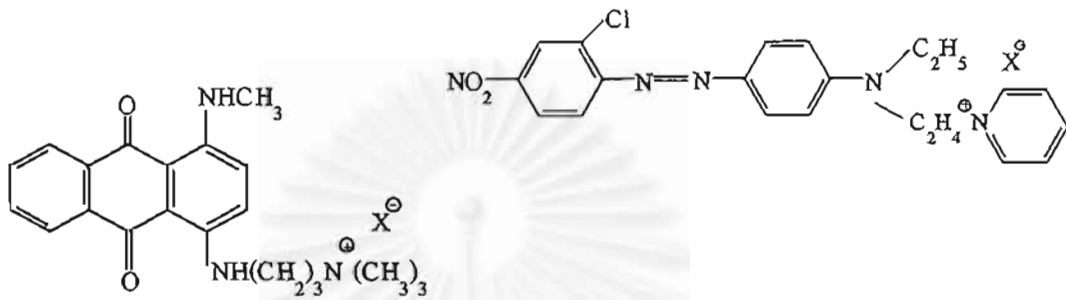
C.I. Basic Blue 22 (Anthraquinonoid)   C.I. Basic Red 18 type (Azo)

Figure 2.12 Examples of localized basic dyes.
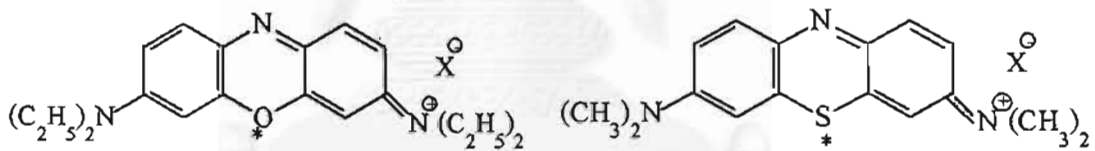
C.I. Basic Blue 3 (Oxazine)   C.I. Basic Blue 9 (Thiazine)
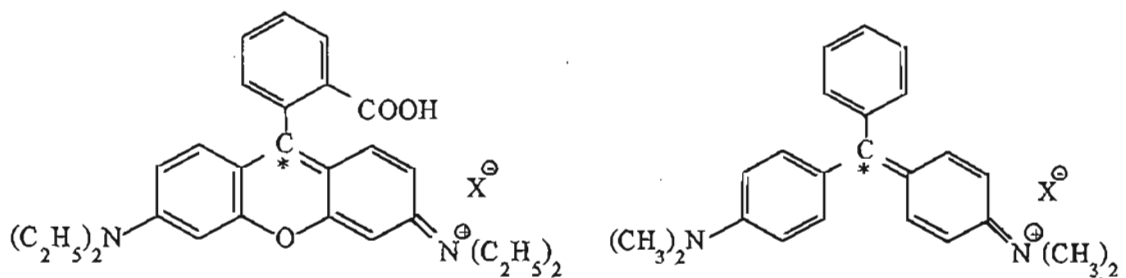
C.I. Basic Violet 10 (Xanthene)   C.I. Basic Green 4 (Triphenyl methane)

Figure 2.13 Examples of delocalized basic dyes.
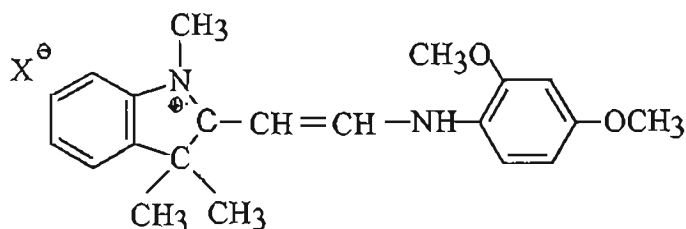
C.I. Basic yellow 11 (Azacarbacyanine)
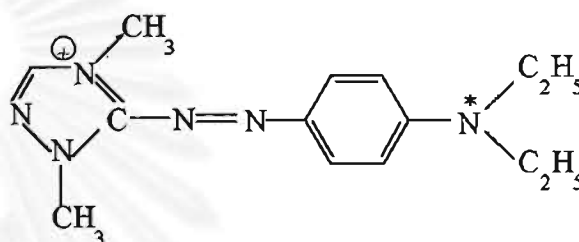
C.I. Basic Red 22 type (Diazohemicyanine)

Figure 2.14 Some types of polymethines.

Basic dye may also be classified in two main types according to their positive charge location, firstly localized or pendant cationic dyes, in which the positive charge is localized on one atom, usually a nitrogen atom. Secondary, delocalized dyes, as examplified by Figure 2.13 to 2.14, in which the positive charge is delocalized over the entire dye molecule (alternate locations for the positive charges are shown with asterisks (*)). It is those basic dyes with delocalized charges which are responsible for the intense colors associated with the basic dyes. Most of localized basic dye are azo or anthraquinone types, often with a localized quaternary ammonium group isolated from the chromophoric grouping by a saturated aliphatic chain, as in Figure 2.12. Such the dyes often exhibit better light fastness than the traditional delocalized types [16].

2.2.6 Reactive dyes

Reactive dyes are the only textile colorants designed to bond covalently with the substrate on application. This, of course, offers a higher degree of color fastness as the dye cannot be easily washed out of the substrate. Reactive dyes are colored compounds which have suitable groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye molecule and an oxygen, nitrogen, or sulphur atom of a hydroxyl (-OH), amino (-NH$_2$), or a mercapto group (-SH), respectively, of the substrate. So, commercial reactive dyes have been developed for both wool and polyamide but, undoubtedly, the major success has been in the application to cotton and its blends[10].

Generally, reactive dye structures thus produced are essentially in three parts, the chromogen, solubilizing group, and reactive system, and it is convenient to consider them separately since many chromogens and solubilizing groups are common to several dye ranges and only the reactive systems differ. The characteristic structural features of a reactive dye are shown in Figure 2.15. In some cases the reactive dye group is attached directly, i.e., without a bridge, to the chromogenic system[21].
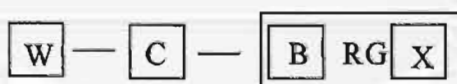
RG = reactive group

B = bridge link

X = leaving group

C = chromogen

W = water – solubilizing group

Figure 2.15 Characteristic features of a typical reactive dye molecule.

2.2.6.1 Chromogens in the reactive dye structure

The colored part of a reactive dye (i.e., the chromogen) is identical to those found in other dye classes, and very often contains an azo group (Metallized and unmetallized) or an anthraquinone group. Other chromogenic groups include phthalocyanine, triphenodioxazine and formazan.

2.2.6.2 Solubilizing group

Most cotton textile dyeing is carried out in water, and so solubilizing groups are added to the dye structure. All reactive dyes contain commonly sodium sulphonate groups for solubility, and dissolve in water to give colored sulphonate anions and sodium cations. Most reactive dyes have from one to four of these sulphonate groups[22].

In the cellulosic dyeing the overall surface charge is negative when immersed in water. Negative potential at fiber surfaces will resist the approach of similarly charged ions such as the sulfonate anion dye. And at the high concentration used in dyeing with more sulphonate anion dye, the fiber is also increased fixed sulphonate anion build–up or repulsion effect, which prevented further dye from being absorbed and fixing on the substrate. So the large concentration of salt is used in the dyeing to promote dye absorption and serve to screen the negative charge surface.

2.2.6.3 Reactive system

During the early years of development of reactive dyes it was soon recognized that the important reactive systems could be classified into two distinct categories, depending on the mechanism of formation of the dye–fiber bond and the stability of this bond to subsequent treatments[9]. In the first class, the reactive system most are heterocyclic rings (such as triazines, pyridines, quinoxalines and benzothiazoles) containing one or more halogens as leaving groups; these react with ionized hydroxyl groups or any other negatively charged fiber substituent (-NH group in wool or

polyamides) by nucleophilic substituent mechanism, as shown in Scheme 2.3. The second class of this dyes contains β-sulphatoethyl sulphone group or related species that, in the presence of alkali, are converted into a vinyl sulphone group which reacts with substrate by nucleophilic addition to form the dye–fiber bond (see Scheme 2.4). Because of the ionization of the cellulosic fibers requires the alkaline condition, hydroxyl anions (i.e., -OH⁻) will always be present and therefore be in competition with the cellulosate anion as nucleophilic reagent; the dye is hydrolyzed as a result of reaction with the hydroxyl anions. With the possible exception of the Procion T (ICI) range of dyes, all reactive dyes of cellulosic fiber undergo hydrolysis.

Procion T, reactive dyes which react under acidic condition were introduced in 1977 by ICI[23]. These dyes contain phosphonic acid groups which readily undergo esterification reaction in the present of cyanamide or dicyanamide. The mechanism of fixation of phosphonic acid to cellulosic fiber is particularly interesting, the overall fixation process being represented by the simplified Scheme 2.5. The fixation process involves baking at 200^0C for 2–3 minutes and requires mildly acidic conditions (pH 5–6)[10], so that the dyes are suitable for dyeing polyester/cotton blends by a single stage process, since the alkaline conditions normally required to fix reactive dyes are avoided. The Procion T dyes were withdrawn from the market due to their disadvantages, which particular the high temperature is required for fixation and conjunction with acidic condition, that sometimes caused tendering of fiber damage[23].

Dichlorotriazine dye   Transient species   Dyed fiber (X = O-cellulose)

or Partly hydrolyzed dye

(X=OH)
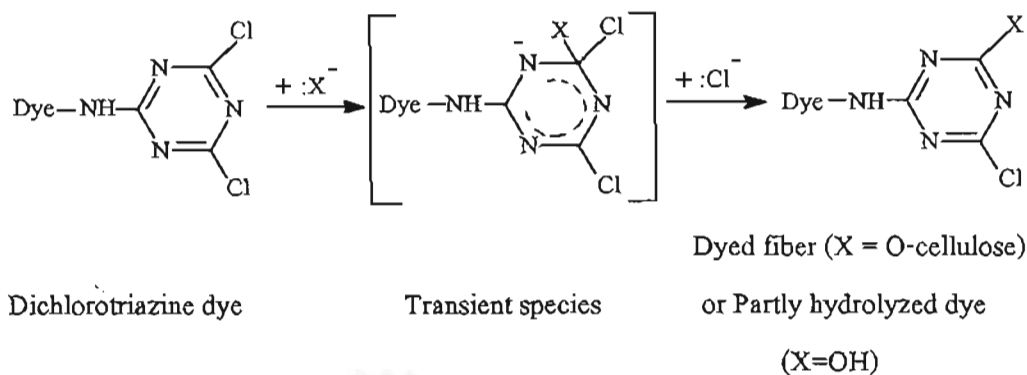
Scheme 2.3 The nucleophilic substitution mechanism of dichlorotriazinyl dye[9].

Vinylsulphone dye   Transient species   Dyed fiber (X=O-cellulose)

or hydrolyzed dye (X=OH)
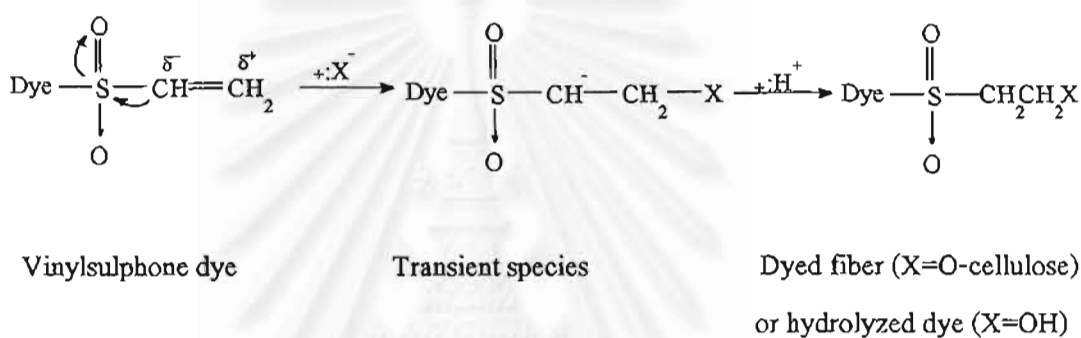
Scheme 2.4 The nucleophilic addition mechanism of vinyl sulphone dye[9].

Where R = H (cyanamide) or R = (dicyanamide)
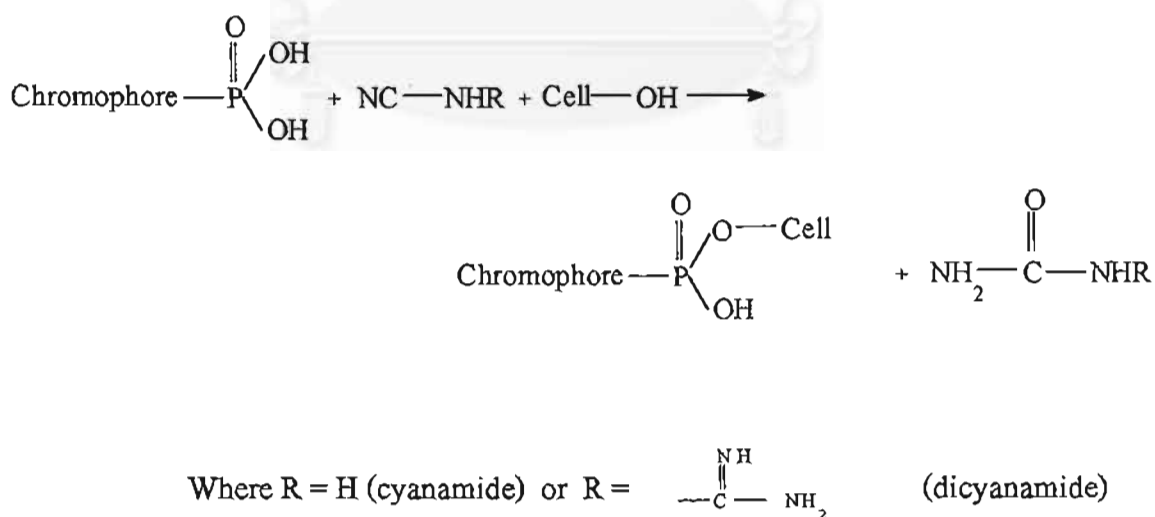
Scheme 2.5 Proposed mechanism for fixation of phosphonic acid reactive dye on cellulose fibers[17].

Reactive system of reactive dye have several specific structural features of their own. These are of two main principal types: nitrogen–containing heterocyclic ring structures and masked vinyl sulphones [22].

2.2.6.3.1 Nitrogen – containing heterocyclic ring

A very large number of the dyes of this type carry reactive groups based on nitrogen – containing heterocyclic groups. The heteroatom in the heterocyclic ring activate the system for nucleophilic substitution reaction because of their electronegativity, cause an electron deficiency at the adjacent carbon atoms which are then susceptible to reaction with nucleophile substances [24]. The attacking nucleophile can be either a cellulosate anion or a hydroxide ion, the former leading to fixation on the fiber and the latter resulting in hydrolysis of the dye. The electron deficiency of the carbon atoms is increased with the number of nitrogen atoms; this is shown by the calculation of the electron distribution in the series of heterocycles containing 1 to 3 nitrogen atoms [25].
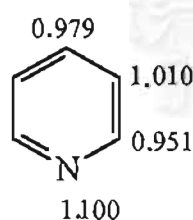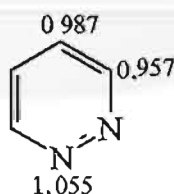
Pyridine   Pyridazine   Pyrimidine
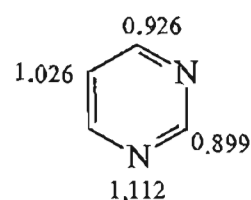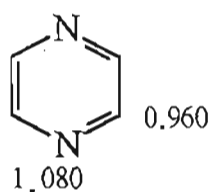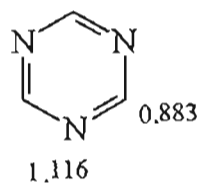
Pyrazine   s – Triazine

The activity of this reactive dye type depending upon the positional relationship between the hetero–nitrogen atoms and the substituent[25]. The high reactivity shown by the dichloro–s–triazine dye arises from the presence of three ideally situated heteronitrogen atoms in the s–triazine ring, most of the other reactive systems in use having not more than two such nitrogen atoms. The arranged in reactivity of this reactive type in order of gradually increasing reactivity: trichloropyrimidine (TCP); monochlorotriazine (MCT); monofluorotriazine (MFT); difluorochloropyrimidine (FCP); and dichlorotriazine (DCT)[22]. The structures of major types of these reactive system and the commercial band name are shown in Figure 2.16.
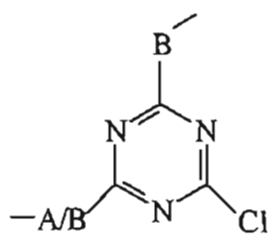
a) monochlorotriazine

(e.g. Procion H, Cibacron)
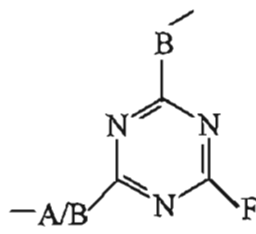
b) monofluorotriazine

(e.g. Cibacron F)
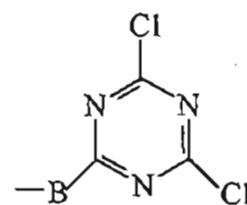
c) dichlorotriazine

(e.g. Procion MX)
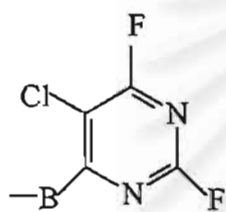
d) difluorochloropyrimidine

(e.g. Drimarene K, Levafix E-A)
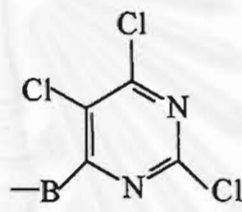
e) trichloropyrimidine

(e.g. Drimarene Z and X)
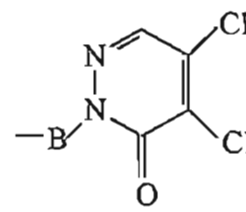
f) dichloropyridazone

(e.g. Primazin P)
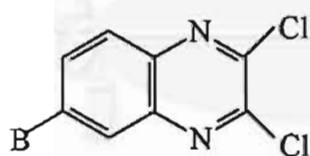
g) dichloroquinoxaline

(e.g. Levafix E)
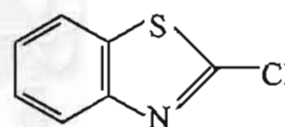
h) chlorobenzothiazole

(e.g. Reatex)

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

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

amide linkage

Figure 2.16 Selected heterocyclic reactive group.

Replacement of one or more of the halogen atoms (e.g., leaving groups) heterocyclic systems by other substituents affects the reactivity of the remaining halogen atoms to a greater or lesser extent according to the electrochemical character of the substituent, the positional relationship in the ring between the halogen atom and the substituent, and also the type of bonding between them[25]. For example, the dichlorotriazine dyes are highly reactive and can be applied to cellulosic fiber at temperatures of 30–40^{0}C, but when one of chlorine atom of this dye is displaced by other substituent such amino alkoxy or aryloxy, the reactivity of the remaining monochlorotriazine dyes are greatly decreased and are used in the higher temperature than dichlorotriazine dyes .

The leaving groups (X) are attached initially at carbon atoms adjacent to a ring nitrogen, chlorine is the most common choice as displaceable substituent on the heterocyclic reactive system. Whilst other potential leaving groups include fluoro groups (-F) and methyl sulphonyl group (CH_3SO_2-).

More than 50% of the reactive dyes in the market are based on the s–triazinyl systems[10]. A major class of s–triazine derivatives used in preparing reactive dyes are generally obtained from cyanuric chloride or 2,4,6–trichloro–s–triazine (Figure 2.17) owing to its high reactivity and versatility in chemical reactions and to its low cost. So, in this study is also used cyanuric chloride in preparing reactive system for the novel reactive dye.
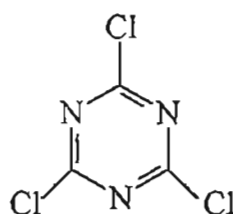
Figure 2.17 The structure of cyanuric chloride.

2.2.6.3.2 Vinyl Sulphone

The second major class of reactive dye based on a vinylsulphone system, which react by a nucleophilic addition mechanism. The vinylsulphone groups are actually written : $-SO_2-CH=CH_2$, this group is not normally present in the commercial dyes since it is more convenient to use a less reactive precursor such as the β-sulphatoethyl-sulphone group obtained from the corresponding β-hydroxyethylsulphone compounds[24].

The bridging group is the sulphone ($-SO_2-$), portion of the structure, which withdraws electrons from the rest of the group so that, in the alkaline condition, the leaving group departs with a hydrogen ion(from the carbon next to the sulphone group) and generate the vinyl group(see equation I).

$$Dye-\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}-CHCH_2-OSO_3^- \longrightarrow Dye-\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}-CH=CH_2 + HSO_4^-$$

(I)
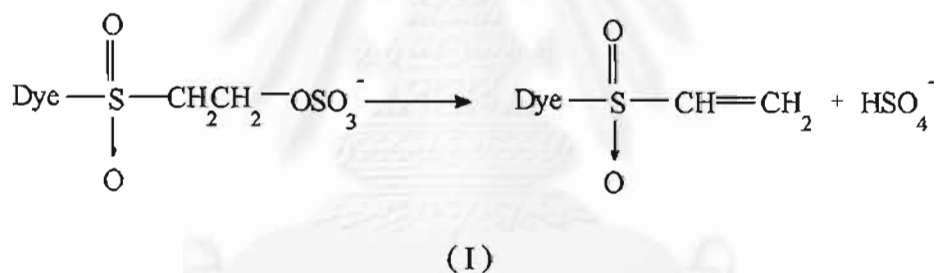
In vinylsulphone group, the carbon–carbon double bond is polarized by the powerfully electron–attracting sulphone group. This polarization imparts a positive charge to the terminal carbon atom, so that nucleophilic addition of nucleophiles (such as cellulosate anion, hydroxyl ion) to occur. Finally, the addition of proton completes the dye–substrate reaction (see Scheme 2.4).

These dyes were first introduced by Hoechst, which markets them under the band name Remozol[16]. The reactivity of these dyes are intermediate between the mono– and dichlorotriazine dyes requiring an exhaustion dyeing temperature of $50-60^0C$, depending on pH.

2.3 Previous research works on an attempt to improve the dyeability of cellulose with reactive dyes

2.3.1 Chemical modification of cellulosic fibers to enhance dyeability.

There are however certain environmental problems which may arise from the use of reactive dyes and associated chemicals. The problems occur from using high salt concentrations and only moderate efficiency of dye utilization[3]. There are several ways to solve this problem, many studies have been devoted to improving the substantivity of cellulose towards reactive dyes will greatly reduce the need for electrolyte in the dyebath, and also improve dyebath exhaustion, serving to lessen color in dyehouse effluent. Several papers have been reported as follows:

The fixation of reactive dyes on substrates containing amino groups is much higher than hydroxyl group on cellulose substrates. Thus wool can be dyed with reactive dyes under slightly acidic to neutral condition to give very high fixation efficiencies and without the need to add electrolyte in the dyebath[5]. It is therefore not surprising that a large amount of work has been done to introduce amine groups into the cellulose substrates to improve their dyeability, which have appeared in the review paper of Lewis and McIlroy[1].

El–Alfy et al.[26] introduced diethyl amino ethyl group into the cellulose substrates to improved their dyeability. Diethylaminoethylcellulose (DEAE cellulose) can be prepared by reacting the cotton with 2–chloroethyldiethylamine hydrochloride in the presence of an alkali (Scheme 2.6)

$$\text{Cell—OH} + \text{Cl—CH}_2\text{CH}_2\text{—} \overset{\overset{\displaystyle \text{C}_2\text{H}_5}{|}}{\underset{\underset{\displaystyle \text{C}_2\text{H}_5}{|}}{\overset{+}{\text{N}}\text{—H}}} \quad \overset{\text{NaOH}}{\longrightarrow} \quad \text{Cell—O—CH}_2\text{CH}_2\text{—N} \overset{\text{C}_2\text{H}_5}{\underset{\text{C}_2\text{H}_5}{}}$$
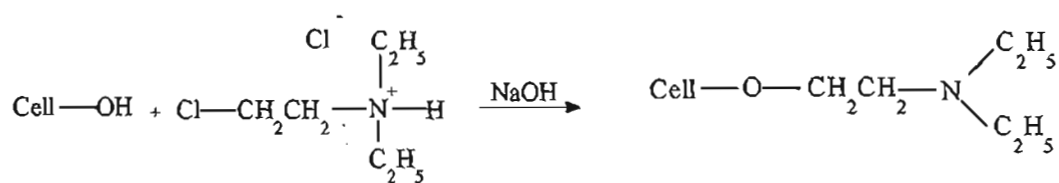
Scheme 2.6 The reaction between cellulose and 2–chloroethyldiethylamine hydrochloride.

The DEAE–cellulose could be dyed, in the absence of salt, with direct, acid and reactive dyes. The dyeing properties of this modified cotton were investigated and compared with those of untreated cotton and cotton treated with NaOH under condition similar to that used for chemical modification but in the absence of the etherifying agent. The results show that the color strength of DEAE–cellulose is significantly higher than the alkali–treated and untreated cellulose, respectively. This was observed irrespective of the dye used. Of particular interest were the results obtained with the reactive dye. Which the action of DEAE groups acted as "built–in catalyst" was used to explain phenomenon of covalent fixation between the reactive dye and cellulosic hydroxyl group under neutral and acidic conditions. The proposed reaction for the 2,4– difluoromonochloropyrimidine type reactive dye with the modified cellulose can be written[1]:
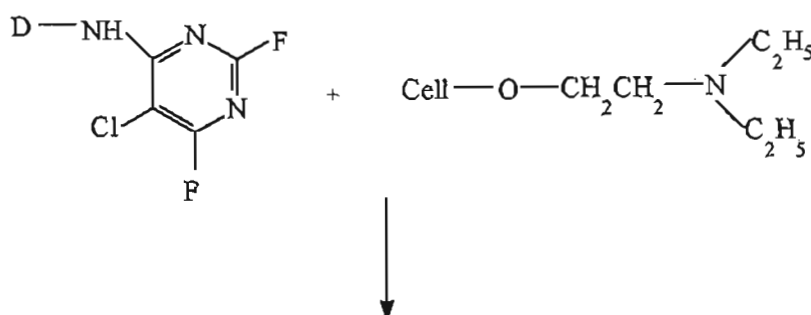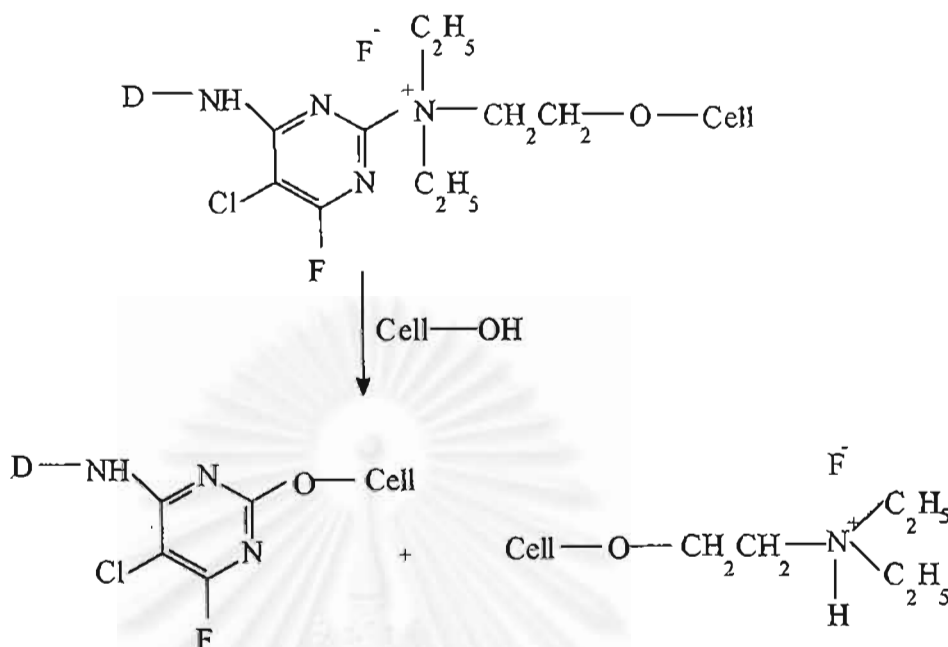
Waly *et al.*[27] used an alternative method to introduce tertiary amino groups into cotton, based on etherification with epichlorohydrin and triethanol amine. The technique adopted involved padding the cotton fabric with sodium hydroxide solution followed by impregnating in a nonaqueous solution consisting of a mixture of epichlorohydrin/ triethanol amine (3:1 mole) in acetone. Dyeing was carried out according to the conventional thermofixation method using either an acid dye or a reactive dye. Aminized cotton with nitrogen content of ca. 0.2 – 0.5% displayed greater dyeability with respect to acid dye. The situation is much more promising with reactive dye with which the tertiary sites for ionic bond formation between themselves and the dye anions.

Burkinshaw, Lei and Lewis[28] studied the reactive dyeing of cellulose which pretreated with a reactive polyamide–epichlorohydrin resin (Hercosett 125). A commercial polyamide–epichlorohydrin polymer solution, Hercosett 125 is a cationic, reactive polymer prepared by a condensation of adipic acid and diethylenetriamine followed by reaction and partial cross–linking with epichlorohydrin. NMR studies have

shown that the reactive group in this polymer is the azetidinium cation (Figure 2.18) rather than the γ- chlorohydrin or epoxide residue.
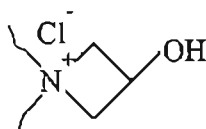
Figure 2.18 Azetidinium cation

The polyamide–epichlorohydrin (PAE) cotton can be easily dyed under neutral pH conditions in the absence of salt using reactive dyes of high reactivity, giving high fixation efficiency and good dyeing quality. The wash fastness properties of PAE–treated and dyed cotton were excellent, although light fastness was down by 1–2 points compared with control dyeing on untreated cotton. Because of, but during the drying stage it is cured and insolubilized at the surface of the fiber. The location of the resin encourages subsequent surface coloration, and this makes the dyeing particularly susceptible to photofading.

It is know that cotton fabric when pretreated with polymeric compounds, poor light fastness of subsequent reactive dyeing was associated with ring dyeing. Pretreatments with lower molecular mass compounds did not exhibit this problem when dyed. Lewis and Lei[3] also modified cotton with the low molecular mass reactive species 1,1–dimethyl–3–hydroxyazetidinium chloride (DMA–AC) to study the light fastness of subsequent dyeings. DMA–AC has similar characteristics to the Hercosett polymer in that it is water soluble and consists of cationic, reactive azetidinium groups capable of reaction with hydroxyl nucleophiles of cellulose. The compounds may be prepared by reaction of dimethylamine and epichlorohydrin as following :

$$H-N\overset{CH_3}{\underset{CH_3}{}} \quad + \quad Cl-H_2CHC\overset{O}{-}CH_2 \quad \longrightarrow \quad \overset{H_3C}{\underset{H_3C}{}}N^+\overset{}{}OH \quad Cl^-$$
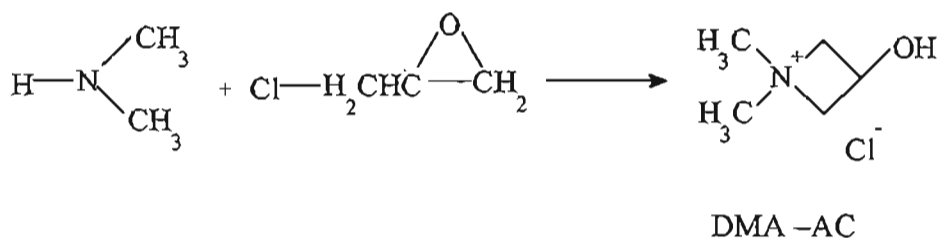
DMA –AC

DMA–AC was applied to cotton fabric by pad dry bake methods. The presence of a strong alkali, such as NaOH, was necessary to provide sufficient levels of covalent bonding between DMA–AC took place with reactive dyes at the boil, at pH 7 in the absence of salt. Dye fixation was extremely high and dyeing results showed good light fastness on the pretreated cellulose. Improved neutral fixation of DMA–AC pretreated cotton can be ascribed to the presence of tertiary and quaternary amino groups in the modified cotton. By increasing cellulose hydroxyl ionization due to the proximity of strongly basic groups.

Burkinshaw et al.[29] , Lei and Lewis[30] again studied the dyeability of cellulose substrates modified with alternative method of PAE resin system, which consists of PAE/thiourea and PAE/ethylenediamine system, respectively. The dyeing procedure can be carried out under neutral pH conditions in the absence of salt. Excellent build up properties, dye fixation and wash fastness properties were achieved when modified with both systems. However, the problem of reduced light fastness remained unresolved.

Wu and Chen[31] proposed the method to improve dyeability of cellulose fibers by pretreating cotton with polyepichlorohydrin–dimethylamine (PECH–amine) polymer. The likely chemical structure of the active species is shown in Figure 2.19.

$$\text{---}(CH_2\text{---}\underset{\underset{CH_2Cl}{|}}{CH}\text{---}O)_n\text{---}(CH_2\text{---}\underset{\underset{CH_2N^+H(CH_3)_2Cl^-}{|}}{CH}\text{---}O)_m\text{---}$$
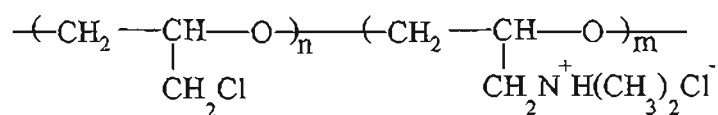
Figure 2.19 Likely chemical structure of PECH – amine cationic agent.

Pretreatment of cotton with PECH–amine increased the dyeability of the modified cotton for reactive dye by introducing cationic amino groups. The pretreatment can be applied by both the exhaustion method and the pad–dry process. Excellent build–up properties were achieved with dyes of both low and high reactivity under neutral dyeing conditions; low reactivity dyes required only 10% of the normal salt usage and high reactivity dyes required no salt. The wash fastness of dyed PECH–amine–treated cotton was excellent, although a drop in light fastness of 1–2 points was reported.

Evans et al.[32] studied the modification of cellulosic fiber with reactive colorless quaternary compounds (Figure 2.20) is a means of introducing fixed cationic sites which have a marked effect on the uptake of anionic dyes in subsequent dyeing.
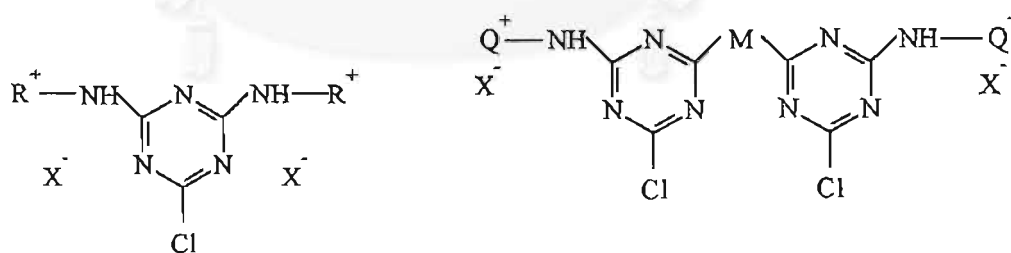
Mono–reactive bis–quaternary compounds.   Bis–reactive bis-quaternary compounds.

(R = aliphatic amine, aromatic amine or pyridinium moiety,

Q = aliphatic or aromatic amine, and M = bridging)

Figure 2.20 Quaternary compounds capable of bonding covalently to cellulose to enhance dyeability

The both type of reactive quaternary compounds were applied to cellulose fiber by different method owing to differences in their reactivity and substantivity. Mono–reactive bis–quaternary compounds, recognized to have low substantivity for cellulose, were applied by a semi– or fully continuous method and the compounds also showed poor penetration of the fiber due to migration of the agents to the surface during dyeing. For bis–reactive bis–quaternary type, recognized to have higher substantivity for cellulose were applied by exhaustion in the absence of electrolyte. Twelve reactive dyes were tested in subsequent dyeing, resulting in some extreme hue and brightness changes when compared with untreated fiber.

The novel compound 2,4–dichloro–6–(2'–pyridinoethylamino)–s–triazine (DCPEAT) has been studied by Lewis and Lei[33] in an attempt to improve substantivity in the no–salt dyeing. The activated fiber can be produced by the use of this cationic reactive compound. When applied to cotton under weakly alkaline conditions one of the chlorine atoms in triazine ring will be displaced by the nucleophilic cellulosate anion to form a covalent bond with the fiber. The treated fiber contains mono–chloro–s–triazine residues that can undergo reaction with the more nucleophilic amino–alkyl dyes. DCPEAT was applied to cotton both by exhaustion and pad–batch processes. Dyeing was carried out at the boil, pH 9, in the absence of salt. The resulting dyeing were bright, of similar hue to that of the respective parent dye applied by the classical method to untreated cotton; similar washing and light fastness levels were achieved as in conventional dyeing. The preparation of this activated fiber is shown in Scheme 2.7.
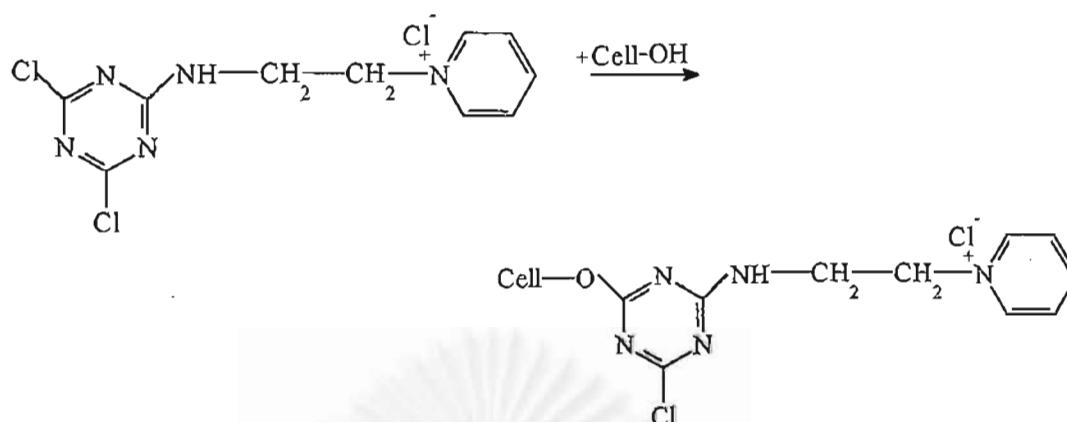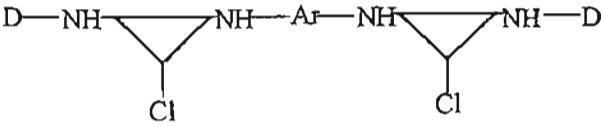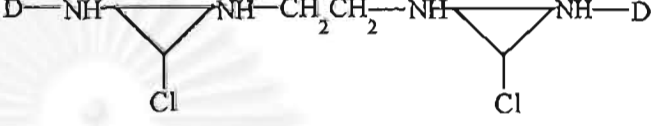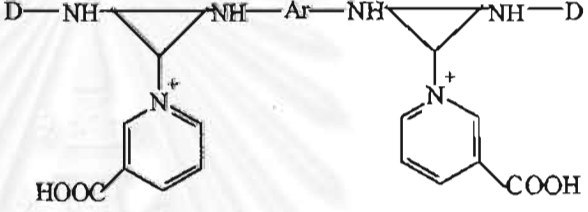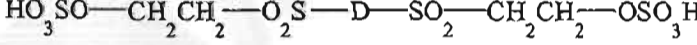
Scheme 2.7 The preparation of activated cellulose with DCPEAT

2.3.2 Developments of high substantive reactive dyes.

Other development to improve the dyeing of cellulose fiber with reactive dye include the introduction of more than one reactive group into the dye molecule. The objective was to produce multifunctional reactive dye for exhaust dyeing that exhibited substantially higher substantivity, exhaustion and fixation values compared with corresponding monofunctional reactive dyes. Table 2.4 and 2.5[5] summarize the present market status of multifunctional reactive dyes from the main dye manufacturers; Table 2.4 covers the so–call homofunctional dyes while Table 2.5 lists those bifunctional reactive dyes having different reactive groups on the same dye molecule (so–called heterobifunctional dye).

40

Table 2.4 Examples of symmetrical multifunctional reactive dyes for cellulosic fiber[a].
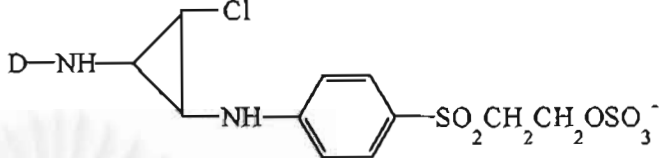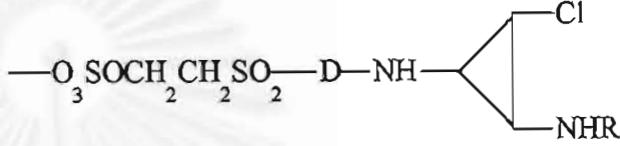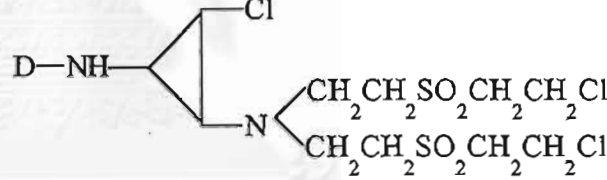
Dye range	Dye structure
Procion H – E (Zeneca) Procion H – EXL	
Drimarene XN (S)	
Kayacelon React (HDE)	
Selected Remozol (HDE) (e.g. Remozol Black B)	HO_3SO—CH_2CH_2—O_2S—D—SO_2—CH_2CH_2—OSO_3H
Cibacron LS (CGY)	

[a] D is sulphonated chromophore

△ is s–triazine

Ar is aromatic residue

Table 2.5 Examples of multifunctional reactive dyes containing mixed reactive groups.

Dye range	Dye structure
Sumifix Supra (NSK)	D—NH—[triangle: Cl / NH—phenyl—$SO_2CH_2CH_2OSO_3^-$]
Diamara SN (Mitsubishi Kasei Hoechst)	$O_3SOCH_2CH_2SO_2$—D—NH—[triangle: Cl / NHR]
Cibacron C (CGY)	D—NH—[triangle: F / NH - alk- SO_2^- $CH=CH_2$]
Remozol Brilliant Red SBB (HDE) Remosol SN/S (HDE)	D—NH—[triangle: Cl / N⟨ $CH_2CH_2SO_2CH_2CH_2Cl$ / $CH_2CH_2SO_2CH_2CH_2Cl$]

These bifunctional dye molecules, having about twice the molecular size of analogous monofunctional dyes, are much more substantive. This allows them to achieve excellent exhaustion onto the fibers and a high fixation ratio. Luttringer[2] has found the advantages of the Cibacron C dyes, especially when applied to cotton by the cold pad– batch process, i.e. very high fixation (often in excess of 90%), good washing– off properties and high fastness levels.

In the search for easier–to–apply reactive dyes, Nippon Kayaku went beyond the conventional concept of alkaline bath dyeing with its Kayacelon React dyes, which can be applied and fixed from a neutral bath (pH 7.0–7.5) at high temperature. Because of, these dye contain quaternary leaving group, which much more reactive than the parent chloro–s–triazines[14,16].

2.4 Concepts of Novel highly substantive reactive dyes

It is well known that a major problem of dyeing of cellulosic substrates with conventional anionic reactive dyes is that high percentage of dye exhaustion could not be achieved without the addition of salts in dyebath. This is due to the repulsive interaction between dye anions and negatively charged fiber surface. The addition of salts will suppress negative charge on the surface, hence allowing dye anions to diffuse from dyebath to the fiber (as illustrated in Figure 2.21). The amount of salts required varies in the range between 20–100 g/l depending on the designed structure of individual dye and depth of color shade.

The problems associated with the use of salts concern not only causing a environmental imbalance to ecological system, but also affecting the consistancy degree of dye exhaustion, if its concentration in the dyebath is different from batch to batch, which then leads to poor reproducibility of dyeing.
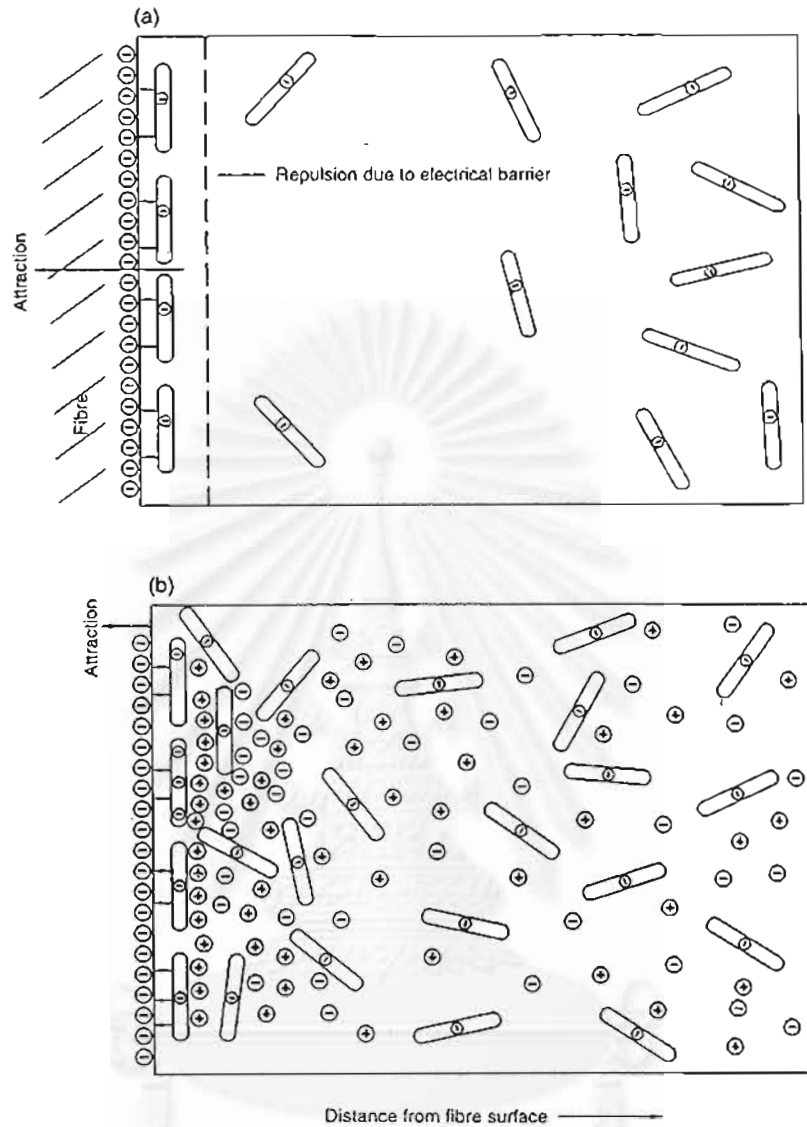
Figure 2.21 Adsorption model of conventional reactive dye on the cellulosic fiber.

((a) in the absence of salt, (b) in the presence of salt)

Recently, reactive dye ranges which are claimed to consume low amount of salts are commercially available and their market share is rising. However, it is still necessary to be applied in the presence of salt.

The aim of this project was to search for novel reactive dye which can be applied in the absence of salt. The fundamental idea on how to achieve such kind of dye type with high substantivity characteristic was based on the exploitation of the attractive interaction between the negatively charged fiber surface and positive charge containing dye. However, the use of commercial positive charge containing dye, so called basic or cationic dyes, for coloring cellulosic substrates is impractical for industry due to their deteriorating fastness to the sunlight.

The purpose of this project is, therefore, to design the reactive dye containing releasable cationic group. Such novel reactive dye generally have three distinct features: a chromogen, a reactive group and releasable cationic solubilizing group.

The synthesis of this dye may be prepared by the modification of commercial disperse dyes which contain free amino group. By reacting amino group containing disperse dye with cyanuric chloride, hence reactive group is incorporated into the dye chromophore. In the final step, releasable cationic group is introduced by the reaction between one leaving group of reactive system of dye chromophore with suitable quaternary ammonium compound such as N–(2-aminoethyl)pyridiniumchloride hydrochloride. The quaternary ammonium compound used in this experiment will also be prepared in our laboratory. The overall reactions involved in the synthesis of novel releasable cationic reactive dye can be summerized as shown in reaction Scheme 2.8

Chromophore—NH$_2$ + [triazine with Cl substituents] → Chromophore—NH—[triazine with Cl substituents]

+ H$_2$NCH$_2$CH$_2$N$^+$[pyridine]

Chromophore—NH—[triazine]—NHCH$_2$CH$_2$N$^+$[pyridine] Cl$^-$
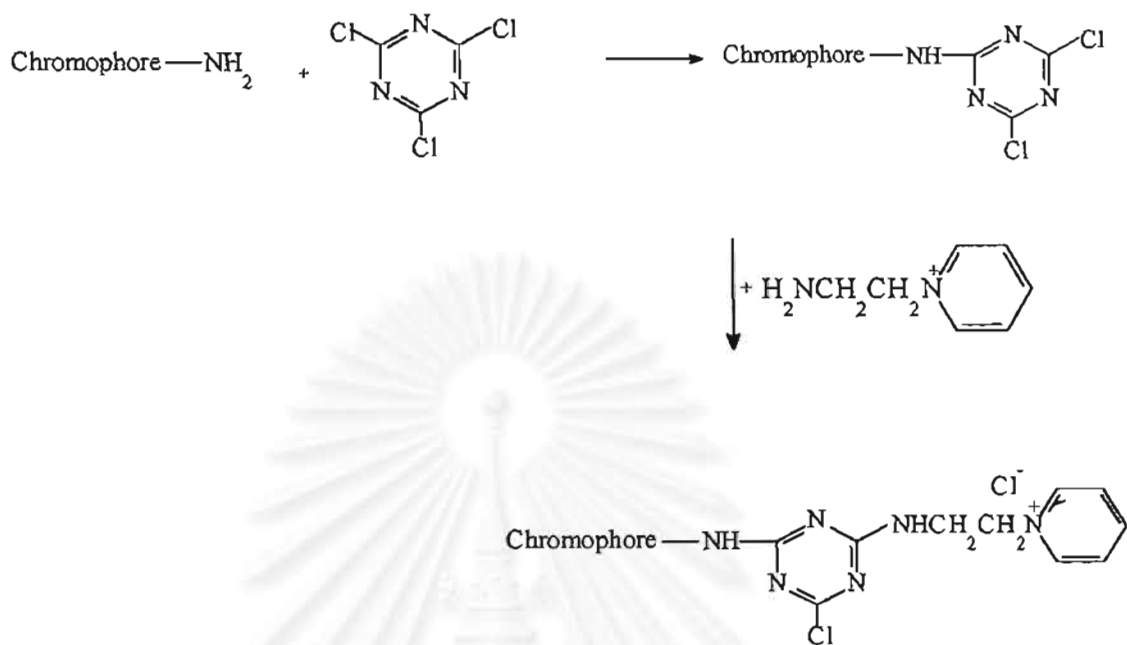
Scheme 2.8 The preparation of releasable cationic reactive dye

The reaction of cellulose with the systhesized dye and the possible mechanism of the cleavage of cationic group are proposed as follows:

Dye—NH—[triazine with Cl]—NHCH$_2$CH$_2$N$^+$[pyridine] Cl$^-$ + Cell—OH

$$\downarrow \begin{array}{c} Na_2CO_3 \\ 80\text{-}85^0c \end{array}$$

O—Cell

Dye—NH—[triazine ring]—NHC$_2$H$_4$N$^+$ [pyridinium] Cl$^-$

$$\downarrow 100^0c \text{ (detergent)}$$

O—Cell

Dye—NH—[triazine ring]—NHCH$_2$CH$_2$OH   +   :N [pyridine]   or a product of ring cleavage of pyridinium group.
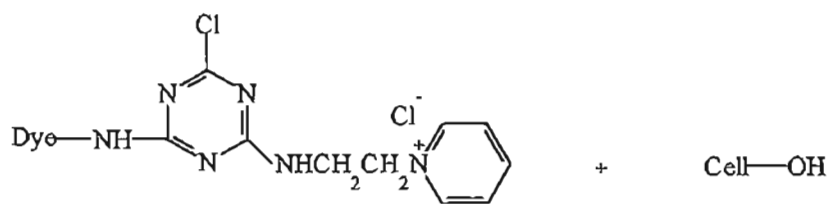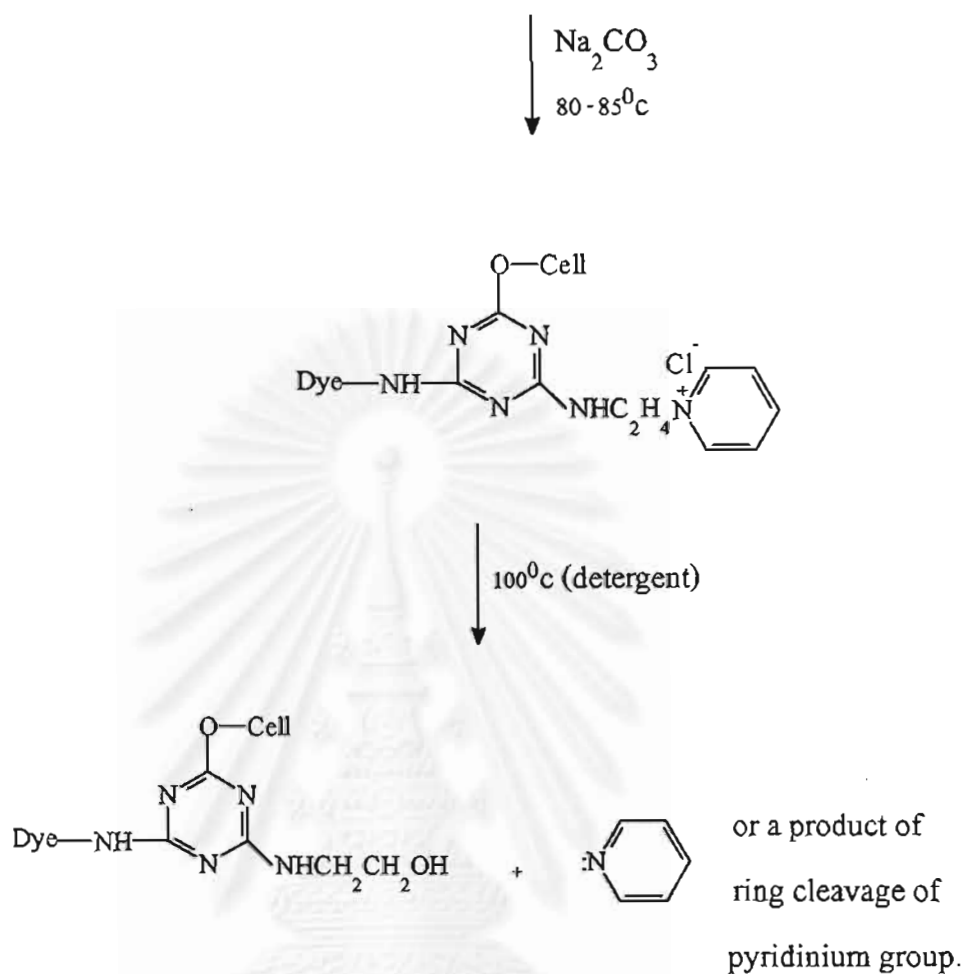
The application of the synthesized dye onto cellulosic substrate will be investigated using exhaustion dyeing method in the absence of salt. It is believed that without the presence of salt, high dye exhaustion would be achieved due to the attractive interaction between cationic group of the dye and negatively charged fiber surface as schematically illustrated in Figure 2.22.
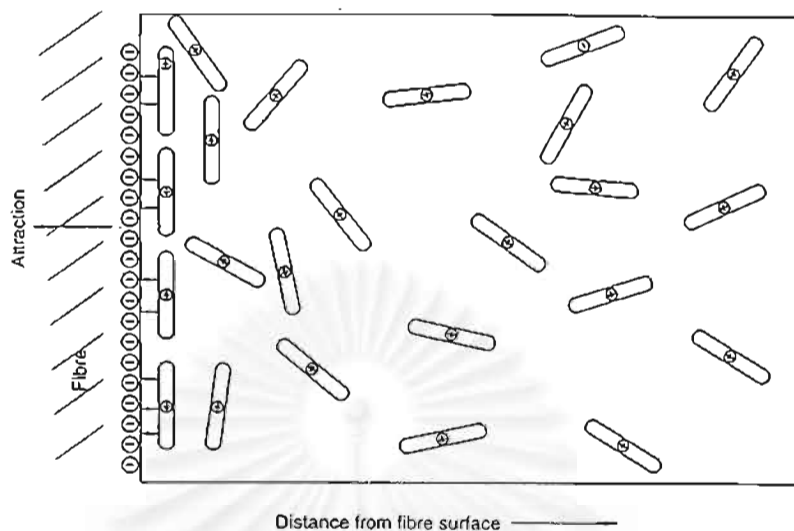
Figure 2.22 The model of the interaction of novel reactive dye with the cellulose fiber.

The percentage of dye exhaustion and fixation of novel reactive dyes were evaluated and compared to those obtained from conventional salt/alkali process. Finally, the fastness properties including wash fastness and light fastness of novel reactive dyes are also presented.

CHAPTER III

Experimental

3.1 **Materials**.

Cotton Fabric : Bleached and unmercerized plain woven fabric was used throughout this work.

Chemicals : The chemicals used in this project were laboratory reagent grade.

Table 3.1 List of chemicals used in this project

Chemicals	Formula	Company
Cyanuric chloride	$C_3N_3Cl_3$	Fluka
2-Chloroethlylamine hydrochloride	$ClCH_2CH_2NH_2 \cdot HCl$	Fluka
Pyridine	$N(CH)_4CH$	Carlo-Erba
Sodium hydroxide pellet	NaOH	J.T.Baker
2-Propanol	$CH_3CH_2CH_2OH$	Merck
Sodium carbonate anhydrous	Na_2CO_3	APS Ajax Finechem
Sodium sulfate anhydrous	Na_2SO_4	Fluka
N,N-dimethyl formamide	$HCON(CH_3)_2$	Cralo-Erba
Acetic acid	CH_3COOH	J.T.Baker
Hydrochloric acid	HCl	J.T.Baker
Acetone	$(CH_3)_2CO$	Bank Trading
Toluene	$C_6H_5CH_3$	Bank Trading
Nonionic detergent	-	U.N.T.Chemical Co.,ltd

Dyes : All of the dyes were of commercial grade. The dyes used in this experiment are listed in Table 3.2

Table 3.2 Commercial dyes used in the this project.

Commercial name	Manufacture	C.I .Generic name	C.I.Constitution number
Palanil Violet 3B	BASF	C.I. Disperse Violet 8	62030
Cibacron Blue LS-3R high conc.	Ciba-Geigy	undisclosed	undisclosed
Drimarene Blue X-BLN	Clariant	undisclosed	undisclosed
Astrazon Blue BG 200%	DyStar	C.I. Basic Blue 3	51004
Astrazon Blue FGLN 200%	DyStar	C.I. Basic Blue 22	61512

3.2 **Equipment**

1. Laboratory dyeing machine, Ahiba Polymat®

2. UV-VIS spectrophotometer, Model UV-160A , Shimadzu Corporation

3. Fourier-transform infrared spectrophotometer, Nicolet Impact 400D

4. Elemental analyzer, Perkin Elmer PE 2400 series II

5. Nuclear magnetic resonance spectrometer, JEOL JNM-A500

6. Macbeth reflectance spectrophotometer, Color-eye 7000

7. Rotary vacuum evaporator, Tokyo Rikakikai Co.,ltd.

8. Magnetic stirrer, Framo-Gerätetechnik model M21/1

9. Heater mantle , Electromantle MA

10. Thin layer chromatography sheets, Silica gel 60 F_{254} , layer thickness 0.2 mm.

11. pH meter, Hanna model 400

12. pH paper 0-14, Merck

13. Filter paper, Whatman No.40 and 42

14. Magnetic bar

15. Glasswares e.g. three-neck round bottom flask, soxhlet extractor, buchner funnel, suction flask, condenser, beakers, pipettes.

3.3 Isolation of 1,4-diamino-5-nitroanthraquinone from commercial disperse dye grade.

The structure of 1,4-diamino-5-nitroanthraquinone is shown in Figure 3.1. This dye is produced by BASF and has a commercial name as Palanil Violet 3B (C.I. Disperse Violet 8).
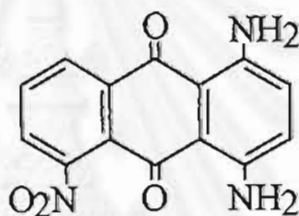
Figure 3.1 Structure of 1,4-diamino-5-nitroanthraquinone.

Commonly, disperse dye powder contains about 60% dispersing agent by weight[34], occasionally more, in order to give stable dispersion during dyeing. It is necessary that all impurities must be removed prior to the modification step.

Isolation of 1,4-diamino-5-nitroanthraquinone from dispersing agent and other impurities was carried out by soxhlet extraction using acetone as a solvent. The purified dye was precipitated in distilled water, filtered out and then dried in an oven.

Identification of 1,4-diamino-5-nitroanthraquinone was carried out using FT-IR technique. The method of sample preparation used in this experiment is pressed-disc technique by mixing sample in potassium bromide (KBr). The spectra of commercial disperse dye and purified 1,4-diamino-5-nitroanthraquinone were obtained on a Nicolet Impact 400D FT-IR spectrometer and all of the spectra were transferred to the computer

for further analysis performed by ommic softwere. For ^{1}H NMR technique, the spectrum of 1,4-diamino-5-nitroanthraquinone was recorded on a JNM 500 MHz from Jeol, Japan. The chemical shifts are expressed in δ ppm. and were internally referenced to the residual protonated solvent ($\delta = 2.5$ ppm. for DMSO)

3.4 Synthesis of N-(2-aminoethyl)pyridiniumchloride hydrochloride

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 hours on a heating mantle unit equip 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% . The reaction scheme may be written as follows:

| Pyridine | 2-chloroethyamine hydrochloride | N-(2-aminoethyl)pyridinium chloride hydrochloride |
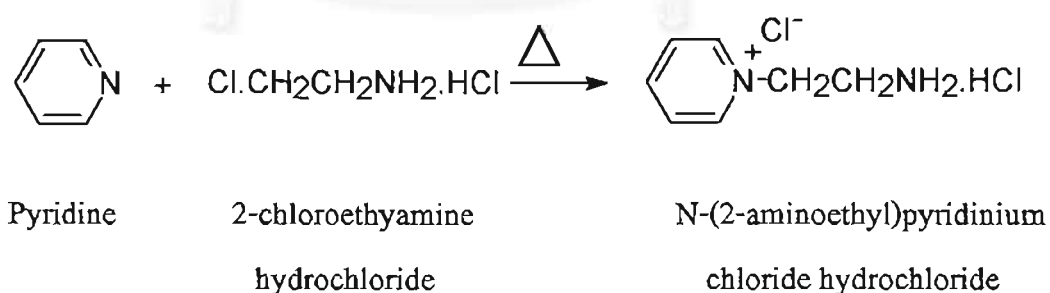
Scheme 3.1 The synthesis reaction of N-(2-aminoethyl)pyridiniumcbloride hydrochloride.

In this study, the identification of N-(2-aminoethyl)pyridiniumchloride hydrochloride was carried out using elemental analyzer, FT-IR, and ^{1}H NMR techniques.

The total nitrogen, hydrogen and carbon content of N-(2-aminoethyl)pyridinium chloride hydrochloride was measured according to the rapid combustion method and quantitatively detected by thermal conductivity detector by using elemental analyzer (Perkin Elmer PE 2400 series II : option CHN).

Infrared analysis of both 2-chloroethylamine hydrochloride and N-(2-amino ethyl)pyridiniumchloride hydrochloride were measured using the Nicolet Impact 400D FT-IR spectrometer with diffuse reflectance attachment. Samples were mixed with KBr powder and pressed into pellet before taking IR spectra.

The ^{1}H NMR spectra was recorded by the Jeol JNM-A500 500 MHz spectrometer. Samples were dissolved in D_2O and DSS (4,4-dimethyl-4-silapentane sulphonic acid) was used as the internal reference.

3.5 Synthesis of highly substantive reactive dye from 1,4-diamino-5-nitroanthra-quinone as a model cationic reactive dye

A solution made by mixing cyanuric chloride (2.766 g, 0.015 mole) and 50 ml. of acetone was added dropwise into the stirred mixture of 1,4-diamino-5-nitroanthra-quinone (2 g, 0.0075 mole) and acetone (400 ml.). The mixture was continuously stirred for four hours at room temperature. The reaction of cyanuric chloride with 1,4-diamino-5-nitroanthraquinone was checked by TLC technique until the reaction was completed.

To follow the reaction by TLC technique, a starting material and reaction mixture taken at various times of reaction were spotted on a TLC plate and dried. The developing solvent used were toluene/acetone mixture (20:1 by volume)[35]. The complete reaction would be observed when spot of 1,4-diamino-5-nitroanthraquinone on the TLC plate totally disappeared.

Then, a solution of N-(2-aminoethyl)pyridiniumchloride hydrochloride (8.763 g, 0.045 mole) and distilled water (200 ml.) which was adjusted to pH 6.5 - 7.0 using 20 wt% of sodium hydroxide stock solution, was added dropwise into above solution in the course of 10 -15 minutes. The pH value of reaction mixture was maintained between 6.5 and 7.0 by the addition of 20wt% of sodium hydroxide solution and the temperature was raised and kept between 45 and 50°C. The complete reaction was judged by no change in pH value of reaction mixture observed and was confirmed by TLC technique using toluene/acetone mixture (20:1) as eluent.

After that, acetone was removed under vacuum using a rotary evaporator at 50°C. The impurities were removed by filter off and then the synthesized dye was isolated by stirring with 2-propanol, the dye was filtered, washed with acetone and dried in a desiccator.

The overall reaction scheme may be written as follows:

1,4-diamino-5-nitro-   Cyanuric chloride   1-(4,6-dichloro-2-triazinylamino)-
anthraquinone   4-amino-5-nitroanthraquinone

Cationic reactive dye
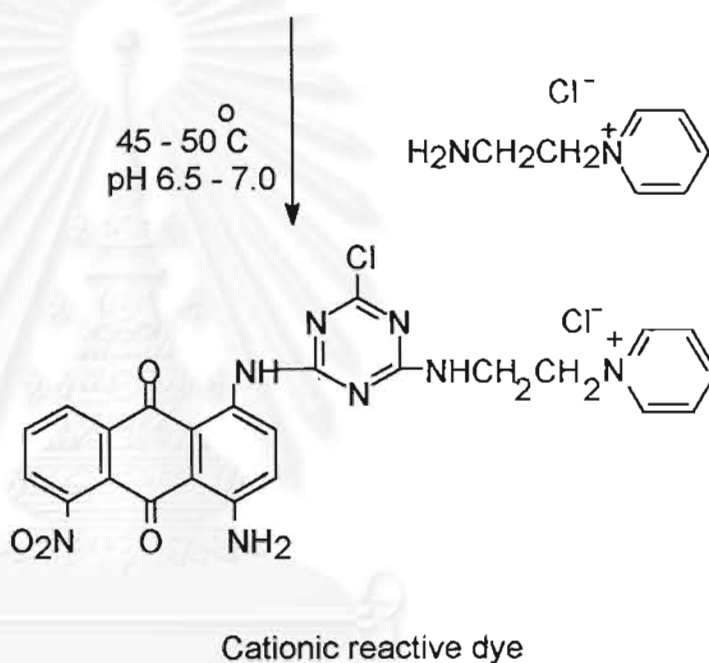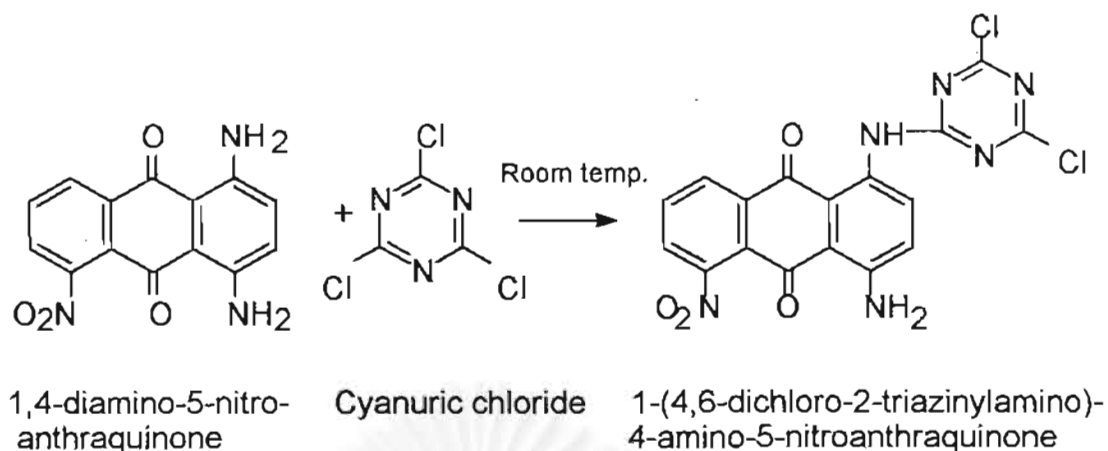
Scheme 3.2 The overall reaction scheme of the preparation of novel highly substantive

reactive dye.

An identification of the chemical structure of the synthesized cationic reactive

dye was carried out using the Nicolet Impact 400D spectrometer for FT-IR spectra and

Jeol JNM-500 spectrometer for ^{1}H NMR spectra. The preparation of sample for

characterization was used the same methods as described earlier.

3.6 Application of novel cationic reactive dye to cotton fabric in the absence of electrolyte by exhaustion dyeing method.

The material used was bleached cotton fabric. The novel cationic reactive dye was applied at a depth of shade of 1%, 2%, 3% and 4% o.w.f. (on weight of fabric) in an Ahiba Polymat® laboratory dyeing machine (Figure 3.2) at liquor ratio of 10:1. All dyeing were commenced at room temperature. The temperature was raised to 85°C over 25 minutes (2°C/min.) 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 at 85°C for a further 45 minutes. The dyed fabric was then taken out and rinsed thoroughly in running tap water. After that, rinsed fabrics were soaping- off in the boiling solution of nonionic surfactant.

The dyeing process diagram of novel cationic reactive dye may be illustrated in Diagram 3.1

where   A   =   Cotton fabric

          B   =   Novel cationic reactive dye

          C   =   Sodium carbonate
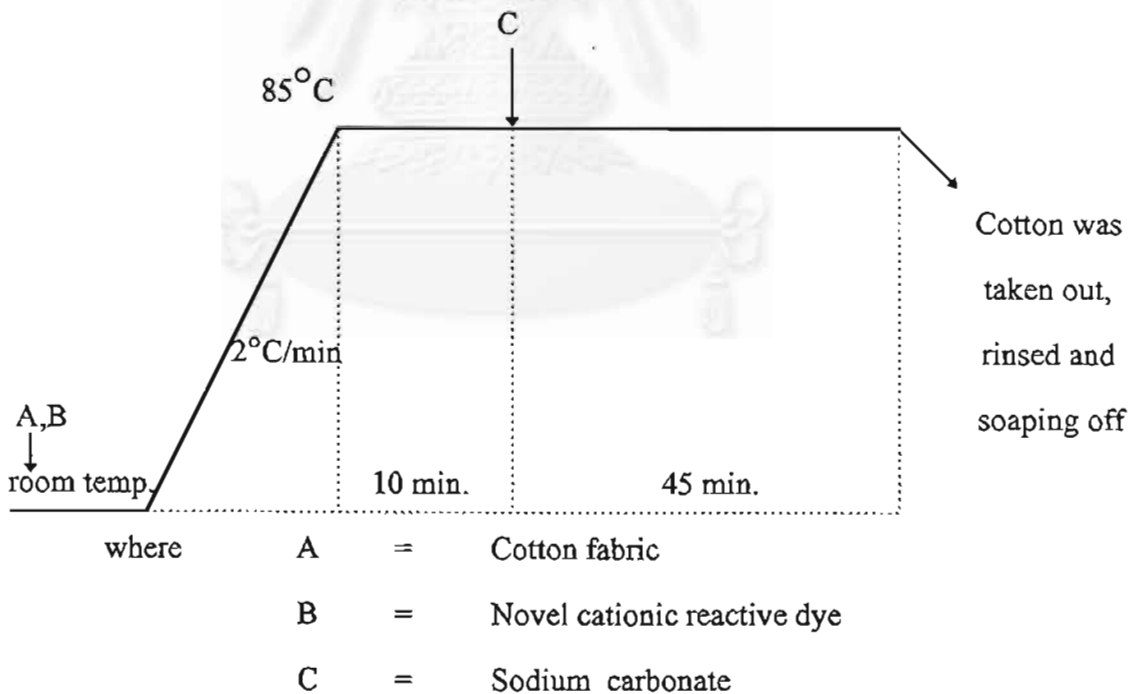
Diagram 3.1 The dyeing process diagram of novel cationic reactive dye
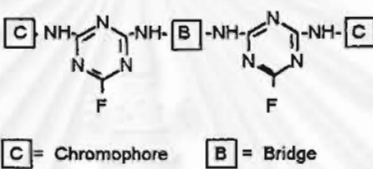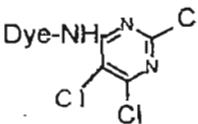
Figure 3.2 Ahiba Polymat® laboratory dyeing machine

3.7 Dyeing of commercial reactive dyes by conventional method for a comparison purpose

Two types of commercial reactive dyes, low salt and high salt types, were applied to the cotton fabric by dyeing method recommended by manufacturer's (salt/alkali conventional method). The percentage of dye exhaustion and the degree of fixation obtained from commercial reactive dyes were compared with those obtained from the synthesized reactive dye. Cibacron Blue LS-3R high conc and Drimarene Blue X-BLN were selected to represent low- and high-salt application reactive dye ranges, respectively. Table 3.3 shows the general data of selected commercial reactive dyes.

Table 3.3 The general data of commercial reactive dyes used.

	Cibacron Blue LS-3R high conc	Drimarene Blue X-BLN
Manufacturer	Ciba-Geigy	Clariant
Suitable dyeing method	Exhaustion method	Exhaustion method
Reactive system	Bis(monofluoro-s-triazine) (bifunctional reactive dye)	Trichloropyrimidine (monofunctional reactive dye)
Chemical structure	[37]	[21]
Minimum/maximum amount of salt recommended	10-30 g/l [37]	20-90 g/l [38]
Optimum fixation temperature	70°C	90-95°C

Dyeing of cotton fabric with the selected dyes was carried out using a Ahiba Polymat® laboratory dyeing machine at a liquor to fabric ratio of 10:1. Dyeing with depths of shade of 1%, 2%, 3% and 4% o.w.f. was also studied. Dyebath preparation and dyeing method were conducted accordingly to the manufacturer's literature[37,38]. The dye manufacturer's recommended process for both the selected dyes are shown in Diagram 3.2 and 3.3.

Diagram 3.2 The dyeing diagram of Cibacron Blue LS-3R high conc (Isothermal method/70°C)
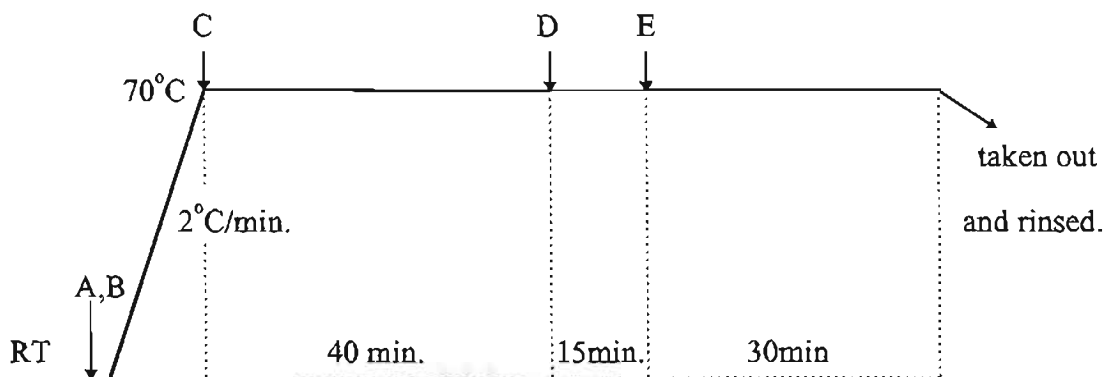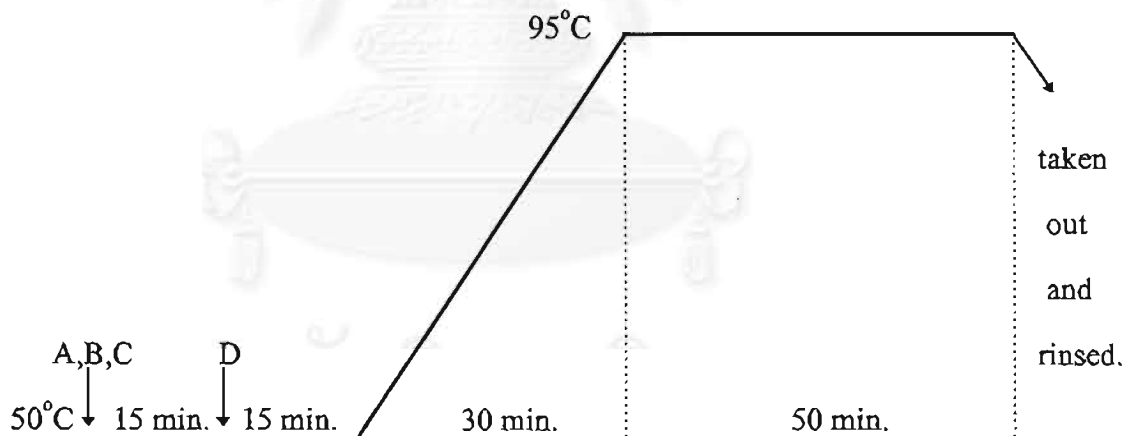
where   A = Cotton fabric

         B = Sodium sulphate 20 g/l

         C = Cibacron LS dyes

         D = Sodium carbonate 5 g/l

         E = Sodium carbonate 10 g/l

where   A = Cotton fabic

         B = Sodium sulphate 80 g/l

         C = Sodium carbonate 20 g/l

         D = Drimarine X dyes

Diagram 3.3 The dyeing diagram of Drimarene Blue X-BLN (All-in process)

For Cibacron Blue LS-3R high conc, all salt was added at the start. The temperature was raised from room temperature to 70°C at 2°C/minutes and then the dye added to the dyebath. After 40 minutes for dye exhaustion, sodium carbonate was added in two portions at an interval of 15 minutes for dye fixation. Dyeing was then continued for another 30 minutes. The dye fabric was removed and rinsed with tap water.

In the case of Drimarene Blue X-BLN, all-in process method is suitable for this type of dyes. Both of salt and alkali were added into the dyebath at the initial dyeing. The temperature was started at 50°C and then the dye was added afterward 15 minutes. Dyeing was continued at this temperature for 15 minutes; then the temperature was raised to 95°C within 30 minutes and dyeing was held at this temperature for 50 minutes. Finally, the fabric was taken out and rinsed thoroughly in water.

3.8 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. UV/Vis spectroscopy is the most commonly used technique for quantitative determination of dye concentration. Usually the Beer-Lambert law is employed to determine the concentration of the dye in the solution from a measurement of absorbance at the wavelength of maximum absorption of the dye[38].

$$\text{Absorbance} \quad = \quad \log(I_o/I) \quad = \quad acl$$

where I_o = 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. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max}) of the dye using a UV-Visible spectrophotometer model UV 160A. The percentage dye exhaustion (%E) was calculated using the following equation :

$$\%E = \frac{(Abs)_o - (Abs)_1}{(Abs)_o} \times 100$$

where $(Abs)_o$ and $(Abs)_1$ were absorbance of the initial dye solution and final dyeing process respectively.

For the dyeing cotton with novel highly substantive reactive dyes, the first step, the cotton was immersed in dye solution in the absence of salt. The dyebath exhaustion at the end of this stage is called the primary exhaustion. Then, an alkali is added to the dyebath to promote fixation and also dye absorption. The exhaustion of the dyebath at the end of dyeing process is referred the secondary or final exhaustion. In the case of conventional reactive dye, only final exhaustion of the dye was determined.

3.9 **Measurement of dye fixation**

The degree of dye fixation was determined spectrophotometrically with an Instrumental Color System (I.C.S.) spectrophotometer which was used to measure the reflectance values of the coloured samples in the visible region of the spectrum (400-700 nm). The colour strength of the dyed fabrics were expressed as K/S values calculated by the Kubelka-Munk equation[8].

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

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. So, 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 of nonionic detergent at the boil for 30 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 the I.C.S. Macbeth reflectance spectrophotometer (Figure 3.3). The measurement parameters were as follows: 10°observer; illuminates D65; specular reflectance included; U.V. reflectance included; large aperture; and average 5 times.

Figure 3.3 I.C.S. Macbeth spectrophotometer (Color-eye 7000)

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

$$\%F \quad = \quad \frac{(K/S)_1 \times 100}{(K/S)_o}$$

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

where $(K/S)_o$ and $(K/S)_1$ are the K/S values of the dyed sample 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.
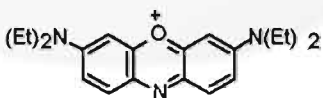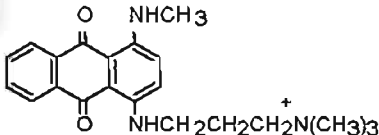
3.10 Color fastness comparison of novel highly substantive reactive dye with traditional cationic dyes on the cotton fabric.

The light fastness properties of dyed cotton fabric between synthesized cationic reactive dye and traditional cationic dyes were evaluated to compare the photocatalytic effect of cationic dyes. Two kinds of cationic dyes, Astrazon Blue BG 200% and Astrazon Blue FGLN 200% were selected which represent types of cationic dyes which contain cationic charge inside- and outside-chromophore structure, respectively. The general data of selected traditional cationic dyes are given in Table 3.4

Traditional cationic dyes have a 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. So, the washing fastness of traditional cationic dye and synthesized cationic reactive dye were also investigated.

Table 3.4 The general data of traditional cationic dyes in the experiments.

	Astrazon Blue BG 200%	Astrazon Blue FGLN 200%
Position of cationic group	cationic group is part of chromophore	cationic group locates outside the chromophore molecule
Manufacturer	DyStar	DyStar
C.I. Generic name	C.I. Basic Blue 3	C.I. Basic Blue 22
C.I. Constitution No.	51004	61512
Dye class	delocalized cationic dyes	localized cationic dyes
Chromophoric system	oxazine	anthraquinone
Dye structure[39]	(Et)2N—[O+]—N(Et)2	O NHCH3 / O NHCH2CH2CH2N(CH3)3+

The color fastness properties were tested on the dyed fabrics at a depth of shade of 1%, 2%, 3% and 4% o.w.f; For the synthesized reactive dye, dyed samples after washing off process were used; and for conventional cationic dyes dyed samples were just rinsed in tap water prior to testing. The fastness tests were carried out in accordance with the recommendations of the International Organization of Standardization (ISO).

Specific tests used were: ISO 105-B01:1994 color fastness to light (daylight) and ISO 105-C03:1989 color fastness to washing (test 3).

3.10.1 Dyeing method of traditional cationic dyes on the cotton fabric.

Cotton fabrics were dyed by varying the dye concentration in the range of 1-4% o.w.f. Dyeing procedure of Astrazon Blue FGLN 200% was carried out in similar manner to the dyeing of novel highly substantive reactive dye in section 3.6. In the case of Astrazon Blue BG 200%, addition of alkali was not required because of its sensitively to alkali. The dyeing were started at room temperature and raised to the boil at rate of $2^{\circ}C/minute$ and then held for a further for 45 minutes. After dyeing, both cationic dyed fabrics were rinsed with clean water in three washing bath for 3 minutes, L:R 50:1 and then fabric was squeezed and dried. The process diagram of Astrazon Blue BG 200% is shown in Diagram 3.4.
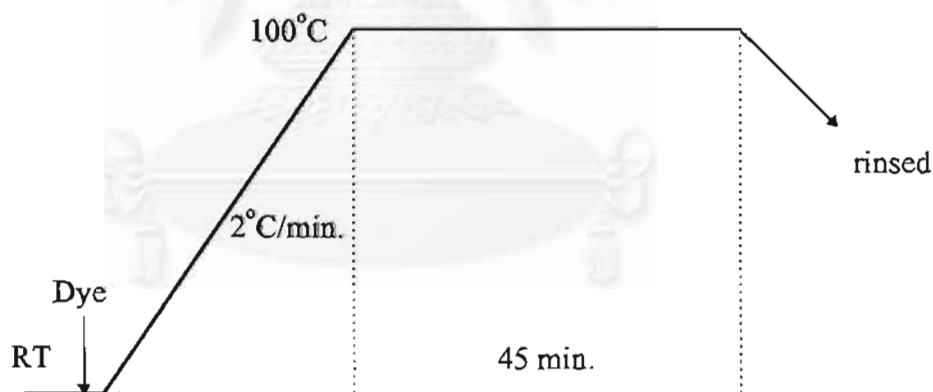
Diagram 3.4 The process diagram of Astrazon Blue BG 200% used in this experiment.

3.10.2 Determination of light fastness (daylight)

The ISO 105-B01 color fastness to light[40] was used to determine the resistance of the color of textile to the action of daylight. The light fastness of a dye is usually assessed against a set of standard dyeing. ISO has chosen a set of eight blue dyes (Table

3.5) which vary in light fastness on wool from very poor (grade 1) to excellent (grade 8). The dyes have been selected carefully so that an increase of one grade is approximately equivalent to doubling the light fastness[6]. In the test, a dyed fabric is exposed to daylight under prescribed conditions along with eight dyed blue wool as references. 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).

Table 3.5 Dyes for blue wool references 1 to 8[40]

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

3.10.3 Determination of washing fastness

The ISO 105-C03 color fastness to washing: test 3[41] 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 5 g/l of anhydrous sodium carbonate in distilled water and previously heated to $60^{\circ}C$, to gave 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 both the grey scales and determined as the color difference (ΔE) values by using I.C.S. Macbeth spectrophotometer. The settings on the I.C.S. were as follows: 10°observer; illuminates D65; specular and U.V. reflectance included; small aperture; average 2 times; and used CIELAB equation.

CHAPTER IV

Results and Discussion

4.1 FT-IR Analysis of purified 1,4-diamino-5-nitroanthraquinone

1,4-diamino-5-nitroanthraquinone was isolated from commercial disperse dyes by solvent extraction method as described in section 3.3. The fourier transform infrared spectroscopy (FT-IR) was carried out to identify the characteristic structure and purity of isolated 1,4-diamino-5-nitroanthraquinone. The FT-IR spectra of the commercial disperse dye and purified 1,4-diamino-5-nitroanthraquinone are shown in Figure 4.1 and Figure 4.2, respectively. The results of functional group analysis are also summarized in Table 4.1 to 4.2.

Commercial disperse dyes often contain high amount of anionic dispersing agents and other additives. The presence in such a high concentration of those auxiliaries, as indicated by the dominance of their absorption bands (see Figure 4.1)causes a severe interference to the identification of FT-IR spectrum of the dye. The broad band found at ~3700 -3000 cm^{-1} is the region of the presence of –OH stretching and –CH stretching in which the $–NH_2$ stretching band of 1,4-diamino-5-nitroanthraquinone dye also appears. However, the distinct characteristic of $-NH_2$ stretching which shows two sharp peaks could not be observed due to the interference. The absorption bands in the region of near 1200 cm^{-1} and the band at the 1037 cm^{-1} are also found, which correspond to the presence of sulphonic group (SO_3^-) of anionic dispersing agent[35]. On the other hand, these absorption bands disappear from the FT-IR spectrum of the purified dye (Figure 4.2). The disappearance of both broad bands in the region of 3700–3000 cm^{-1} and the sulphonate group absorption band indicate that anionic dispersing agents as well as other additives are no longer present. Comparison of

FT-IR spectra of commercial disperse dye and its corresponding purified product (1,4-diamino-5-nitroanthraquinone) are shown in Figure 4.3.

Primary amine group of 1,4-diamino-5-nitroanthraquinone dye is readily recognized as sharp, well separated bands at 3440 and 3310 cm^{-1}. The other main absorption bands of purified 1,4-diamino-5-nitroanthraquinone can be also found in the region of 1610, 1530 and 1390 cm^{-1}, respectively, which are assigned to the presence of carbonyl group and nitro group (asymmetric and symmetric stretching), respectively.
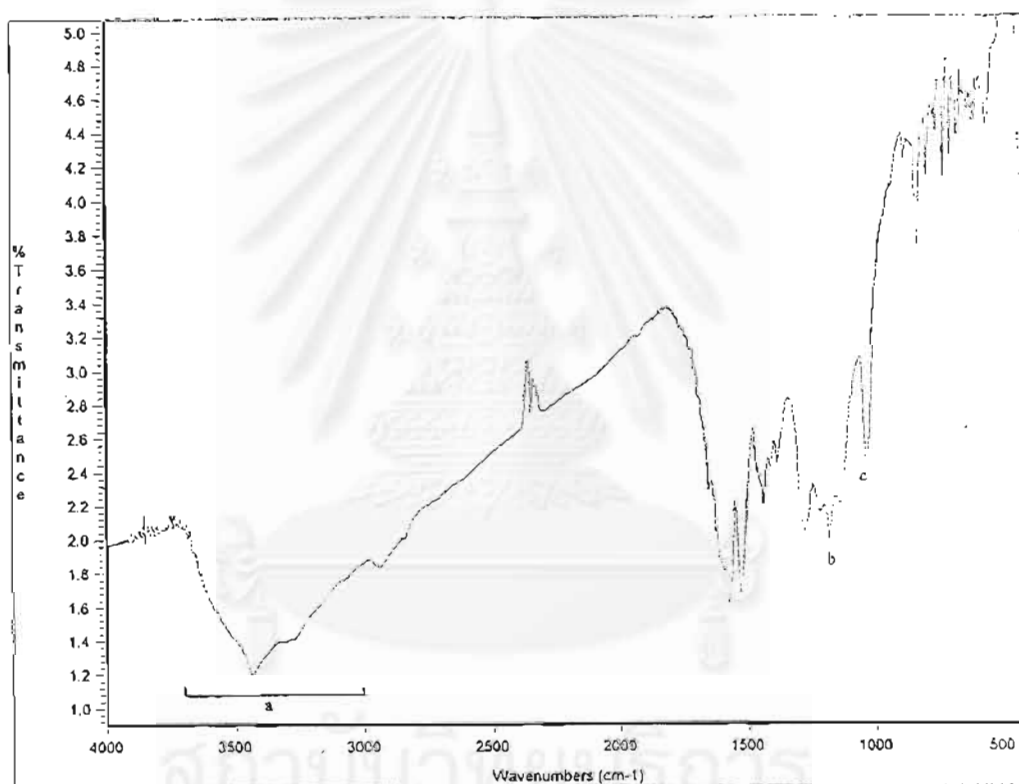
Figure 4.1 FT-IR spectrum of commercial disperse dye (Palanil Violet 3B)

Tables 4.1 Functional group analysis of commercial disperse dye (Palanil Violet 3B)

Assignment	Wave number (cm^{-1})	Interpretation
a	3000 – 3700 (broad band)	Overlapping of –OH stretching (impurities), -CH stretching and -NH$_2$ stretching (dye) bands.
b	1189	-SO$_2$- asymmetric stretching band of sulphonate group.
c	1037	-SO$_2$- symmetric stretching band of sulphonate group.
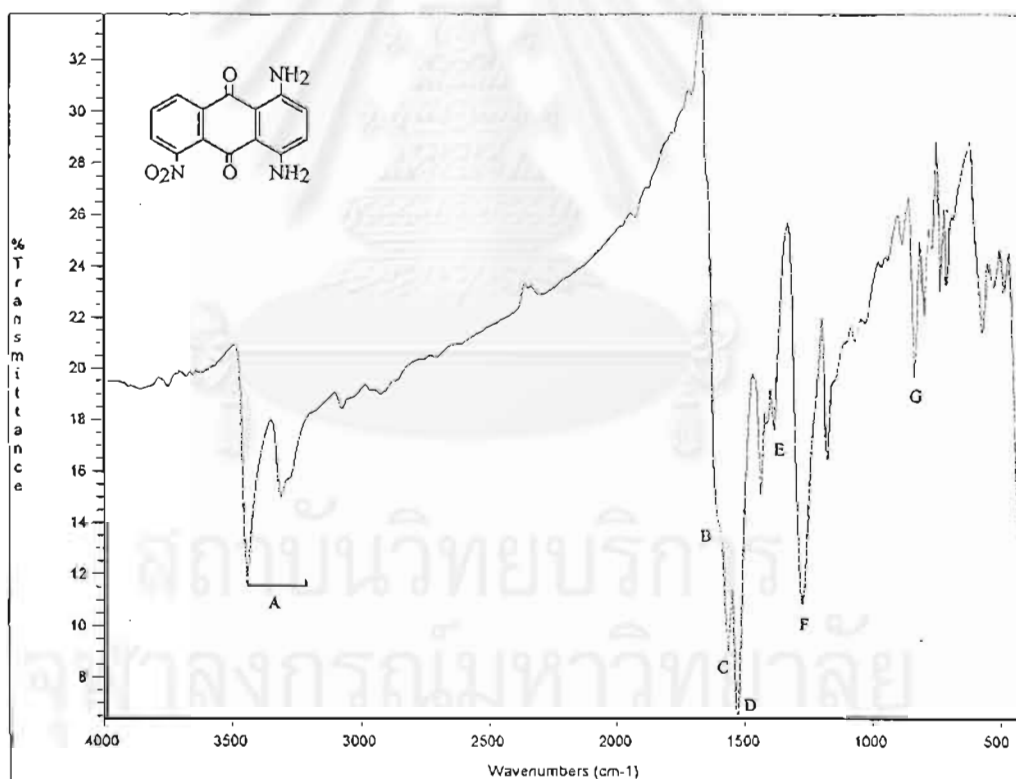
Figure 4.2 FT-IR spectrum of purified 1,4-diamino-5-nitroanthraquinone.

Table 4.2 Functional group analysis of purified 1,4-diamino-5-nitroanthraquinone.

Assignment	Wave number (cm^{-1})	Interpretation
A	3440, 3310	-NH stretching of NH$_2$.
B	1610	Overlapped of –C=O stretching with –NH bending.
C	1570	-C=C ring stretching.
D	1530	-NO$_2$ asymmetric stretching.
E	1390	-NO$_2$ symmetric stretching.
F	1265	-C-N stretching of -NH$_2$.
G	840	-C-N stretching of -NO$_2$.
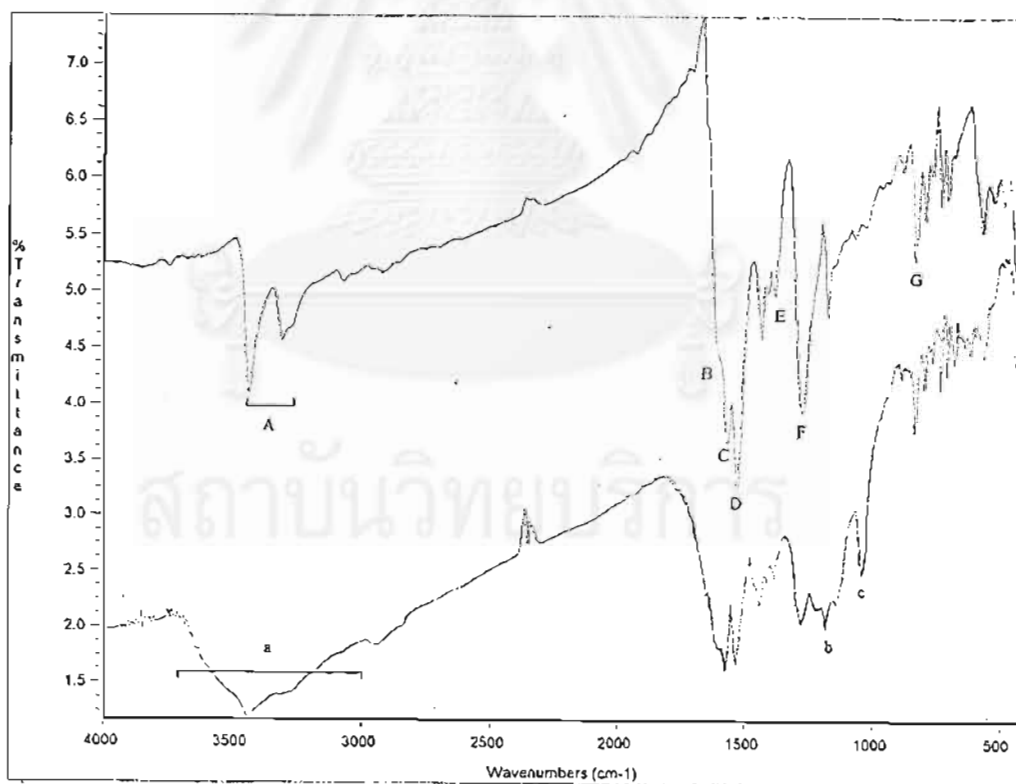
Figure 4.3 Comparison of FT-IR spectra of purified 1,4-diamino-5-nitroanthraquinone (top) and commercial disperse dye (below).

4.2 ¹H NMR Analysis of purified 1,4-diamino-5-nitroanthraquinone

The ¹H NMR spectroscopy was also used to confirm the chemical structure of purified 1,4-diamino-5-nitroanthraquinone. The ¹H NMR spectrum of this compound in DMSO-D_6 is shown in Figure 4.4 and the chemical shifts of all protons are summarized in Table 4.3.
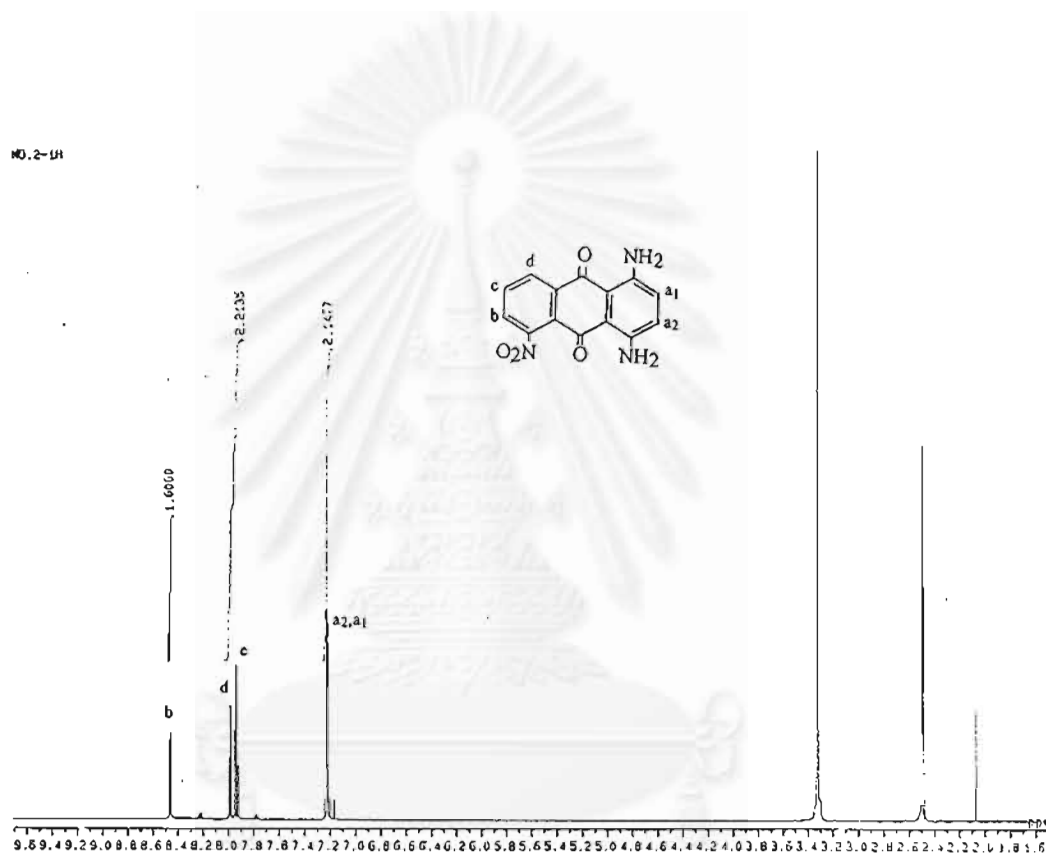
Figure 4.4 ¹H NMR spectrum of purified 1,4-diamino-5-nitroanthraquinone in DMSO-D_6.

Table 4.3 Chemical shifts of purified 1,4-diamino-5-nitroanthraquinone.

Chemical Shift (δ)	Multiplicity	Assignments.
8.457	Doublet of doublet	b
7.982	Doublet of doublet	d
7.938	Triplet	c
7.223	Doublet	a_1 or a_2
7.21	Doublet	a_1 or a_2
6.4 – 10	Broad band under aromatic proton patterns	$-NH_2$
3.3	Singlet	absorbed water of DMSO-D_6
2.5	Singlet	Methyl proton DMSO-D_6

The ^1H NMR spectrum (Figure 4.4) exhibited the peaks at 7.2-8.5 ppm. corresponding to the signals of aromatic protons. In fact, the signals in this region of an anthraquinone dye are often quite complicated because the spectra are not first-order[42]. The signal of H_b and H_d appeared as a doublet of doublet at 8.457 and 7.982 ppm., respectively, due to the long range coupling between these proton and H_c. Similarly, the signal of H_c appeared as a triplet at 7.938 ppm. Other signals at 7.323 and 7.21 ppm showed doublet splitting and smaller $\Delta v/J$ ratio corresponding to the signals of nonequivalent H_{a1} and H_{a2}, respectively.

4.3 **Elemental Analysis of N-(2-aminoethyl)pyridiniumchloride hydrochloride**

N-(2-aminoethyl)pyridiniumchloride hydrochloride was synthesized by the method described in the section 3.4 and used as an intermediate for synthesizing cationic reactive dye. This compound has the following formula:
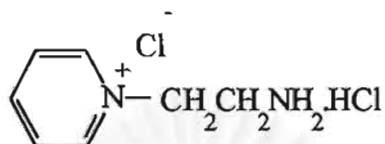
Elemental quantitative analysis included carbon, hydrogen and nitrogen contents of N-(2-aminoethyl)pyridiniumchloride hydrochloride was carried out using elemental analyzer. The purity of synthesized product is referred in the terms of the percentage of relative yield, which calculated from the actual carbon, hydrogen and nitrogen content, are shown in the Table 4.4.

Table 4.4 Total carbon, hydrogen and nitrogen content of N-(2-aminoethyl) pyridiniumchloride hydrochloride.

Element	Analyzes. (%)		% Relative yield[*]
	Calculated	Found	
Carbon	43.096	42.039	97.547
Hydrogen	6.200	6.445	103.952
Nitrogen	14.359	13.890	96.734

* % Relative yield = [Found/Calculated value] x 100

From above results, the actual contents of carbon, hydrogen and nitrogen of synthesized product found with nearly the same value as those of theoretical calculation value. Furthermore, the percentage of relative yield value indicates that the purity of

synthesized product gives a minimum value about 96.734% for nitrogen content. But the percentage of relative yield for the hydrogen content was more than 100% which may be attributed to the presence of moisture in the product.

4.4 FT-IR Analysis of N-(2-aminoethyl)pyridiniumchloride hydrochloride

The FT-IR spectra of N-(2-aminoethyl)pyridiniumchloride hydrochloride and 2-chloroethylamine hydrochloride are shown in Figure 4.5 and Figure 4.6, respectively. The FT-IR spectrum of N-(2-aminoethyl)pyridiniumchloride hydrochloride shows the presence of a pyridine ring as evidenced by the strong absorption bands at 1630, 1500, 1165 and 790 cm^{-1} due to the $-C=N$ stretching, $-C=C-$ aromatic stretching, $-C-N$ aromatic stretching and $-C-H$ aromatic bending, respectively. The assignments of the FT-IR absorption bands of this compound is summarized in Table 4.5.
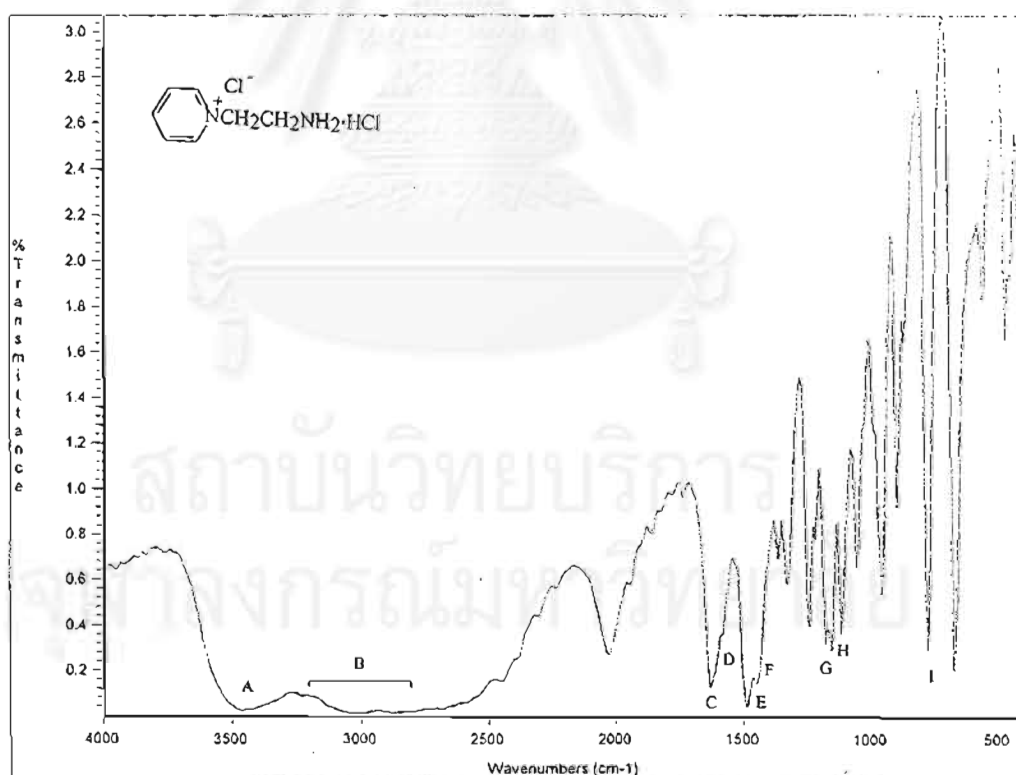
Figure 4.5 FTIR spectrum of N-(2-aminoethyl)pyridiniumchloride hydrochloride.

Table 4.5 Functional group analysis of N-(2-aminoethyl)pyridiniumchloride

hydrochloride

Assignment	Wave number (cm^{-1})	Interpretation
A	3400 – 3500	-N-H stretching of amine
B	2800 – 3200	-NH$_3^+$ stretching overlapped with -C-H stretching
C	~ 1630	-C=N aromatic stretching
D	1590	-N-H bending
E	~ 1500	-C=C- aromatic stretching
F	~ 1450	-C=C- aromatic stretching overlapped with -C-H- aliphatic bending
G	~ 1165	-C-N aromatic stretching
H	1120	-C-N aliphatic stretching
I	790	-C-H aromatic bending

The FT-IR spectrum of 2-chloroethylamine hydrochloride (Figure 4.6) which exhibited the adsorption band of –CH$_2$-Cl group at 1293 and 843 cm^{-1} attributable to –C-Cl bending and –C-Cl stretching, respectively. On the other hand, this absorption band completely disappears from the spectrum of N-(2-aminoethyl)pyridiniumchloride hydrochloride, confirming that the reaction of 2-chloroethylamine hydrochloride with pyridine occurred. The summary of adsorption bands assignments of 2-chloroethylamine hydrochloride are presented in Table 4.6 and overlaid FT-IR spectra between this compound and N-(2-aminoethyl)pyridiniumchloride hydrochloride are also shown in Figure 4.7 for comparison purpose.

Cl-CH2CH2NH2·HCl
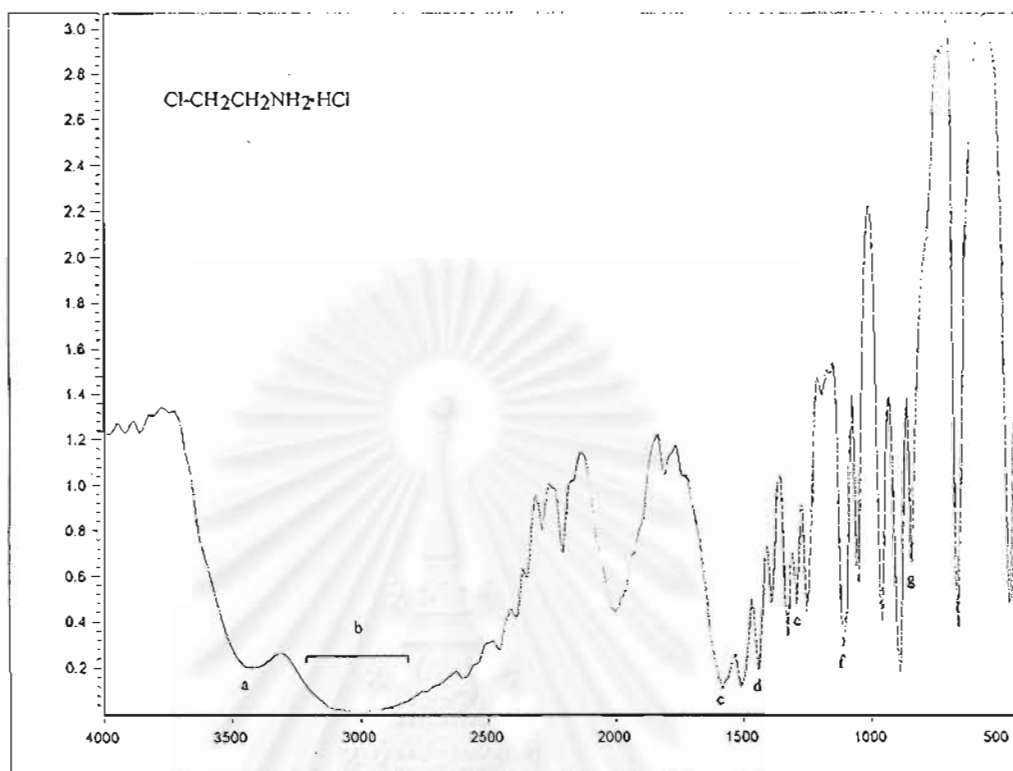
Figure 4.6 FT-IR spectrum of 2-chloroethylamine hydrochloride.

Table 4.6 Functional group analysis of 2-chloroethylamine hydrochloride.

Assignment	Wave number (cm^{-1})	Interpretation
a	3400 – 3500	-N-H stretching of amine
b	2800 – 3200	-NH$_3^+$ stretching overlapped with
		-C-H stretching
c	1590	-N-H bending
d	~ 1450	-C-H bending
e	1293	-C-Cl bending (wagging)
f	~1112	-C-NH$_2$ stretching
g	843	-C-Cl stretching
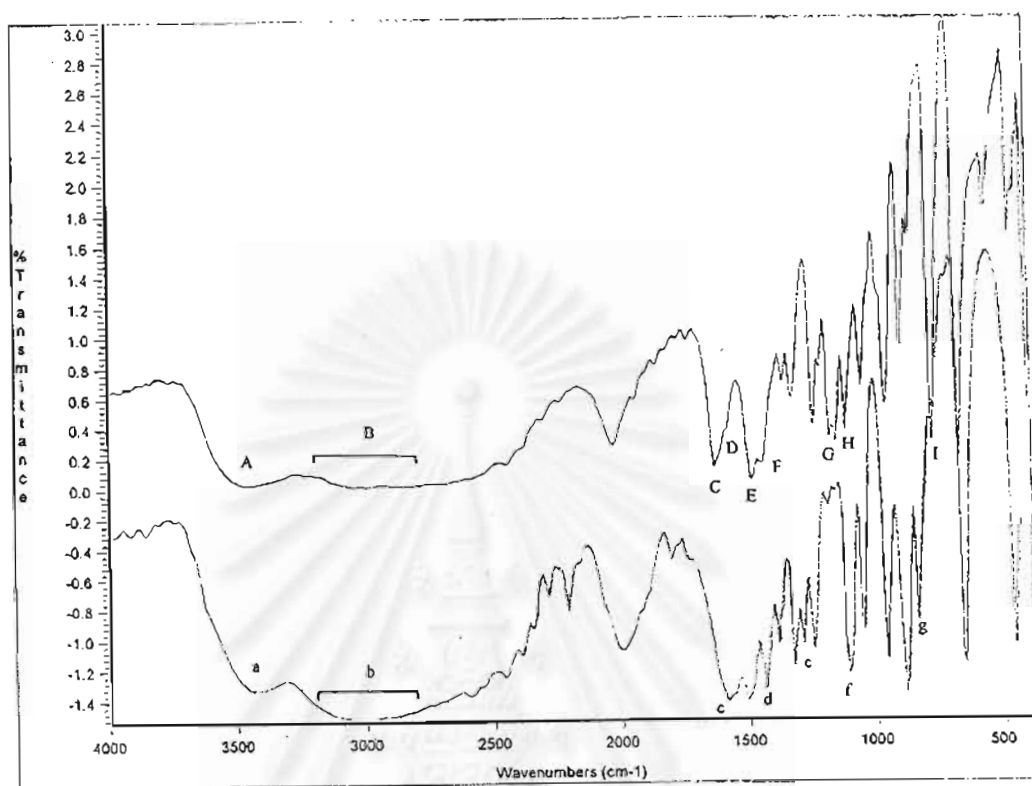
Figure 4.7 Comparison of FT-IR spectra of N-(2-aminoethyl)pyridiniumchloride

hydrochloride (top) and 2-chloroethylamine hydrochloride (below).

4.5 ¹H NMR Analysis of N-(2-aminoethyl)pyridiniumchloride hydrochloride

The ¹H NMR spectroscopy was performed to identify the characteristic structure of N-(2-aminoethyl)pyridiniumchloride hydrochloride. The ¹H NMR spectrum of N-(2-aminoethyl)pyridiniumchloride hydrochloride is shown in Figure 4.7 and its proton chemical shifts are presented in Table 4.8.
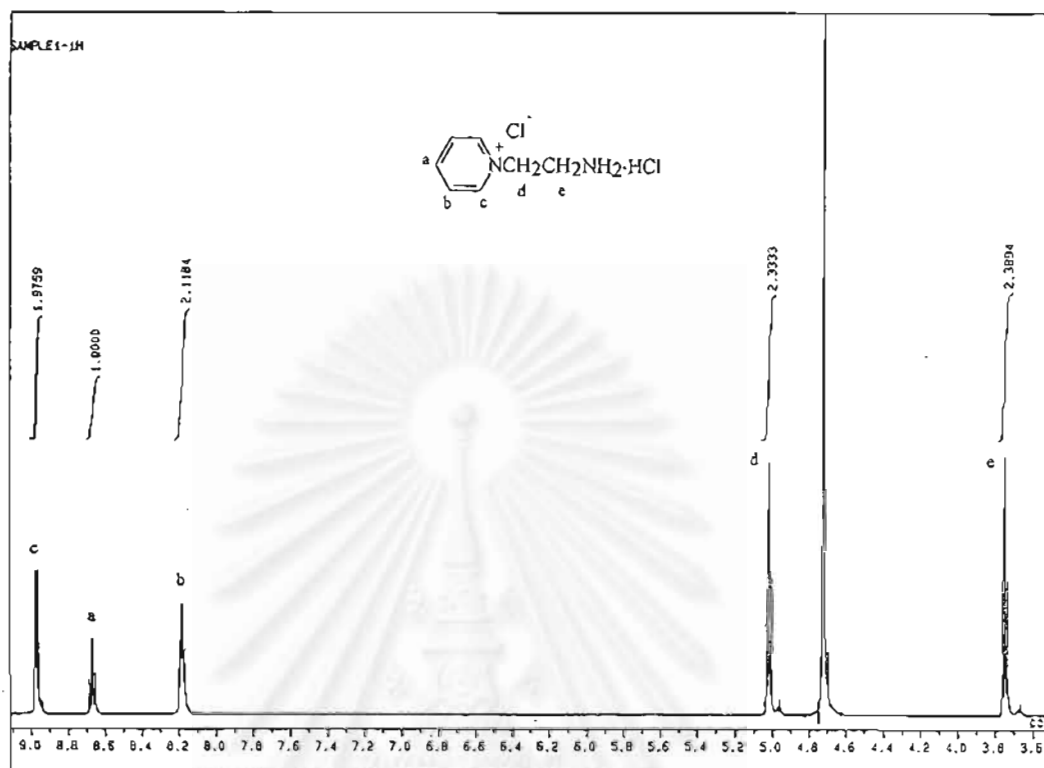
Figure 4.7 ^{1}H NMR spectrum of N-(2-aminoethyl)pyridiniumchloride

hydrochloride in D_2O

Table 4.8 Proton chemical shifts of N-(2-aminoethyl)pyridiniumchloride

hydrochloride

Chemical shift (δ)	Multiplicity	Assignments
9.870	Doublet	c
8.665	Triplet	a
8.180	Triplet	b
5.018	Triplet	d
4.720	Singlet	Solvent
3.745	Triplet	e

From Figure 4.7, the NMR spectrum exhibits the signals of aromatic protons at 9.870, 8.665 and 8.180 ppm corresponding to the signals of H_c, H_a and H_b, respectively. The chemical shifts at 5.018 and 3.745 ppm indicate the aliphatic protons attached to a carbon bearing a pyridine ring ($\rangle$ N-CH$_2$- or H_d) and protonated amine (-CH$_2$NH$_3^+$ or H_e). Clearly, H_d are coupled and split into a triplet by H_e.

4.6 Following the synthesis reaction of novel highly substantive reactive dye by TLC

Thin layer chromatography (TLC) is commonly used as a preliminary test in following dye synthesis. It is quick, convenient and reliable method to check the complete reaction by observing the disappearance of starting material. In this study the reaction of 1,4-diamino-5-nitroanthraquinone with cyanuric chloride and then N-(2-aminoethyl)pyridiniumchloride hydrochloride to produce novel highly substantive reactive dye were followed by TLC technique. The developing solvent used were toluene/acetone mixture of the ratio of 20:1 (by volume) and stationary phase was silica gel-TLC plates. The TLC chromatogram of reaction between 1,4-diamino-5-nitroanthraquinone and cyanuric chloride at various reaction times is shown in Figure 4.8.
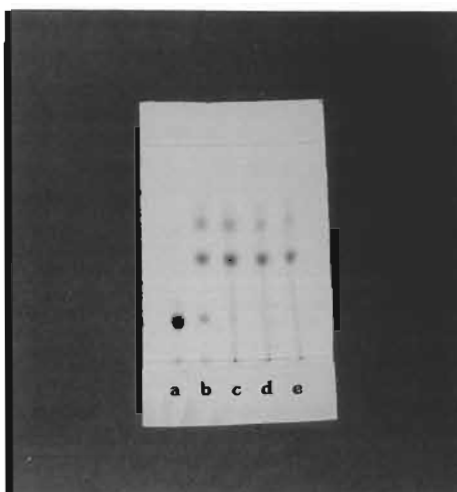
a	=	1,4-diamino-5-nitroanthraquinone (Starting dye)
b	=	reaction mixture taken after 1 hr.
c	=	reaction mixture taken after 2 hrs.
d	=	reaction mixture taken after 3 hrs.
e	=	reaction mixture taken after 4 hrs.

Figure 4.8 TLC-chromatogram of 1,4-diamino-5-nitroanthraquinone and reaction

mixture of 1,4-diamino-5-nitroanthraquinone with cyanuric chloride.

From the above chromatogram, it can be assumed that the reaction between 1,4-diamino-5-nitroanthraquinone dye and cyanuric chloride was completed at the reaction time of 2 hours, confirmed by the total disappearance of the spot of original 1,4-diamino-5-nitroanthraquinone dye. Reaction products are composed of two components with well separate and higher R_f values compared to that of starting dye, due to their high solubility in developing solvent. The major component with intermediate R_f values is assumed to be the product of mono-substitution reaction of the starting dye with cyanuric chloride. While the minor product with fastest R_f value may be a result of mono-substituted dye undergoing further reaction with excess cyanuric chloride to yield bis-substituted product. The resulting products obtained were reacted further with N-(2-aminoethyl)pyridiniumchloride hydrochloride without purification. At this stage, it was

aimed to introduce a releasable cationic group into dye molecule. TLC technique also was employed to confirm the completion of reaction. The TLC chromatogram is illustrated in Figure 4.9.
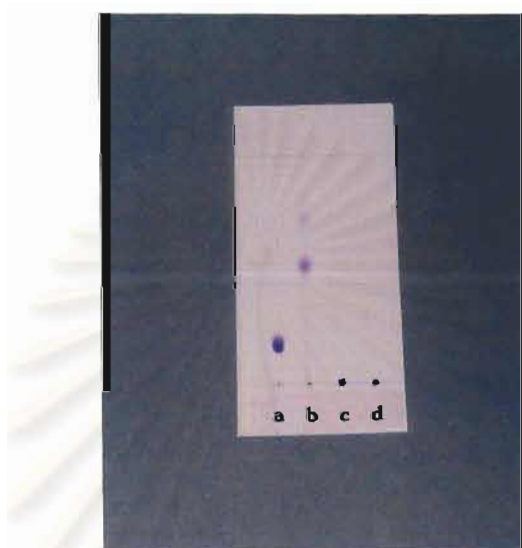
a   =   1,4-diamino-5-nitroanthraquinone

b   =   products of 1,4-diamino-5-nitroanthraquinone and cyanuric chloride

c   =   reaction mixture after 1 hr.

d   =   reaction mixture after 2 hrs.

Figure 4.9 TLC chromatogram of 1,4-diamino-5-nitroanthraquinone, products of 1,4-diamino-5-nitroanthraquinone and cyanuric chloride, and final dye from thus intermediate and N-(2-aminoethyl)pyridiniumchloride hydrochloride.

From resulting TLC chromatogram (Figure 4.9), it shows that the reaction product of dichlorotriazinyl group containing dye (from the first step) with N-(2-aminoethyl)pyridiniumchloride hydrochloride is the water-soluble product, proven by its hardly migration of the dye spot in organically developing solvent.

Finally, conclusion can be drawn that a water-soluble reactive dye which is free from anionic solubilizing group and contains a cationic group could be produced from a disperse dye with free amino group. This type of dye is expected to be appliable to cotton fabric in the absence of electrolyte.

4.7 FT-IR Analysis of novel highly substantive reactive dye

The novel highly substantive reaction dye was synthesized by the method in the section 3.5. The FT-IR spectrum of this synthesized reactive dye is shown in Figure 4.10 which exhibits the important absorption band of C-Cl stretching of chlorotriazinyl group at 802 cm^{-1}, -C=N aromatic stretching of triazine ring overlapped with –C-N aromatic stretching at 1270-1250 cm^{-1} and also the broad band found at 2800-3500 cm^{-1} due to C-H stretching of both aromatic and aliphatic chain overlapped with –NH stretching. The assignments of the FT-IR absorption bands are presented in the Table 4.9.
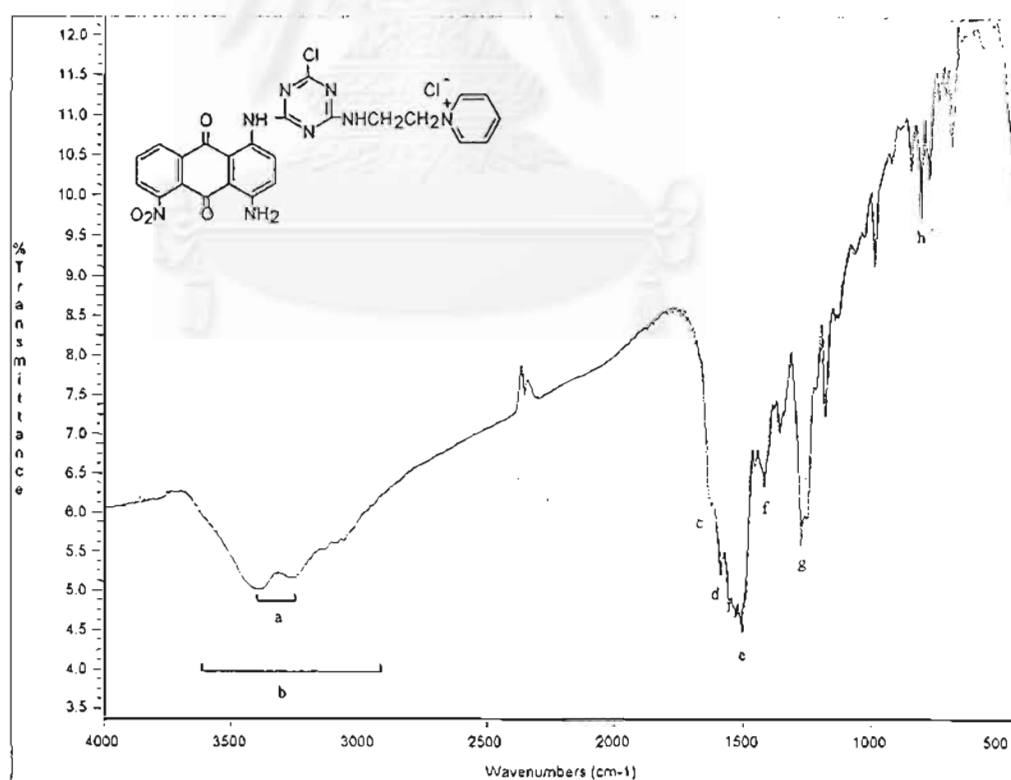
Figure 4.10 FT-IR spectrum of synthesized cationic reactive dye.

Table 4.9 Functional group analysis of synthesized cationic reactive dye.

IR absorption peaks	Wave number (cm^{-1})	Assignment
a	3400 , 3270	-NH stretching of NH_2
b	2800 – 3500	-C-H stretching of both aromatic and aliphatic overlapped with –NH stretching
c	~ 1630	-C=O stretching overlapped with -C=N aromatic (pyridine) stretching
d	~1590	-C=C- aromatic stretching overlapped with –NH bending (aliphatic)
e	1530 – 1500	-C=C- aromatic stretching overlapped with - NO_2 asymmetric stretching
f	1480	-C-H bending of aliphatic chain.
g	1270 – 1250	-C=N aromatic (triazine) stretching overlapped with –C-N aromatic stretching.
h	~ 802	-C-Cl stretching

4.8 ^{1}H NMR analysis of novel highly substantive reactive dye

To confirm the structure of novel highly substantive reactive dye, ^{1}H NMR spectroscopy was used to compare the synthesized reactive dye with an original 1,4-diamino-5-nitroanthraquinone (Figure 4.4) and N-(2-aminoethyl)pyridiniumchloride

hydrochloride (Figure 4.7). The ^{1}H NMR spectrum of this synthesized reactive dye is shown in Figure 4.11 and the chemical shifts of all protons are given in Table 4.10.
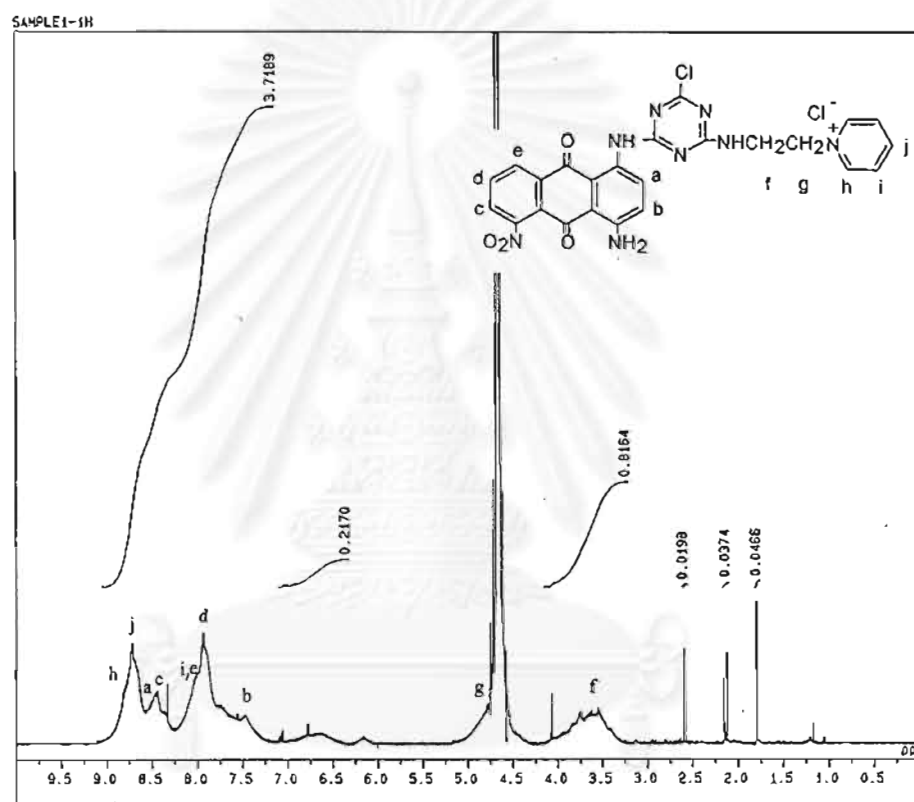
Figure 4.11 ^{1}H NMR spectrum of synthesized reactive dye using D$_2$O as solvent.

Table 4.10 Proton chemical shifts of synthesized reactive dye.

Chemical shift(δ)	Multiplicity	Assignments
~ 8.8	Broad and complex	h
~ 8.71		j
~ 8.51		a
~ 8.45		c
~ 8.05		e and i
~ 7.93		d
~ 7.46		b
4.5 – 5	Overlapped with solvent peak	g
3.3 – 4.05	Broad and complex	f

In this spectrum, the aromatic protons of anthraquinone and pyridinium ring are observed at around 8.8 to 6.0 ppm. The presence of pyridinium ring is evidenced by split signals which has a center around 8.8, 8.71 and 8.05 ppm, and the signals at around 8.51, 8.45, 8.05, 7.93, and 7.46 ppm are assigned to the protons of an anthraquinone ring. The signal at 8.51 ppm is possibly as a result of deshielding effect of adjacent heterocyclic ring proton (H_a). Other broad signals at around 4.5–5 ppm and 3.3–4.05 ppm are probably due to ($>^+$N-CH$_2$ CH$_2$-NH-).

4.9 Dyeing properties of synthesized cationic reactive dye on cotton fabric

The cotton fabrics were dyed with the synthesized cationic reactive using various dye concentrations ranging from 1 to 4% o.w.f. in the absence of electrolyte by exhaustion dyeing method as described in section 3.6. The results of the color yield, %dye exhaustion and the degree of dye fixation were summarized in Table 4.11 and Figure 4.12.

Table 4.11 Color yield, % dye exhaustion and the degree of fixation of the synthesized cationic reactive dye at various concentrations of dye.

Dye concentration (% o.w.f.)	Color yield (K/S)[a]		% Exhaustion[b]		Fixation	
	Before soaping	After soaping	Primary	Secondary	% F	% F_T
1	7.499	6.773	70.683	89.893	90.319	81.190
2	16.591	14.816	43.354	93.510	89.301	83.505
3	21.904	20.06	29.184	94.158	91.581	86.231
4	24.144	22.747	28.639	94.903	94.214	89.412

[a] measured at 570 nm.

[b] measured at 570 nm.
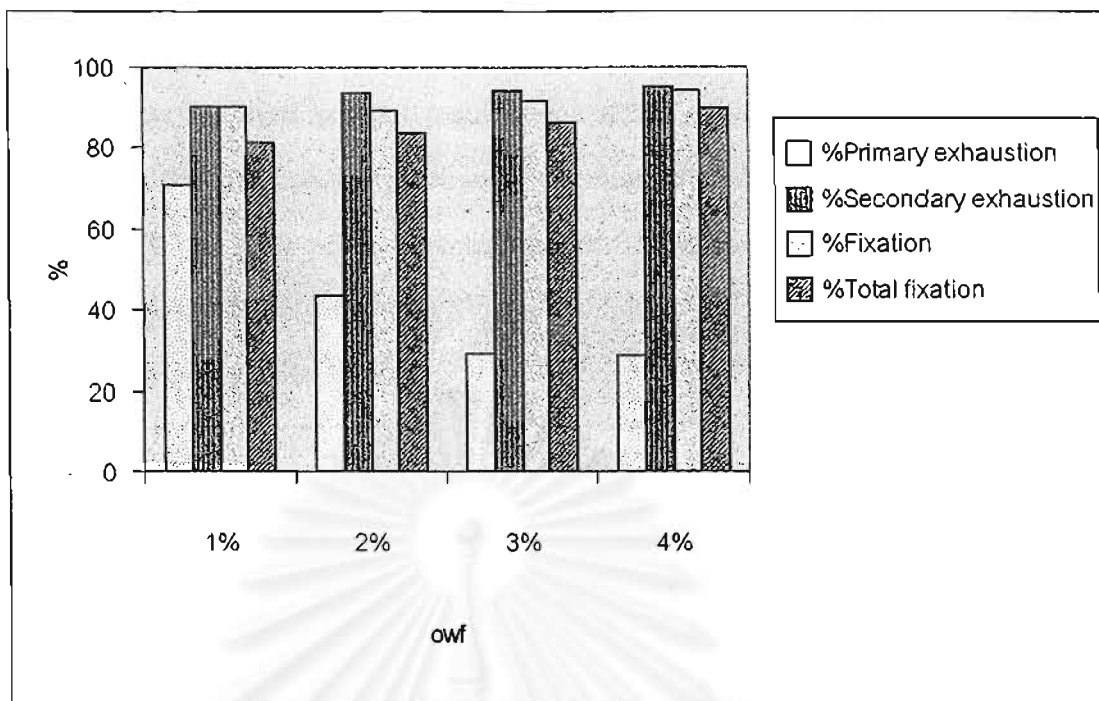
Figure 4.12 The percentage of dye exhaustion, apparent degree of dye fixation
and the total degree of dye fixation of dyeing of novel highly
substantive reactive dye.

The results show that the percentage of primary exhaustion (the first column)
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. After the addition of alkali, dye soluble in the dyebath were capable of
further diffusing into the fiber. The ability of taking up more dyes in this stage was
attributed to the presence of ionized cellulose generated by added alkali. This kind of
ionic interaction attracted cationic dyes to the inner fiber. As can be seen from the

dyeing result, a significant increase in the percentage of dye exhaustion as high as 90% in average was achieved without requirement of the addition of salt. The exhaustion dyes then underwent chemical reaction with cellulose hydroxyl groups under alkaline condition to produce dye-fiber covalent bond. The higher value of dye fixation of cationic reactive dye indicates that almost all dye molecules being absorbed into the fiber can react with cellulosic fiber.

4.10 Dyeing results of commercial reactive dyes by conventional dyeing method for comparison purpose

Two types of commercial reactive dyes, low salt and high salt types, were applied to the cotton fabric by salt/alkali conventional dyeing method recommended by manufacturers as described in section 3.7. Cibacron Blue LS-3R high conc and Drimarene Blue X-BLN were selected to represent low– and high–salt application reactive dye ranges, respectively. The results of the color yield, % dye exhaustion and the degree of dye fixation of both dyes were shown in Table 4.12 to 4.13.

Table 4.12 Color Yield, % dye exhaustion and the degree of fixation of Cibacron Blue LS-3R high conc. at various concentrations of dye.

| Dye concentration (% owf) | Color yield (K/S)[a] | | % Exhaustion[b] | Fixation | |
	Before soaping	After soaping		% F	% F_T
1	11.308	9.953	91.159	87.858	80.090
2	20.653	18.921	92.644	91.614	84.875
3	25.341	24.170	86.135	95.379	82.155
4	27.716	26.927	83.535	97.153	81.157

[a] measured at 620 nm.

[b] measured at 590 nm.
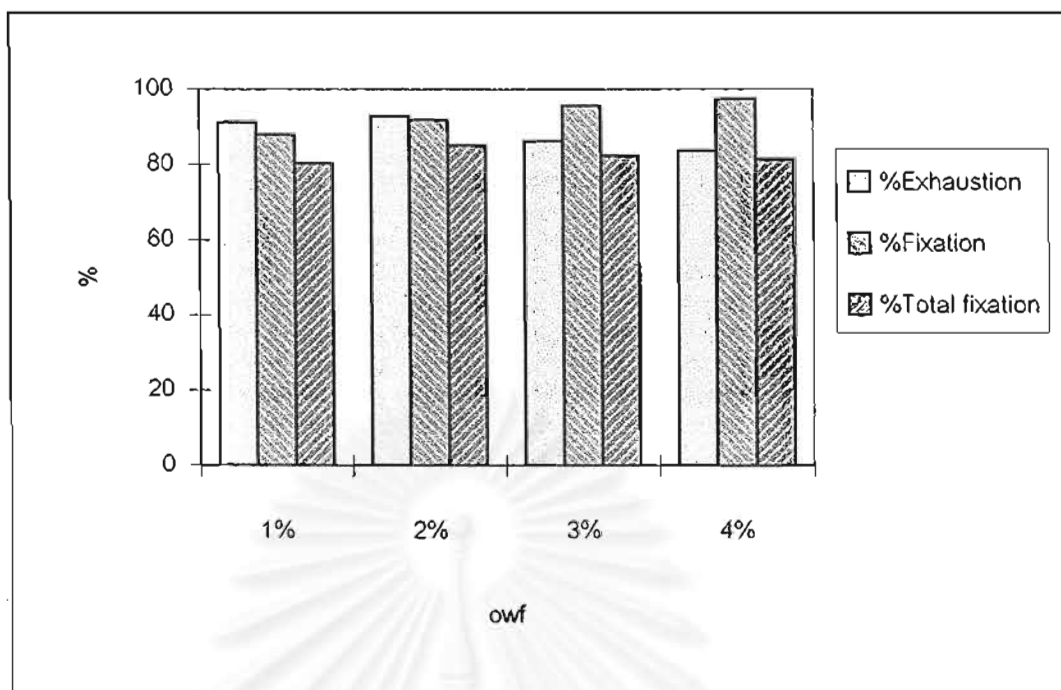
Figure 4.13 Chart of dyeing properties of Cibacron Blue LS-3R high conc. at various dye concentrations.

Table 4.13 Color Yield, % dye exhaustion and the degree of fixation of Drimarene Blue X-BLN at various concentrations of dye.

Dye concentration (% owf)	Color yield (K/S)[a]		% Exhaustion[b]	Fixation	
	Before soaping	After soaping		% F	% F_T
1	11.676	11.325	95.724	96.994	92.847
2	18.773	18.661	93.831	99.403	93.271
3	22.886	22.755	92.685	99.428	92.155
4	25.437	25.018	90.392	98.353	88.903

[a] measured at 640 nm.

[b] measured at 625 nm.
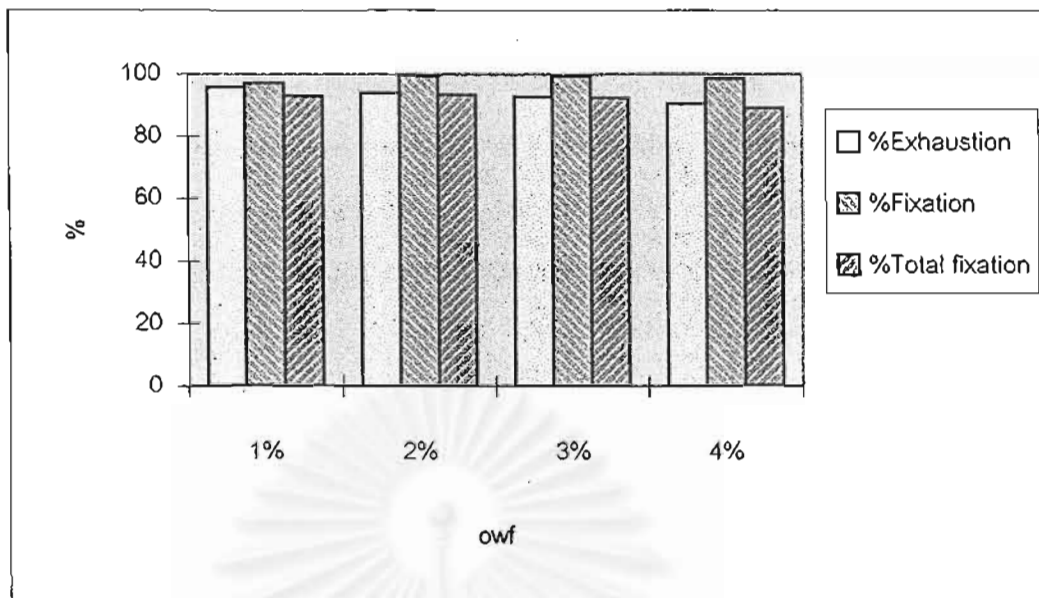
Figure 4.14 Chart of dyeing properties of Drimarene Blue X-BLN at
various dye concentrations.

The percentage of dye exhaustion and the degree of dye fixation obtained from
dyeing of low-salt reactive dye range (Cibacron Blue LS-3R high conc) and high-salt
reactive dye (Drimarene Blue X-BLN) are exceptionally high. However, these good
results would not be achieved without the addition of salts. In addition, both dyes show
the same trend of gradual decrease in % dye exhaustion with an increasing in
concentration of dye. These are due to the negative repulsion effect of fixed dye onto
cellulose at the higher applied depths of shade which retards the further absorption of
dye molecule from the dyebath. The phenomenon did not occur with dyeing of cationic
reactive dye since fixed dyes on cellulose were converted into nonionic dyes, hence
having no influence on the absorption of dye remaining in the dyebath.

4.11 Comparison of dyeing properties between the novel highly substantive dye and commercial reactive dyes.

Comparison between percentage of dye exhaustion, the degree of dye fixation and percentage of overall dye fixation of the synthesized cationic reactive dye and both selected commercial reactive dyes (low– and high–salt application type) are shown in the Figure 4.15, 4.16 and 4.17, respectively.

Figure 4.15 Comparison of % dye exhaustion of synthesized cationic reactive dye with both selected commercial reactive dyes at various dye concentrations.

Figure 4.16 Comparison of % apparent dye fixation(%F) of synthesized cationic reactive

dye with both selected commercial reactive dyes at various dye concentrations.

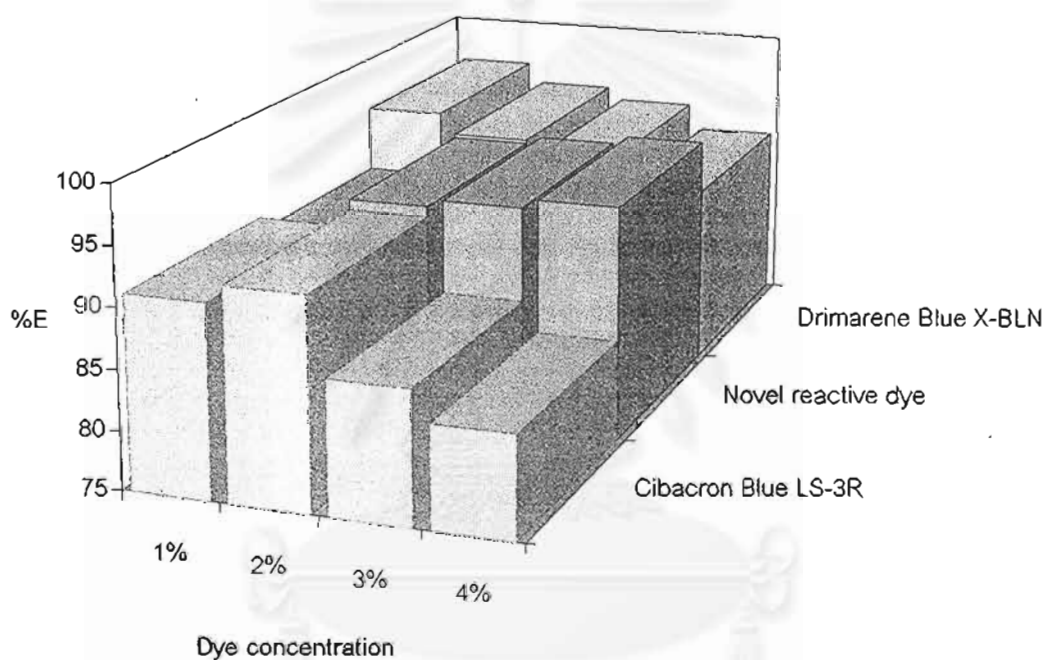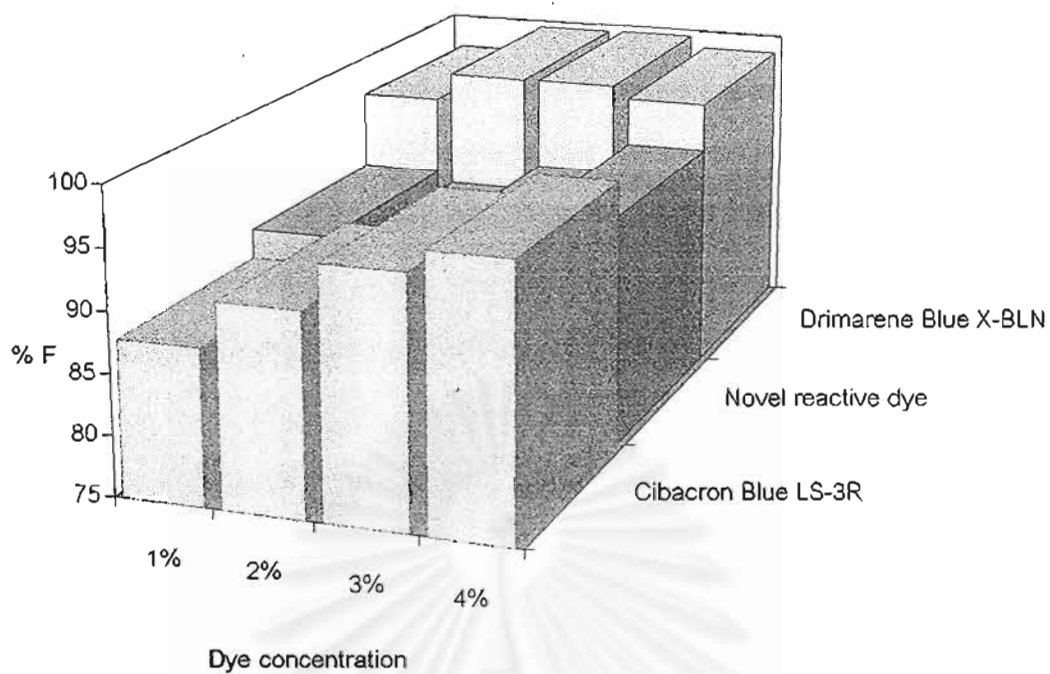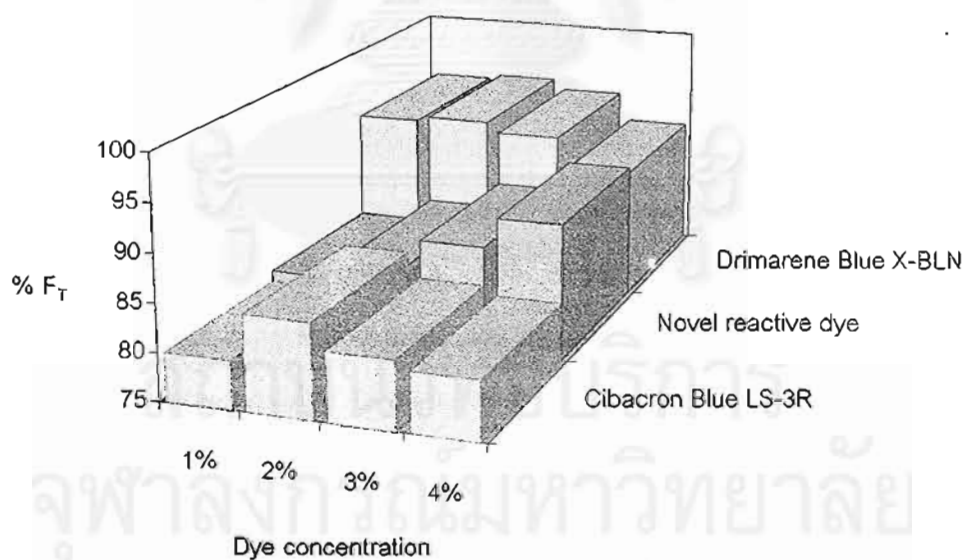Figure 4.17 Comparison of % total dye fixation (%F_T) of synthesized cationic reactive

dye with both selected commercial reactive dyes at various dye concentrations.

Considering cationic reactive dye (see Figure 4.15), the percentage of dye exhaustion increases with an increase in dye concentrations. The reason behind this is that once exhausted dyes being reacted with the fiber under alkaline condition the cationic group of dye could be simultaneously broken off, leading to further increase in dye adsorption as a result of the absence of charge barrier. On the other hand, the percentage of dye exhaustion of both low- and high-salt type reactive dye gradually decreases as the concentration of dye applied increases. It is because the build-up of dye anions in the fiber act as a barrier retarding further adsorption of dye from the solution.

The high substantivity of synthesized cationic reactive dye is visually observed by the comparison of dye concentration before and after dyeing. The photograph of dyebath solution before and after dyeing of synthesized dye, Cibacron Blue LS–3R high conc and Drimarene Blue X-BLN are shown in the Figure 4.18, 4.19 and 4.20, respectively. From the Figure 4.18 the color of dyebath residue after dyeing of synthesized dye at all case of dye concentration (1 – 4 % o.w.f.) is very pale, which is indicative of most dyes in the bath being taken up by the fiber.

By comparison of fixation efficiency, synthesized cationic reactive dye gave the lower % dye fixation than Cibacron Blue LS – 3R high concentration and Drimarene Blue X-BLN. It may be because the nature of cationic reactive dye is susceptible to hydrolysis during alkaline dyeing condition. Another likely contributing factor may be because the application method itself was unsuitable dye to the unsuitable method of dyeing. But the overall dye fixation of this dye gradually increases when the dye concentration increases. This is because the synthesized cationic reactive dye is relatively higher dye exhaustion when compared to both selected commercial reactive dye. Therefore, it may be concluded that the application of the synthesized cationic dye by the absence of electrolyte exhaustion dyeing method offers advantages over conventional reactive dyes in terms of high exhaustion and high fixation, its ease of application as well as its environmental friendliness.

Figure 4.18 The comparison between the color of dyebath solution before (top) and

after (below) dyeing of synthesized cationic reactive dye.
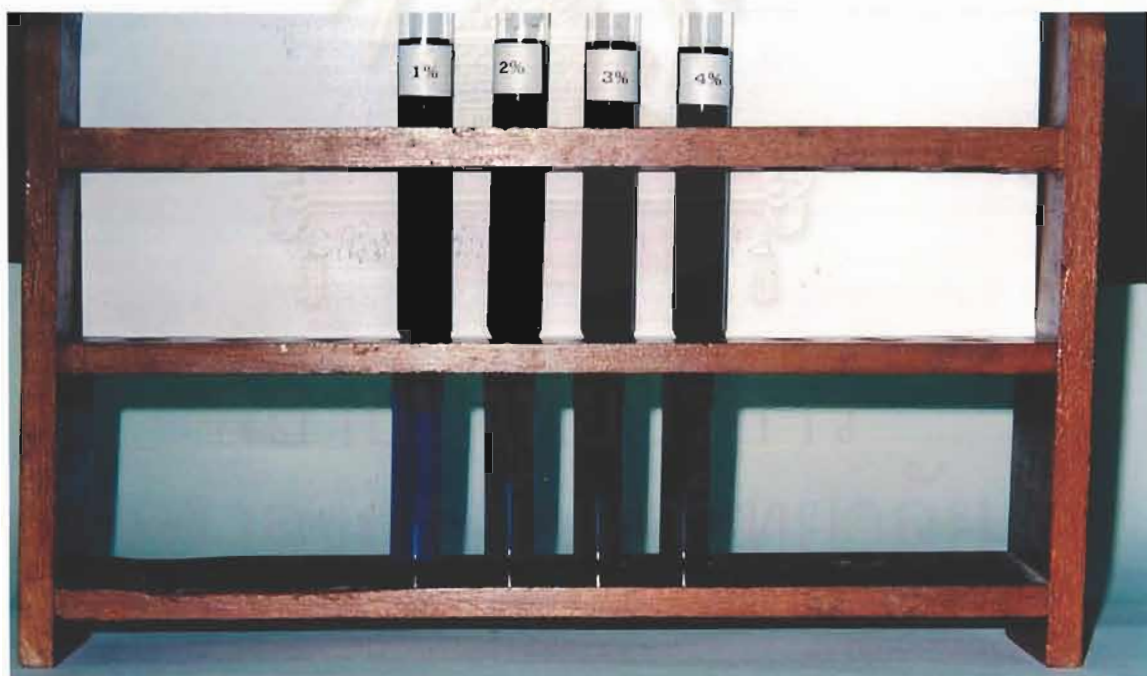
Figure 4.19 The comparison between the color of dyebath solution before (top) and

after (below) dyeing of Cibracron Blue LS-3R high conc.
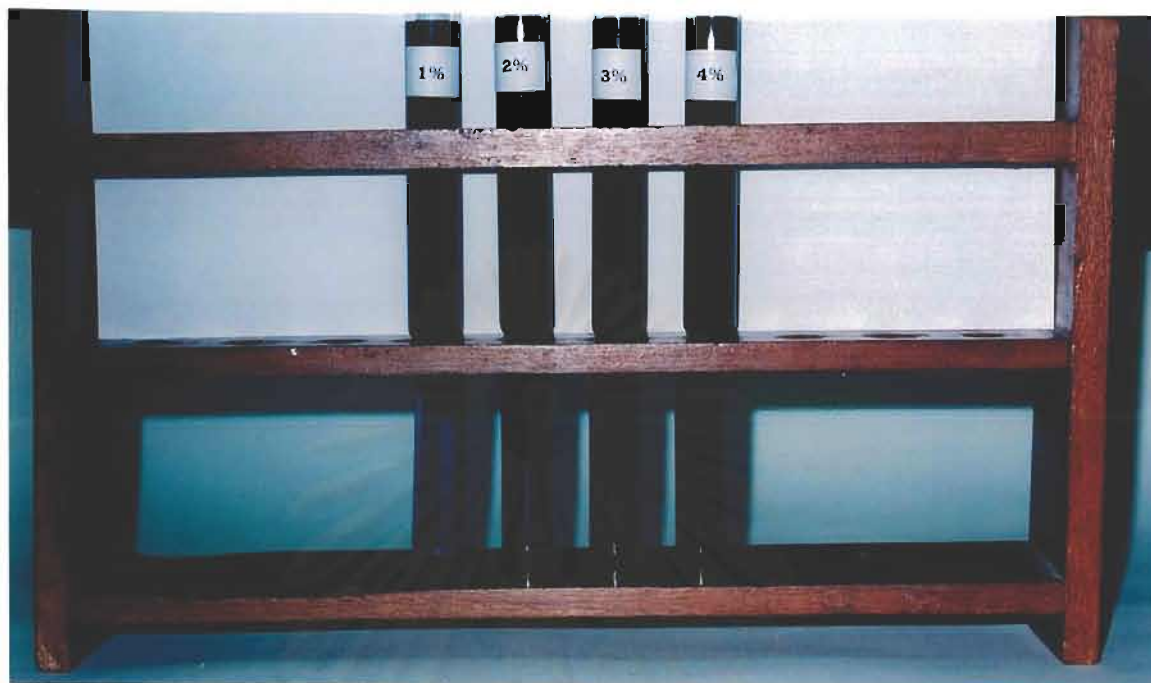
Figure 4.20 The comparison between the color of dyebath solution before (top) and
after (below) dyeing of Drimarene Blue X-BLN.

4.12 Color fastness comparison of novel highly substantive dye with traditional cationic dyes on the cotton fabric.

The synthesized reactive dye and both selected traditional cationic dyes, Astrazon Blue FGLN 200% and Astrazon Blue BG 200%, were dyed by the method described in the section 3.6 and 3.10.1, respectively. The light and washing fastness properties of synthesized cationic reactive dye and two types of traditional cationic dyes, delocalized and localized cationic dye, on the cotton fabrics were evaluated.

4.12.1 Light fastness evaluation.

The dyed fabrics were tested for the resistance of the color to the action of daylight, according to ISO 105-B01 method. The degree of dye fading was assessed using standard blue wool scales.

Color fastness to daylight of the synthesized cationic reactive dye and two types of traditional cationic dyes with different concentrations of dye are shown in Table 4.14

Table 4.14 Light fastness (ISO 105-B01) of synthesized cationic dye and both selected traditional cationic dyes.

Dye Concentration (% owf)	Light fastness		
	Synthesized cationic reactive dye.	Astrazon Blue FGLN 200% (localized cationic dye)	Astrazon Blue BG 200% (delocalized cationic dye)
1	4	2	1
2	4	2 – 3	1
3	5	2 – 3	1
4	5	2 – 3	1 – 2

From the results in Table 4.14, these surprisingly showed that the light fastness of synthesized cationic dye on the cotton fiber was found to be significantly improved, compared with both traditional cationic dyes. In the case of Astrazon Blue FGLN 200%, its chromophore is based on an anthraquinone like cationic reactive dye to eliminate the different effect of type of chromophore on its properties. On the other hand, very low light fastness was recorded when both types of traditional cationic dyes were used in the cellulosic dyeing. This was probably because of the photocatalytic fading effect of positive charge on the traditional cationic dye which seemingly was not the case with

synthesized cationic reactive dye. This is believed that the cationic group of cationic reactive dye was loosely attached to the chromophore and easily removed by alkali at elevate temperature. Another possible reason for good light fastness of synthesized cationic reactive dye may be related to the covalent bonding between this dye and cotton fiber that facilitated the transfer of energy from an excited state of the dye to the fiber, thereby reducing the rate of photodegradation of the dye[43].

4.12.2 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 both the grey scales and determined as the color difference (ΔE) values by using I.C.S. spectrophotometer. Table 4.15 and Table 4.16 demonstrate the washing fastness properties of the synthesized cationic reactive dye and both selected traditional cationic dyes that assessed by using grey scales and I.C.S. spectrophotometer, respectively.

The higher the level number of standard grey scale (level 5) and lower value of ΔE means that there was little change in color of dyed fabric and no dye staining on white adjacent fabric after washing test. In the case of both traditional cationic dyes on the cotton fabric, washing fastness properties were markedly lower than that of synthesized cationic reactive dye which was evidenced by the color change of dyed fabric. However, dye staining of Astrazon Blue BG 200% was more obvious due to degradation of this dye under alkaline testing condition.

Table 4.15 Washing fastness assessment of synthesized cationic reactive dye and both
traditional cationic dyes by using grey scale.

Dye	Conc. of Dye (%owf)	Color change	Color staining[a]					
			Ac	C	N	P	A	W
Synthesized	1	4 – 5	4-5	5	3	5	5	3-4
cationic	2	5	4	4-5	2-3	4-5	5	3
reactive	3	5	4	4-5	2-3	4-5	5	3
dye.	4	4 – 5	4	4-5	2-3	4-5	5	3
Astrazon	1	1	3	4-5	2	4-5	5	4
Blue FGLN	2	1	2-3	4-5	2	4	5	3-4
200%	3	1	2	4-5	1-2	4	5	3
	4	1	2	4-5	1-2	4	5	3
Astrazon	1	1	4-5	4-5	4-5	4-5	5	4-5
Blue BG	2	1	4-5	4-5	4-5	4-5	5	4-5
200%	3	1	4-5	4-5	4-5	4-5	4-5	4-5
	4	1	4-5	4-5	4-5	4-5	4-5	4-5

[a] Ac = Acetate adjacent   P = Polyester adjacent

    C = Cotton adjacent   A = Acrylic adjacent

    N = Nylon6,6 adjacent   W = Wool adjacent

Table 4.16 Washing fastness assessment of synthesized cationic reactive dye and both

traditional cationic dyes by using I.C.S. Macbeth spectrophotometer (as the

color difference (ΔE))

Dye	Conc. of	Color	Color staining[a](ΔE)					
	Dye (%owf)	change	Ac	C	N	P	A	W
Synthesized	1	2.316	2.821	2.588	7.366	1.618	0.776	1.086
cationic	2	1.012	4.372	3.477	8.820	1.806	0.954	5.146
reactive	3	1.535	5.089	3.522	10.073	1.886	1.004	5.578
dye.	4	0.927	5.819	4.006	10.334	2.058	0.974	6.104
Astrazon	1	35.237	8.520	1.483	12.719	1.361	0.480	2.139
Blue FGLN	2	37.968	12.812	2.114	17.472	2.107	1.043	2.934
200%	3	38.949	17.695	2.721	22.102	3.230	1.122	5.826
	4	40.016	18.691	2.778	23.503	3.553	1.229	6.132
Astrazon	1	41.191	3.023	1.175	0.754	0.814	0.560	1.524
Blue BG	2	42.638	2.682	1.302	1.128	1.094	0.601	1.748
200%	3	43.270	2.763	1.430	1.483	1.331	1.017	2.138
	4	43.423	2.617	1.467	1.342	1.207	1.095	2.169

[a]   For key see Table 4.15

4.13 The study on the alkaline treatment of novel highly substantive reactive dye

To confirm that solubilizing cationic (pyridinium) group is erasable from the dye chromophore after complete dyeing process, the solution of synthesized cationic reactive dye and sodium carbonate was heated to the boil for 15 minutes. It was found that the water-soluble dye was converted to water-insoluble dye which then precipitated from the solution. This test visually confirmed that the cleavage of cationic solubilizing group of dye occurred during soaping-off process at high temperature. Comparison of absorbance

of the cationic reactive dye before and after alkaline treatment (see Figure 4.21) shows that nearly similar absorbance curves are observed even though some part of the dye molecule was removed. This means that the cleavage of quaternized group, which attaches indirectly to the dye chromophore via aliphatic alkyl spacer group, brings about little change in shade of resulting dyed fabric.
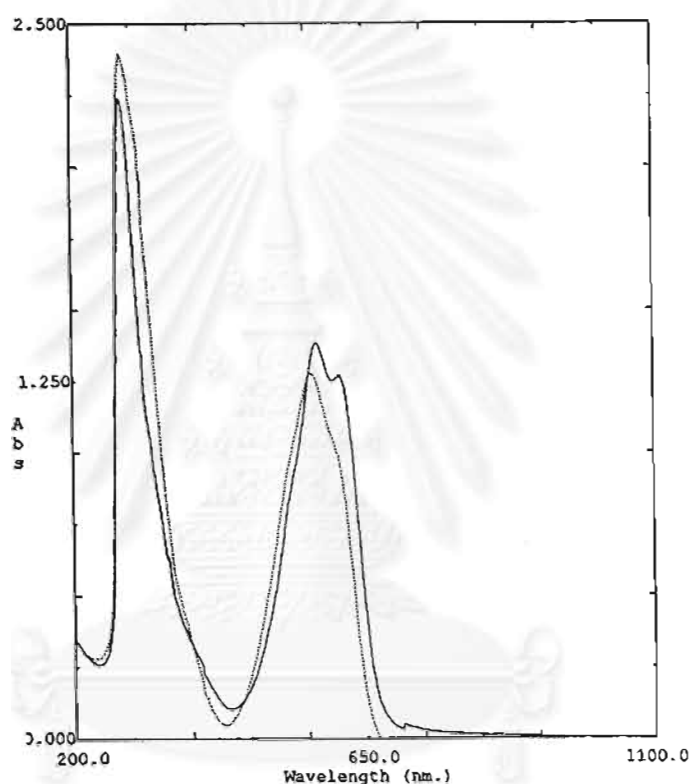

Figure 4.21 Comparison of absorbance curves of synthesized cationic reactive dye before (dot line) and after (solid line) alkaline treatment, using DMF as solvent.

CHAPTER V

Conclusion

The results of the present study show that a model cationic reactive dye can readily be prepared from a purified commercial disperse dye such as C.I. Disperse Violet 8 by modification with cyanuric chloride and followed by N-(2-aminoethyl) pyridiniumchloride hydrochloride. Many analytical techniques including FT-IR, NMR, elemental analysis and TLC techniques were employed to characterize and follow the reactions. The highly substantive reactive dye is different from conventional anionic reactive dye in terms of its solubilizing groups. The use of cationic solubilizing group instead of anionic groups was aimed to facilitate the salt-free dyeing of cotton cellulose with this type of dye. The pyridinium group was selected as a cationic solubilizing group and attached separately to the chromophore via aliphatic alkyl spacer linkage for the reason of its ease of removal without causing a significant color shift.

The results of dyeing showed that very high percentage of dye exhaustion and high fixation value could be achieved when dyeing of this dye in the absence of salt. The high degree of overall dye fixation comparable to the low salt reactive dye available in the market was also achievable. The wash fastness of dyeing was excellent. Advantageously, it was found that this type of dye showed a marked improvement in light fastness over traditional cationic dye on cotton cellulose.

These results revealed that cationic reactive dye could offer not only simpler dyeing recipes than conventional reactive dyes but also possible environmental friendliness. However, at present the cleavage mechanism of pyridinium cationic moiety is not clearly understood.

CHAPTER VI

Recommendation for Future Work

1. To cover the full range of shade, it is interesting to continue further research on the other types of chromophores particularly dyes based on azo chromophore.

2. Effects of dyeing parameters such as temperature, time, amount of alkali, liquor ratio and soaping condition should be studied to find the optimum conditions for the best dyeing results and good color fastness properties.

3. The cleavage mechanism of pyridinium cationic moiety of novel cationic reactive dye should be investigated.

4. The suggested azo chromophores which may be easy to synthesize and characterize are given as follows.
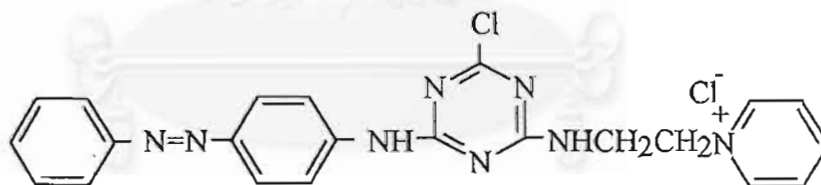
(1) Dye base is mono azo dye (aniline ----> aniline)
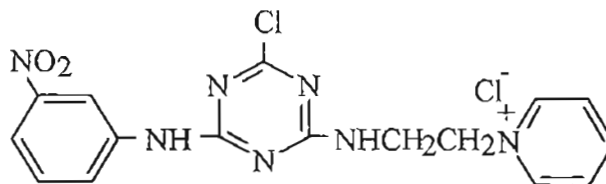
(2) Dye base is 3-nitroaniline

5. Investigation of the dyeability of other types of fibers with novel cationic reactive dye such as wool, silk, nylon and acrylic fibers are quite interesting. In the case of polyamide fiber, the overall charge on the fiber are anion in the neutral condition and the fiber contains amino group which is more reactive than the hydroxyl groups of cellulose. So, the dyeing is possibly carried out under alkali-free condition and not necessary to use associated chemicals. For acrylic fiber, the cationic reactive dye can be used in the dyeing like traditional cationic dye

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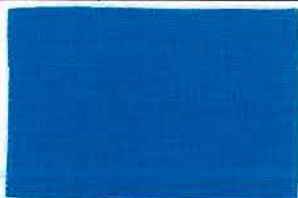
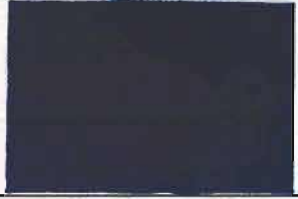24. Peters, R.S. Textile chemistry. Vol.3. The physical chemistry of dyeing. Amsterdam: Elsevier Scientific Publishing, 1975.

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Appendix

Example of dyed cotton fabrics

Dye concentration (% o.w.f.)	Synthesized cationic reactive dye	Cibacron Blue LS-3R high conc (Low salt reactive dye)	Drimarene Blue X-BLN (high salt reactive dye)
1			
2			
3			
4			

BIOGRAPHY

Mr. Pornchai Suntifueangkul was born in Bangkok, Thailand, on September 16, 1973. He received a Bachelor of Engineering degree with a major in Textile Chemistry Engineering from Rajamangala Institute of Technology in 1997. He 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 1997, and completed the programe in September 1999.