CHAPTER I

INTRODUCTION

Reactive dyes are currently widely employed for dyeing cellulose fabrics because of their wide shade range, ease of application and excellent wet fastness properties. The excellent fastness of reactive dyes for cellulose is actually due to the fact that the dye molecules react with the active functional groups of cellulose to form covalent bonds. The substantivity of the reactive dyes is generally quite low, that requires high concentration of salt, sometimes as high as 200% owf or 20:1 liquor ratio at 100 g of dyes per liter of water. The utilization of dye is relatively poor and the dye remained in the waste can be as high as 30-40%.[1] The dyehouse effluents thus contain an unacceptable level of unfixed reactive dyes and salts that can cause environmental hazards. Thus, it is in need of treatment of cellulose fabric to improve the reactive dyes uptake in order to improve the efficiency of dyeing process and reduce the concentration of salt required in the dyeing bath. This thesis relates to a treatment method of the cotton fabric with chitosan for improving its dyeability with reactive dyes contributing to a reduction of the amounts of dyes and salt used in the dyeing process.

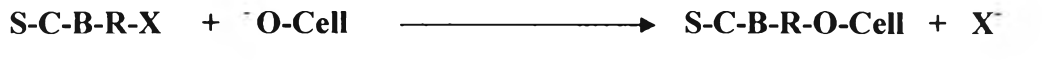
1.1 Reactive dyes [1-2]

Molecular structures of the reactive dyes are generally consisted of five parts briefly described as S-C-B-R-X whereas C = chromophore unit; S = solubilizing group; B = bridging group linking the reactive part of the molecule to the soluble color portion; R = reactive group and X = leaving group. The leaving group can be classified into 2 types: heterocyclic ring such as mono-chloro-triazine and aliphatic chain such as vinyl sulphone. There are generally two main types of reactions involving in the dyeing of the reactive dyes: (1) nucleophilic substitution reaction and (2) nucleophilic addition reaction

(1) Dyes reacting by nucleophilic substitution reaction

A dye of this type has a reactive group of a carbon-nitrogen (heterocyclic) ring with a leaving group attached to the ring carbon atom. For such dye, reaction takes place by the progressive expulsion of the leaving group by either the cellulosate anions from the fiber or by hydroxide ions in the solution, and these anionic

nucleophiles become attached to the same ring carbon atom vacated by the leaving group. The reactive dyes of this type are fiber reactive as sold.



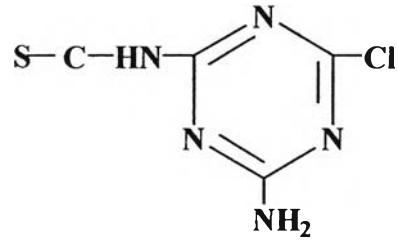
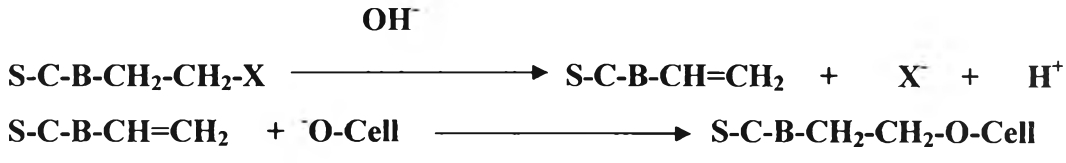


Figure 1.1 Mono-chloro-s-triazine (reactive group).

(2) Dyes reacting by nucleophilic addition reaction

A dye as sold contain a polar substituent group (X) protecting (masking) the reactive vinyl group, and also confer added solubility. Upon the lost of such a substituent may thereby both reveal the hidden vinyl group and lower the dye solubility. The generated vinyl group then reacts with either cellulosate anion or hydroxide ions by nucleophilic addition.



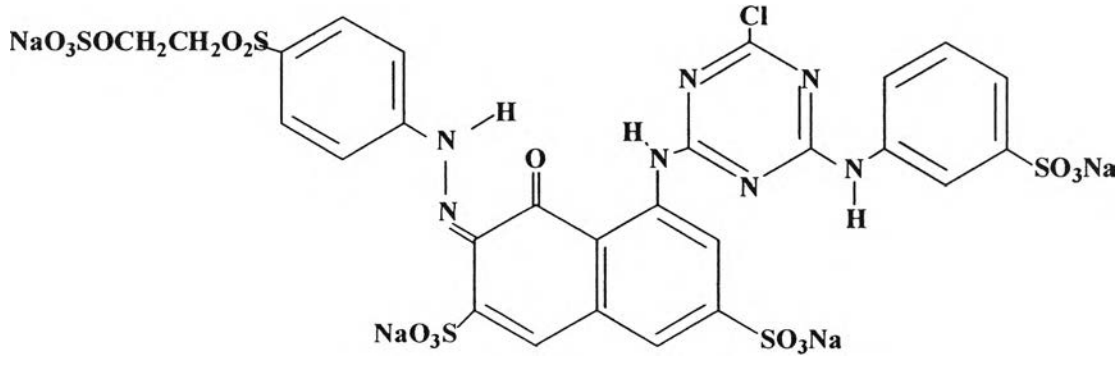


Figure 1.2 β-sulphato ethyl sulphone (reactive group) of C.I. Reactive Red 198.

1.2 Chitosan [3-5]

Chitosan is a deacetylated derivative of chitin, a natural polymer abundantly found in crab and shrimp shell. Structurally, chitosan contains two main functional groups, namely hydroxyl and amino groups **(Figure 1.3)**. Chitosan is generally obtained from the deacetylation of chitin using base hydrolysis **(Figure 1.4)**. The degree of deacetylation (%DD) of commercial chitosan usually ranges from 70% to 95% depending on the temperature and the time used in the hydrolysis. The physicochemical properties of chitosan depend mostly on the degree of deacetylation and the molecular weight. Normally, chitosan is insoluble in water, alkaline and organic solvents but is soluble in aqueous solution of an organic acid when the pH of the solution is lower than 6 where most amino groups of chitosan being protonated to form a polycationic polymer. Acetic and formic acids are two of the most widely used acids for dissolving chitosan. Chitosan has been applied in various fields **(Table 1.1)**.

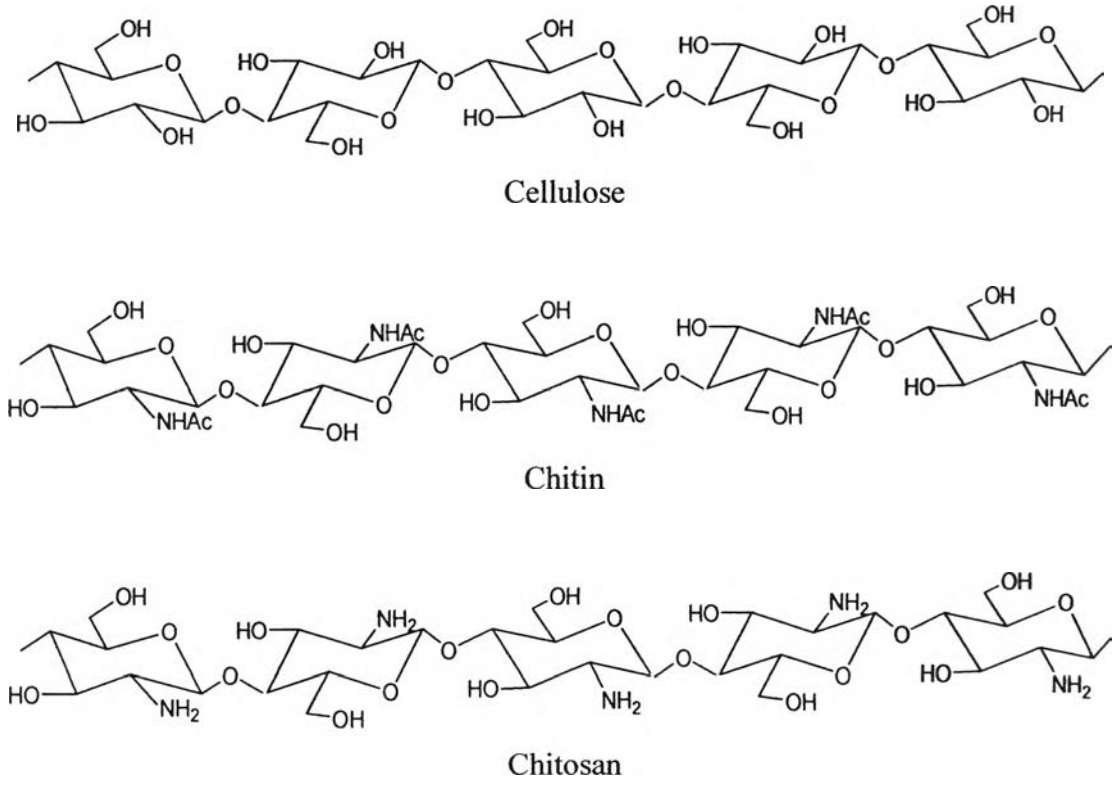


Figure 1.3 The chemical structures of cellulose, chitin and chitosan.

Table 1.1 Applications of chitosan

Application	Example
Water Treatment	Removal of Metal Ions
	Flocculant/Coagulant: Proteins, Dyes, Amino Acids
	Filtration
Pulp and Paper	Surface Treatment
	Photographic Paper
Medical	Blood Cholesterol Control
	Dental/Plaque Inhibition
	Skin Burns/Artificial Skin
	Contact Lens
	Controlled Release of Drugs
Cosmetics	Make-up Powder
	Moisturizers, Bath Lotion
	Face, Hand and Body Creams
Biotechnology	Enzyme Immobilization
	Protien Separation
	Cell Immobilization
	Glucose Electrode
Agriculture	Seed Coating
	Leaf Coating
	Hydroponic/Fertilizer
	Controlled Agrochemical Release
Food	Removal of Dyes, Solids, Acids
	Preservatives
	Animal Feed Additive
Membranes	Reverse Osmosis
	Permeability Control
	Solvent Separation

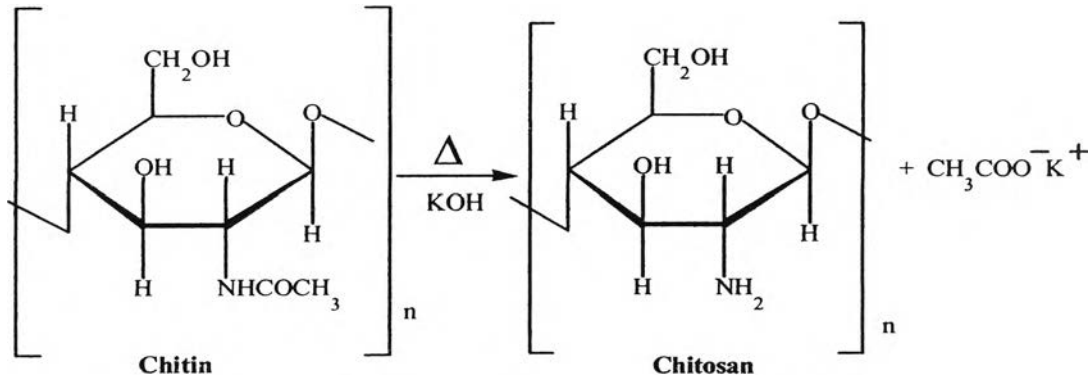


Figure 1.4 Deacetylation of chitin to chitosan.

1.2.1 Molecular weight determination of chitosan by viscometry [6]

Molecular weight is one of the most important structural parameters of polymers. The average molecular weight of a polymer can be determined by various methods such as light scattering, viscometry, gel permeation chromatography (GPC) and mass spectrometry. Among these methods, viscometry is the most economical and convenient method for determination of chitosan.

A polymer chain contains many single bonds around which rotation is possible. If the configurations around successive carbon atoms are independent and unrelated, it will be seen that two parts of the polymer chain more than a few carbon atoms apart are essentially uncorrelated in regard to direction in space. The polymer chain is then "statistically coiled" and resembles a loose tangle of yarn. When the polymer chains behave as statically coils, the molecular weights of the polymers are related to the intrinsic viscosity [η] according to Mark-Houwink equation,

$$[\eta] = KM_v^a$$

where K and a are empirical parameters characteristic for both the polymer itself and the solvent. For chitosan in 0.1 M acetic acid containing 0.2 M NaCl at 25 °C, K= $1.8X10^{-3}$ g/mL and a = 0.93.

The intrinsic viscosity, denoted by [η], is defined as the ratio of the specific viscosity (η_{sp}) to the weight concentration of the polymer (C) at the limit of zero concentration (C→0) experimentally obtained from a Y-intercept in the plot of η_{sp}/C against C;

$$[\eta] = \lim_{C \to 0} (\eta_{sp}/C)$$

The defining equation of specific viscosity η_{sp} can be shown as

$$\eta_{sp} = \eta_r - 1$$

where η_r is the relative viscosity, which defined as the ratio of the viscosity of the solution to the viscosity of the solvent (η/η_o) or the ratio of the falling time of the solution to the falling time of solvent (t/t_o);

$$\eta_r = \eta/\eta_o = t/t_o$$

The molecular weight determination of a polymer by viscometry gives the most accurate result when a polymer whose molecules are all of same molecular weight is said to be monodisperse. Furthermore, the analysis should be done on low concentration solutions in order to decrease interaction between particles of polymer. Viscosity of a dilute polymer solution is usually determined by using an Ubbelohde viscometer tube.

1.2.2 Colloid titration [7-9]

The colloid titration is a way to estimate the net charge density of surfaces, polyelectrolytes, and colloidal materials in an aqueous mixture. What is actually measured is the capacity of the mixture to adsorb a polyelectrolyte of opposite net charge. In the titration of amino groups in chitosan, chitosan was treated with excess acetic acid to produce polycationic polymer. A small amount of indicator (usually toluidine blue-O) is added to the solution of this polycationic polymer. The blue solution is titrated with an anionic polyelectrolyte such as potassium polyvinylsulfate (PVSK) to a purple-pink endpoint **(Figure 1.5)**.

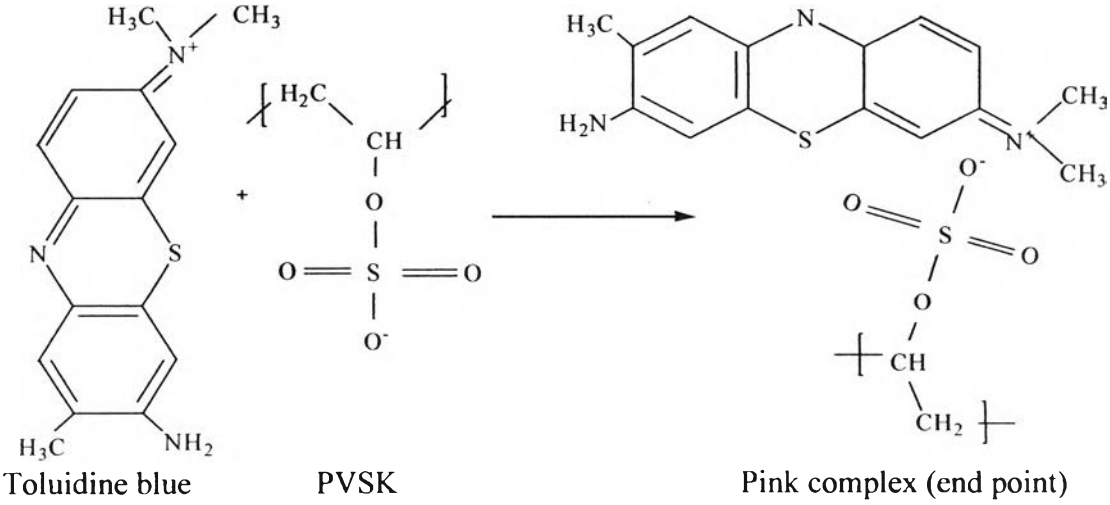


Figure 1.5 Reaction of PVSK and toluidine blue at the end point of colloid titration of chitosan.

1.3 The method for enhancement of reactive dye uptake on cotton fabrics with chitosan and literature reviews

The modification of fabrics with chitosan is interested in this thesis because of chitosan is a natural biopolymer, has a combination of many unique properties such as nontoxic, biodegradability and cationic nature. Amino groups of chitosan increase the attraction between the fibers and anionic dyes. This method enhances dye uptake, reduces the amount of dye used and also contribute to reduce the amount of salt used in dyeing. Various uses of chitosan for textile dyeing and finishing were reviewed in several papers.

Modification of cotton fabrics to improve the reactive dyes uptake can increase the utilization rate of the dyes and reduce the concentration of salt required for dyeing. Considerable attention has focused on the introduction of cationic groups, commonly quaternized amino groups, by means of pre-treatment of the cotton fibers and cotton fabrics to increase the attraction between the fibers and anionic dyes and so enhance the dye-fibers substantivity.[10-12]

As a polycationic polymer, chitosan was investigated to improve the dyeability of cotton fibers with reactive dyes by pad and exhaust processes.[13-17] Chitosan was applied after oxidation by hydrogen peroxide and subsequently stabilized by reducing agent such as sodium cyanoborohydride and sodium borohydride showed improved dyeability with reactive dyes.[18] The modification by oxidizing the cellulose fiber with potassium periodate and subsequent Schiff's base formation is highly specific reaction to convert 1,2-dihydroxyl group to a pair of aldehyde groups without significant side reaction and is widely used in structural analysis of carbohydrates.[19-24] The chitosan content was determined from the nitrogen percentage.

This thesis relates to a method for improving the dyeability of cotton fabrics with reactive dyes by treatment of the fabric prior to dyeing with an aqueous solution of chitosan. The first step, bleached cotton fabrics were first oxidized by potassium periodate to give dialdehyde cellulose which would possess the ability to couple with an amino group of chitosan after reacting with a chitosan solution in acetic acid to provide the formation of a Schiff's base and then stabilizing with sodium borohydride **(Figure 1.6).**

1.3.1 Oxidation

The first step of reaction is the oxidation of the bleached fabrics with potassium periodate under acidic conditions to give aldehyde cellulose which is confirmed by a chemical test with 2,4-dinitrophenylhydrazine (2,4-DNP) **(Figure 1.6).**

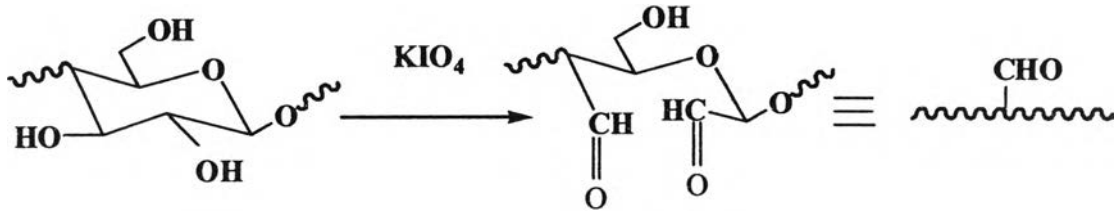


Figure 1.6 Oxidation.

1.3.2 Reductive amination

In the second step, the aldehyde groups in the oxidized fabrics are allowed to react with amino groups of chitosan to form iminic schiff base followed by a reduction with sodium borohydride to generate secondary amine linkage between cellulose and chitosan chains **(Figure 1.7).**

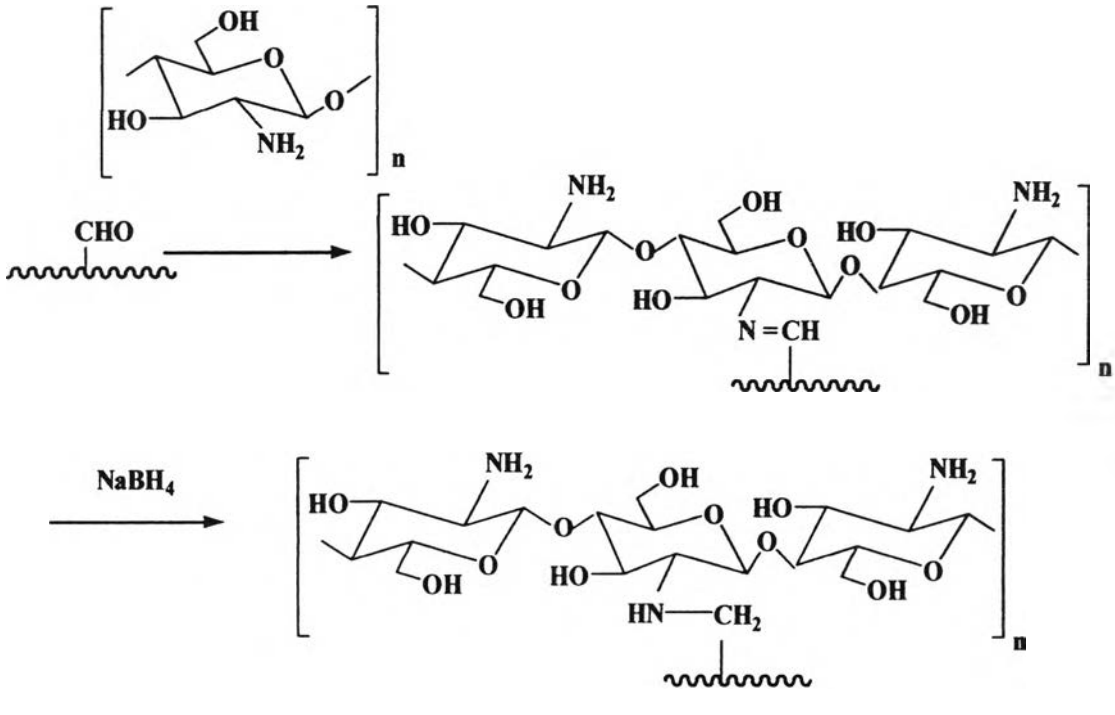
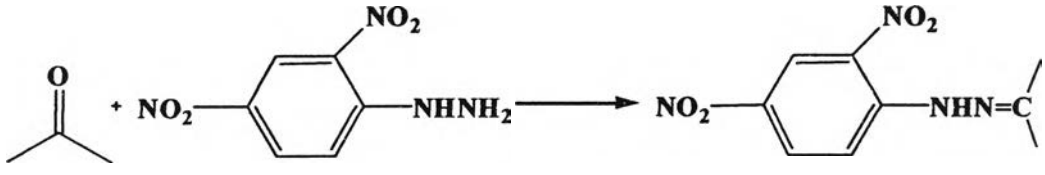


Figure 1.7 Reductive amination.

1.4 Test for carbonyl group with 2,4-dinitrophenylhydrazine [25]

The reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine (2,4-DNP) to form 2,4-dinitrophenylhydrazone probably represents the most studied and most successful of all qualitative tests and derivatizing procedures **(Figure 1.8)**. The color of a 2,4-dinitrophenylhydrazone may give an indication as to the structure of the aldehyde or ketone from which it is derived. The dinitrophenylhydrazones of aldehydes and ketones in which the carbonyl group is not conjugated with another functional group are orange. Conjugation with a carbon-carbon double bond or with a benzene ring shifts the absorption maximum toward red color.



aldehydes and ketones — 2,4-dinitrophenylhydrazine — 2,4-dinitrophenylhydrazone

Figure 1.8 The reaction of carbonyl group with 2,4-dinitrophenylhydrazine (2,4-DNP) to form 2,4-dinitrophenylhydrazone.

1.5 Kjeldahl nitrogen analysis [26]

The Kjeldahl method for nitrogen analysis is composed of three distinct steps: digestion, distillation, and titration.

The purpose of the digestion step is to break the intricate structure and chemical bonds that hold a chemical substance (piece of fabric) down to simple chemicals and ionic structures. Specifically, amino groups of nitrogen are broken down and converted to ammonia. To accomplish this, the sample is placed on a digestion tube with concentrated sulfuric acid (H_2SO_4). Potassium sulfate (K_2SO_4) and a metallic catalyst, usually copper, are then added. The digestion tube is laced into a digestion block where it is heated to the boiling temperature of the mixture. Digestion is usually completed after one hour at 370 °C to 400 °C.

Separation of ammonia from the digestate involves distillation. This is accomplished by raising the pH of the digestate with sodium hydroxide (NaOH). This changes the ammonium (NH_4^+) ion to ammonia (NH_3). It is then possible to distill the

ammonia and collecting the distillate in a suitable trapping medium, usually boric acid solution. The ammonia is bound to the boric acid in the form of ammonium borate.

Determination of the amount of nitrogen on the condensate flask can be accomplished by several methods. The most common is titration of the ammonium borate with a standard hydrochloric acid solution in the presence of mixed indicator, bromocresol green and methyl red.

1.6 Basic on color measurement [27]

People, who believe that the eye is the most important observer of color, argue that judgments of color can be made purely by reference to color cards by visual matching. The clear criticism of this technique of judging color is that everyone's perception of color differs. Besides genetic abnormalities, color vision changes with age due to the build up of yellow macular pigmentation in the eye. For this reason, it is argued that all judgments of color must be based on physical measurements. However, these measurements and their interpretation must be related closely to the responses of visual observers. Therefore, color control is split into two segments: visual and instrumental. In the following pages, color measurement methods will be described.

There are two basic methods for measuring the colors of surfaces. The first is to imitate the analysis made by the eye in terms of responses to three colors, green blue and red known as "tristimulus colorimetry". The second method is to determine reflectance (R) for each wavelength band across the range of the spectrum to which the eye is sensitive, and then to calculate the visual responses by summing products of R and the standard values for distribution of the sensitivity of the three-color responses. The tristimulus method has theoretical advantages where the materials to be measured are fluorescent, but there are serious practical problems in assuming that a tristimulus colorimeter exactly matches human vision, that is, in eliminating color blindness from the instrument. Two commonly used types of color measurement equipment are a colorimeter and a spectrophotometer.

A tristimulus colorimeter has three main components: a source of illumination (usually a lamp functioning at a constant voltage), a combination of filters used to modify the energy distribution of the incident / reflected light and a photoelectric detector that converts the reflected light into an electrical output. Each color has a

fingerprint reflectance pattern in the spectrum. The colorimeter measures color through three wide-band filters corresponding to the spectral sensitivity curves. Measurements made on a tristimulus colorimeter are normally comparative, the instrument being standardized on glass or ceramic standards. To achieve the most accurate measurements it is necessary to use calibrated standards of similar colors to the materials to be measured. This "hitching post" technique enables reasonably accurate tristimulus values to be obtained even when the colorimeter is demonstrably colorblind. Tristimulus colorimeters are most useful for quick comparison of near-matching colors but they are not very accurate. Large differences are evident between the various instrument manufacturers. However, colorimeters are less expensive than spectrophotometers.

To get a precise measurement of color, it is advisable to use a spectrophotometer. A spectrophotometer measures the reflectance for each wavelength, and allows to calculate tristimulus values. The advantage over tristimulus colorimetry is that adequate information is obtained to calculate color values for any illuminant and that metamerism is automatically detected. The negative is that high quality spectrophotometers are very expensive and measurements take longer (although this disadvantage has been greatly reduced by instrument development). In a spectrophotometer, the light is usually split into a spectrum by a prism or a diffraction grating before each wavelength band is selected for measurement. Instruments have also been developed in which narrow bands are selected by interference filters. The spectral resolution of the instrument depends on the narrowness of the bands utilized for each successive measurement. In theory, a spectrophotometer could be set up to compare reflected light directly with incident light, but it is more usual to calibrate against an opal glass standard that has been calibrated by an internationally recognized laboratory. Checks must also be made on the optical zero, e.g. by measurements with a black light trap, because dust or other problems can give rise to stray light in an instrument (which would give false readings). Today's spectrophotometers contain monochromators and photodiodes that measure the reflectance curve of a product's color every 10 nm or less. The analysis generates typically 30 or more data-points, with which a precise color composition can be calculated.

1.6.1 CIELAB method

An organization called CIE (Commission Internationale de l'Eclairage) determined standard values that are used worldwide to measure color. The values used by CIE are called L*, a* and b* and the color measurement method is called CIELAB. L* represents the difference between light (where L*=100) and dark (where L*=0): a* represents the difference between green (-a*) and red (+a*), and b* represents the difference between yellow (+b*) and blue (-b*). Using this system any color corresponds to a place on the graph shown in **Figure 1.9**. Variables of L*, a*, b* or E* are represented as ΔL^*, Δa^*, Δb^* or ΔE^*, where $\Delta E^* = \Delta (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})$. ΔE^* represents the magnitude of the difference in color, but does not indicate the direction of the color difference.

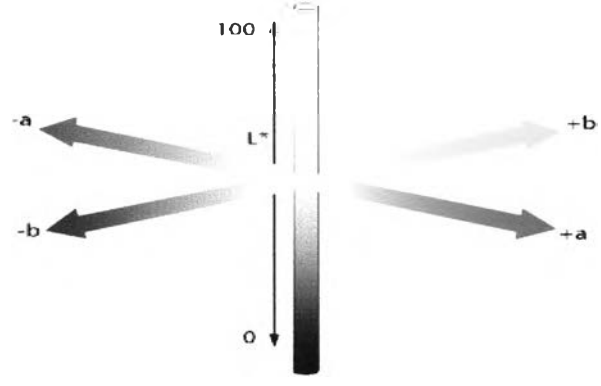


Figure 1.9 CIELAB coordinate system.

1.6.2 Color yield (K/S) [28]

To evaluate the permanent fixation of a dye onto a fabric, the color yield (K/S) is measured. This factor is obtained by reflectance spectroscopy. The color yield (K/S) value is calculated according to the Kubelka-Munk equation:

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

Where K-absorbance, S-scattering and R-reflectance. The reflectance (R) of the dyed samples were measured on a spectrophotometer.

1.7 %Exhaustion measurement [29]

The %exhaustion indicated the qualitative amount of dyes absorbed by textile fiber. This value was obtained by the measurement of absorbance of dye solution at the beginning and the end of dyeing process. The %exhaustion (%E) is calculated according to the following equation:

$$\%E = 100(A_0-A)/ A_0$$

where A_0 is the absorbance before dyeing at λ_{max} of the dye used and A is the absorbance after dyeing.

1.8 Colorfastness

Colorfastness is the ability of dye to retain its color after exposure to certain conditions or treatments. To the ordinary consumer of dyed goods, fastness to washing, water, perspiration, rubbing, sun (light) are the properties most desired.

The term fastness is a relative one; a dye may be reasonably fast to washing and only moderately fast to light. The amount of fading or staining is the gauge of the ability of the color to meet standard requirements and specifications on yarn or fabric.

Colorfastness to washing is the resistance in color loss and abrasive action resulting from solution and/or various action of laundering with or without chlorine.

Colorfastness to water is the resistance to water of dyed, printed, colored textile, yarns and fabrics of all kinds

Colorfastness to perspiration is the fastness of colored textile to the effects of human's sweat.

Colorfastness to rubbing is the resistance to in color loss and abrasive action resulting from rubbing with a dry rubbing cloth and with a wet rubbing cloth.

The factors that effected the fastness to washing are solubility of dyes, rate of movement of dyes outward from the fiber, chemically bond to the fiber

Colorfastness to light is a term applied to dyed fabric that will not fade under normal exposure to sunlight or under standard tests. Molecules of dye (organic coloring matter) absorb energy in form of light that cause the dye's molecule is not stable and become to the excited state. In this condition, dye may react with oxygen or fiber and decompose. Effect of excitation of dye calls "photochemical reaction".