

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 The chemical structure of fiber

Textile fibers are composed of molecules that are very long and flexible, as are the fibers themselves. These molecules are polymeric, meaning they are composed of a large number of small repeating units. The units may be either all the same or of several types, occurring at intervals along the length of the molecule. Such molecules are usually referred to as molecular chains. The principal repeating units of the more important fiber molecules are as shown in Figure 2.1 and Figure 2.2 [3].

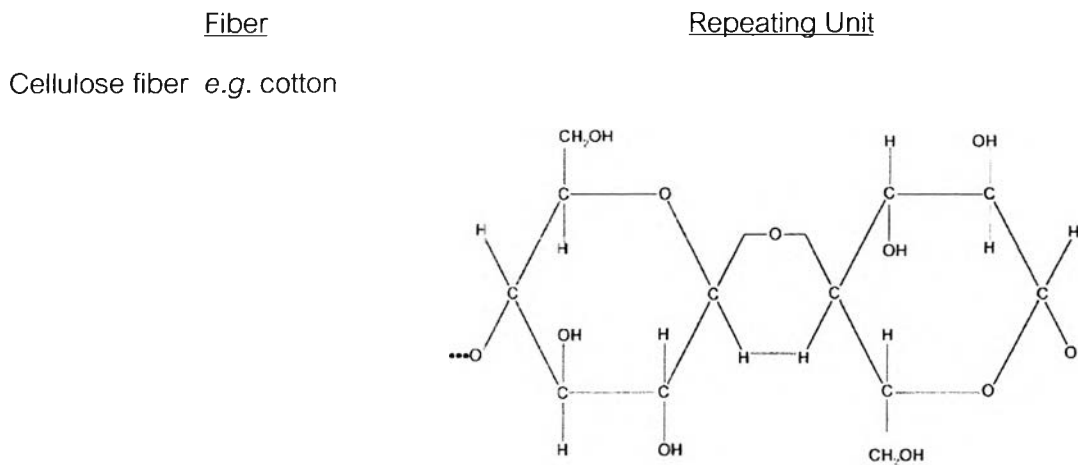


Figure 2.1 Repeating unit of cellulose fiber.

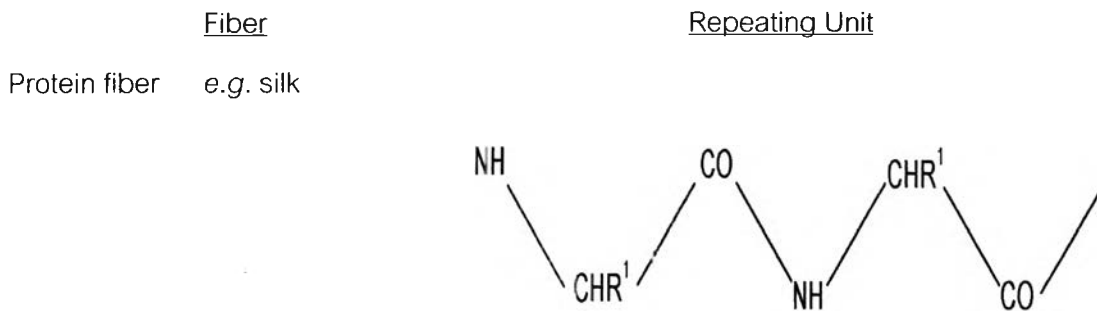


Figure 2.2 Repeating unit of protein fiber.

From the Figure 2.2, the protein fibers R^1 represent side-chains, of which about 20 different kinds are present of these a number terminate in amino ($-NH_2$) or carboxyl ($-COOH$) groups, which are important because of their influence on dyeing. One of the side-chains in silk or wool is the cystine group ($-CH_2-S-SCH_2-$), which, can form a link between parallel molecular chains. This phenomenon helps improving the rigidity and colour permanence of the fiber.

Fiber has interesting property where the molecular chains are not folded as in wool, but are almost fully extended and packed closely together. As with all fibers, there are some amorphous areas between the crystalline areas. For example, water is strongly attracted by portions of the molecular chains of most fibers, and so quickly enters the amorphous regions, forcing them apart so that the whole fiber structure becomes interpenetrated by minute pores and channels. These pores allow substance dissolved in the water, to enter the fiber. The fiber in this water-swollen state is something in the nature of a sponge. Perhaps a better analogy would be to compare it with a loofah, which is a highly porous network of longitudinal strands. The relative size and shape of pores and strands being similar to those of the pores and molecular chains of the textiles fiber, but on a vastly different scale.

2.2 The physical structure of fiber

2.2.1 Cotton fiber

Raw cotton is creamy white in colour. The fiber is a single-cell, which during growth, pushes out of the seed as a hollow cylindrical tube over one thousand times as long as it is thick. The quality of cotton depends on the number of convolutions, and the brightness of the fiber [9]. Following is cotton characteristics;

(i) Length: Cotton fibers range from $\frac{1}{2}$ to 2 inch in length, depending on the variety.

(ii) Convolutions: Convolutions or ribbonlike twists characterize the cotton fibers as seen in Figure 2.3.

(iii) Width: Cotton fibers vary from 16-20 microns in diameter. The cross-sectional shape varies with the maturity of the fiber. Immature fibers tend to be U-shaped and the cell wall is thinner; mature fibers are more nearly circular, with a very small central canal as seen in Figure 2.4.

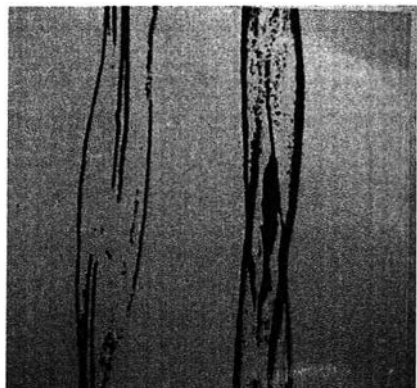


Figure 2.3 Photomicrograph of cotton fiber [10]. Longitudinal view 500x



Figure 2.4 Photomicrograph of cotton fiber [10]. Cross-section 500x

2.2.2 Silk fiber

Silk is a natural continuous filament fiber [11]. It is a solid fiber, smooth but irregular in diameter along its shaft. The filaments are triangular in cross-section with rounded corners as seen in Figure 2.5. Figure 2.6 shows its characteristic of longitudinal striations.



Figure 2.5 Photomicrograph of silk fiber [10]. Longitudinal view 500x

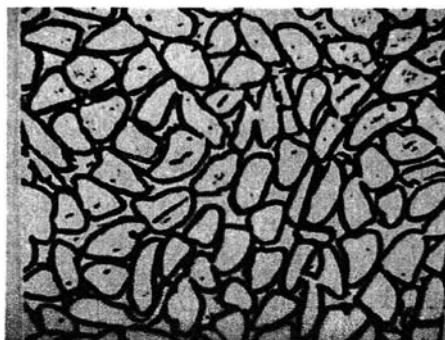


Figure 2.6 Photomicrograph of silk fiber [10]. Cross-section 500x

2.3 The chemistry of dyeing

2.3.1 The internal surface of fibers and its importance

The natural fibers; such as the cellulosic and protein fibers, have exceedingly large internal surfaces. These are the walls of the channels between the bundles of long-chained molecules composing the fiber. The number of such channels immense of the order of ten million in the cross-section of cotton or silk fiber, and the total surface of their walls is of the order of $100 \text{ m}^2/\text{g}$, or five acres per lb. [3].

When the fiber is wetted, water rapidly penetrates and swells a large proportion of these channels. Dyes in solution are then able to diffuse into the channels or pores.

Dyes are surface-active substances, when they are dissolved in water their molecules tend to concentrate more closely together at a surface than in the body of the solution. The surface or interface can be between the solution and either air or a fiber. The first action in any dyeing operation is therefore the concentration of dye molecules at as much of the internal surface of the fiber as they can reach.

2.3.2 Chemical forces responsible for dyeing

Broadly four main chemical effects are subsequently responsible for the substantivity of the dye for the fabric [1]. There are hydrogen bonds, non-polar or Van der Waals' forces, electrostatic or ionic forces, and covalent bonds. The first three of these seldom act in isolation. However, depending on the dye and the fiber and the dyeing conditions, one of these physical forces of interaction will predominate. Additionally the so-called "hydrophobic bond" interaction may be involved [3]. Following are details about these bonds or forces.

2.3.2.1 The hydrogen bonds

This is the "secondary valency". For example, a hydrogen atom in a hydroxy group can form a weak association with another atom. The most familiar example of this effect is seen in the properties of water, which has much higher melting

and boiling points than would otherwise be expected, because its molecules are held together by hydrogen bonds as seen in Figure 2.7. Most fibers and dyes contain groups that can take part in this form of combination. There is evidence for the importance of hydrogen bonds in dyeing some man-made fibers, e.g. cellulose acetates and possibly cellulosic and protein fibers [12]

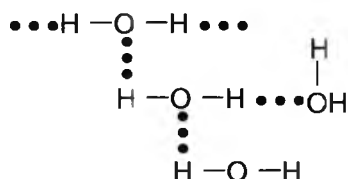


Figure 2.7 Hydrogen bonding in water.

2.3.2.2 Van der Waals' forces or Non-polar forces

These are a manifestation of the universal tendency of atoms and molecules to attract on another, and the Van der Waals' forces are usually divided into two types:

- (a) Polarisation forces.
- (b) Dispersion or London forces.

Both dyes and fibers are polar molecules and as such can attract each other by their permanent dipoles or as a result of induced dipoles. Dye and fiber molecules must therefore approach each other very closely before mutual attraction exists, and lower-range repulsion forces may have to be overcome before this can happen.

2.3.2.3 Ionic forces

A third form of physical attraction between a dye and a fiber may be due to a difference of charge between them. In water all textile fibers become negatively charged and, since most water-soluble dyes are anionic, adsorption does not occur readily. It is then necessary to reduce or even reverse the charge on the fiber before the dye anion can approach closely enough for attractive forces to become effective.

2.3.2.4 Covalent bonds

Reactive dyes are attached to the fiber by a covalent bond, which is much stronger than the previously mentioned forces and difficult to break down.

2.4 Principle of textile dyeing with natural dyes

There are three methods which are dyeing for direct dyes, mordant dyes and vat dyes [13]. Following are details of these dyeing phenomenon.

2.4.1 Direct dyes

As the name suggests, direct dyes colour the fiber without a mordant or vatting. A direct dye forms a positive or negative charge which is electrostatically attracted to a negative or positive charge on the fiber. For example, the direct dye picric acid is a strong acid and interacts with the basic side chains in wool to form a salt linkage between it self and the fiber. The picric acid gives up its proton to some basic group on the fiber and becomes an anion, which strongly binds to a cationic group on the fiber by ionic interaction. This interaction is illustrated below in Figure 2.8

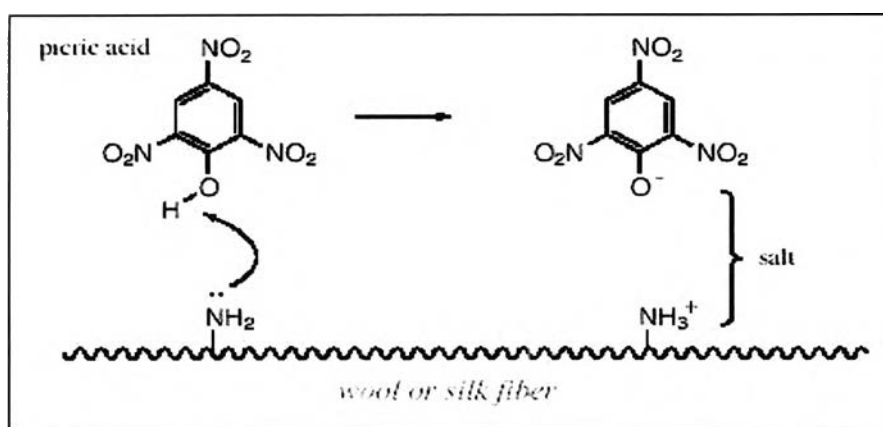


Figure 2.8 The direct dye picric acid and interacts with the basic side chains in wool or silk fiber

2.4.2 Mordant dyes

Certain dyes form chelated complexes with heavy metal such as copper, chromium, tin, iron and aluminum. Cotton, wool, and silk can also coordinate with these metals. To dye a fabric with a mordant dye, the fabric is first treated with a mordant, or the salt of a heavy metal. The fabric is then treated with the dye, the dye complexes with the mordant, and is thus linked to the fabric. Different metals (mordants) can lead to different colours with the same dye. Alizarin (an anthraquinone dye) in a typical mordant dye, show below in Figure 2.9 in a chelated complex with cotton using chromium as the mordant.

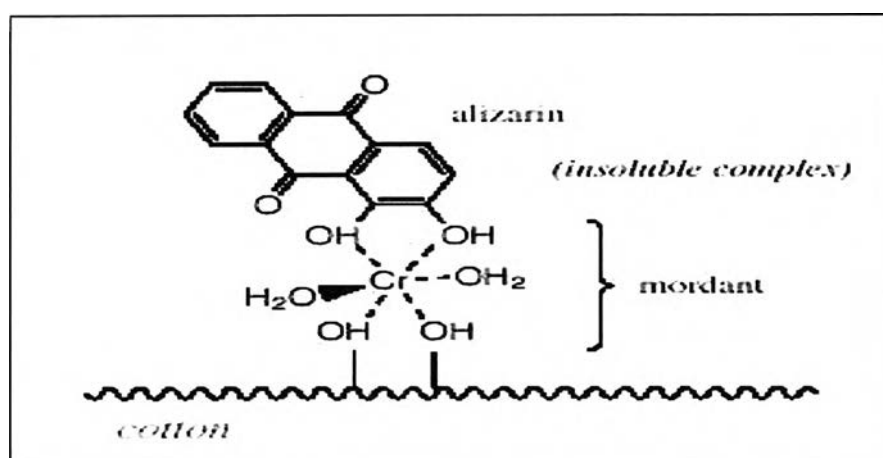


Figure 2.9 A chelated complex with cotton using chromium as the mordant

With some mordant dyes, especially the triphenylmethane dyes (e.g., malachite green and crystal violet, cationic dyes) tannic acid is used as the mordant. Tannic acid is actually a mixture of tannin structures and is isolated from the bark of different plants.

2.4.3 Vat dyes

Vat dyes can be used for all fibers, both natural and synthetic. Most vat dyes are soluble (and colourless) in water in their reduced form, but become insoluble and

coloured when oxidized. They are introduced to fabric in their soluble form and then oxidized or "developed" to precipitate both on the inside and out side of the fabric. In the vat process for indigo, the fabric is impregnated with the soluble leuco indigo in a hot dye bath or vat. Then, the fabric is removed from the vat, and the leuco indigo is allowed to be oxidized by air to the insoluble indigo. The indigo precipitates both inside and on the surface of the fabric. Since the indigo is insoluble in aqueous solution, the dye is fast. The reaction involved is illustrated in figure 2.10

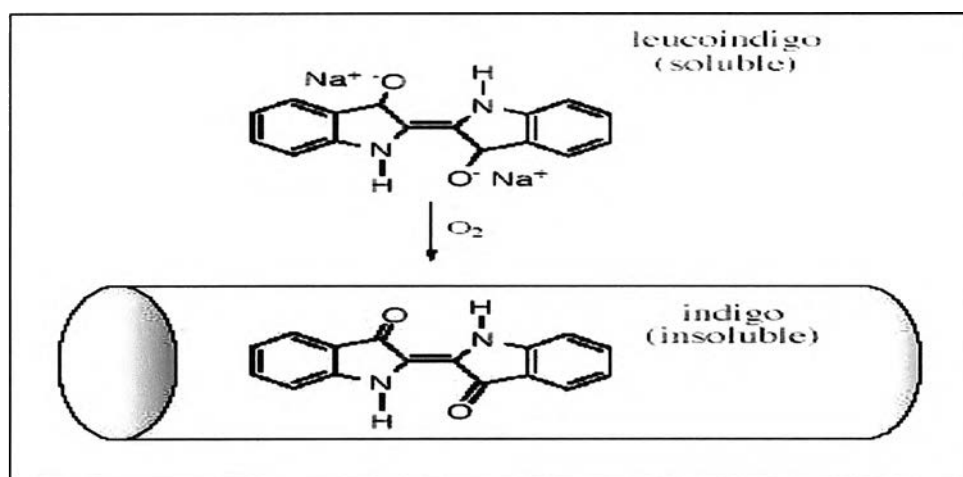


Figure 2.10 The reaction of vat dye.

2.5 Extraction theory

Extraction is the physical process by which a compound (or mixture of compounds) is transferred from one phase into another. Extraction important matter from plants may be done in many ways depending on the extracted matter. The property of the matter in case of heat resistance and solvent type depends on the way of extraction. Each way will result in difference advantages and limitaticns. Different ways of extraction is described below [14].

2.5.1 Maceration

Maceration is an extracting process to extract important matter from plant by fermenting plant with solvent in closed container such as Erlenmeyer flask or blow. Fermenting time is seven days, during these time try to shake or stir often. When the time ups, pour the extracted matter from marc as much as possible. Collect the extracted matter and distil them. In case extracting of all the matter is required, repeat the process may times. The this advantage of this extracting technique is using a lot of solvent.

2.5.2 Percolation

Percolation is a continuously extracting process. The process will be done by "percolation machine" Fermenting plant with solvent. Leave it for an hour to let it extremely swell and then contain plant dust layer by layer into the percolation. Pour solvent into the container until above the plant dust approximately 0.5 cm. And leave it 24 hours. After that separate the extracted matter from marc. Beware drying plant keep pouring solvent above the plant. Keep the extracted matter until the process is completed. Try to take the extracted matter from marc as much as possible and then distil them from marc.

2.5.3 Soxhlet extractor

Soxhlet extractor is continuous extracting process using a low boiling solvent. The extraction is evaporation solvent in flask and then distil it in thimble which containing plant dust. When solvent extracting chamber is as high as appropriate level, siphon will be happen. The flask is heated by heating metal, so the solvent evaporates and the extracting matter is leave in flask. When the stem solvent contact condenser it will be distilled and become a new extraction. The process will be repeated until the extraction is completed. The extraction by heat may cause some chemical decomposition.

2.5.4 Liquid-Liquid extractor

Liquid-Liquid extractor is extraction liquid solution into the other solvent, which is not able to mix with the first solvent. It could be devised into two types

2.5.4.1 Extraction lighter

Extraction lighter is solvent which use lighter solvent to be solution

2.5.4.2 Raffinate lighter.

Raffinate lighter is solvent which use heavier extractor than solvent using to melt matter.

2.6 Colourimetric Fundamentals [15]

The CIE 1976 $L^*a^*b^*$ colour space is the most widely used method for measuring and ordering object colour for example the colour of textile, inks, paints, plastics, paper, printed materials and other objects. It is sometime referenced to as the CIELAB colour difference metric

2.6.1 CIELAB colour system

The CIELAB colour space can be visualized as a three dimensional space, where every colour can be uniquely located. The location of any colour in the space is determined by its colour coordinates; L^* (the lightness coordinate), a^* (the red / green coordinate, with $+a^*$ indicating red, and $-a^*$ indicating green) and b^* (the yellow/ blue coordinate, with $+b^*$ indicating yellow, and $-b^*$ indicating blue). The L^* , a^* , b^* colour coordinates are calculated as follows:

- 1) The object is measured by a spectrophotometer.
- 2) A light source (illuminant) is selected.

- 3) An observer (2° or 10°) is selected
- 4) Tristimulus values(X, Y, Z) are computed from the light –object-observer data.
- 5) L^* , a^* , and b^* are transformed (computed) from the X, Y, Z data, using the CIE 1976 equations.

The L^* , a^* , b^* coordinate axis define the three dimensional CIE colour space in Figure 2.11 [16].

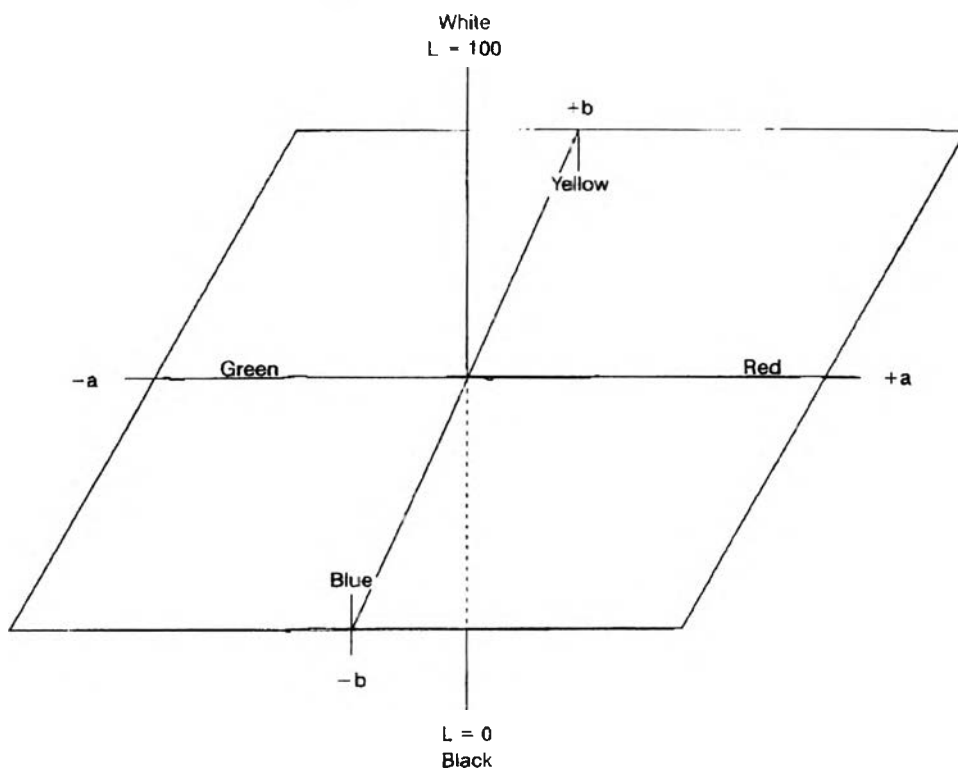


Figure 2.11 CIE $L^* a^* b^*$ color space showing relationships between L , a , and b scales.

2.7 Kubelka – Munk equation (K/S) [2], [3]

Since the numerical range of K/S value is quite extensive for a small range of very low reflection value, K/S is thus, a very sensitive measure of the effect of dyeing. The relation between the reflectance (R) and the concentration of dye (C) for a thick opaque pattern is given by the Kubelka – Munk equation as follows

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

where

K	=	Absorption coefficient
S	=	Scattering coefficient
R	=	Decimal fraction of the reflection of the dye fabric

2.8 Literature Reviews

Carman [1974] studied dyeing with eucalyptus leaves and bark on wool fiber. The dye colours from the eucalyptus are very beautiful. Ranging from red, through various shade of orange to yellow and olive-green up to mordants substance. The dye colours from eucalyptus had good light fastness and the dye colours were also found to have excellent washing fastness [17].

Moeyes [1993] studied dyeing with eucalyptus leaves on silk and cotton fibers in Thailand. It yielded a yellow-brown colour on silk fiber and pale tan colour on cotton fiber. Colours obtained were good fast to the usual washing of silk fiber and excellent fast to light [18].

John and Margaret [1994] studied dyeing with eucalyptus on wool fiber. The colours produced vary considerably according to the seasons. In mid-summer, leaves five soft oranges and browns; unmordanted wool and alum give very similar oranges

with pinkish tones, chrome a pale yellow-orange and copper pinkish-brown. In late autumn, much of the red in the dye disappears and the colours are much more in the yellow range. The pigments are flavonols and are very light-fast. The flavone *hemiphloin*, rhamnosides and tannin are also present [19].

Anansawek, *et al.* [2000] studied and analyzed colour separation in Eucalyptus bark. The study and analysis found that there was tannin 4.0 – 4.8% and 12.44% of phenolic compound in the dried eucalyptus bark. And after dyeing on cotton fiber with those dried eucalyptus bark found that the cotton fiber would be come red-brownish to dark according to used mordant. Moreover it was found that the appropriate used mordant should be copper and ferrous which give a permanent red brown and black colour fastness to light in a satisfactory level [20].

Suree, *et al.* [2000] studied to find out the kind of tannin in Eucalyptus leaves. The research found that the tannin is a kind of disintegrate tannin. The disintegrate tannin will melt to be polyester of phenolic acid and well water soluble sugar melt in weak acid and become phenolic and sugar compound and will be bluish after reaction with ferric chloride [14].