CHAPTER 2

LITERATURE REVIEW

2.1 NATURAL DYEING – A HISTORY

The ability of natural dyes to color textiles has been known since ancient times even though the origin of natural dyes was not to be found (Paul et al 1996). Around 2600 BC, earliest written record of the use of natural dyestuffs in China was found (Chavan 1995).

In more modern times, Alexander the Great mentions having found purple robes dating to 541BC in the royal treasury when he conquered Susa, the Persian capital. Kermes (from the Kermes insect) is identified in the bible book of Exodus, where references are made to scarlet colored linen (Verma et al 1998) and around 550 BC, Romans found painted people "picti" in Gaul dyeing themselves with woad, which is the same chemical content of color as indigo (Agarwal 1992).

By third century papyrus found in a grave contains the oldest dye recipe known, for imitation purple - called Stockholm Papyrus (Agarwal and Garg 1992). It is a Greek work (Garg 1991). By the fourth century AD, dyes such as woad, madder, weld and indigo and a dark reddish-purple were known (Vednere et al 1998).

During the late fourth Century Emperor Theodosium of Byzantium period found certain shades of purple and it was made from a mollusk by
eighth century and clothing made from it was so expensive only the royal family could afford it (Agarwal et al 1993).

A small gastropod mollusk found in all seas or from a crustacean called a Trumpet Shell or Purple Fish, found near Tyre on the Mediterranean coast (Singh et al 1993). Their body secreted a deep purple fluid which was harvested by cracking the shell and digging out a vein located near the shellfish head with a small pointed utensil (Katti et al 1996). The mucus-like contents of the veins were then mixed together and spread on silk. The fact is this dye was worth more than its weight in gold. This expensive dye was also mentioned in the bible, in Acts, where Lydia is a seller of purple (Gupta and Gulrajani 1993).

By twelfth century, Rucellia of Florence, rediscovered the ancient art of making purple dye from lichens sent from Asia Minor (Singh et al 1996). In thirteenth century brazilwood was first mentioned as a dye, source from East Indies and India. The country of Brazil was named for the wood found.

By the fifteenth century, dyes from insects, such as cochineal and Kermes, were becoming more common (Gogoi 1998). By the seventeenth century, dyeing cloth "in the wood" was introduced in England: logwood, fustic, etc (Agarwal 1997).

In the eighteenth century a method of bleaching linen with kelp was introduced in Scotland, a Swedish chemist discovered chlorine destroys vegetable colors and the French began to recommend chlorine water for commercial bleaching. Indigo began to be grown in England, and Cudbear, a natural dye prepared from a variety of lichens, is patented (Gulrajani et al 1992). Another natural dye, Quercitron, from the inner bark of the North American oak, is patented in 1775 (Gulrajani et al 1993).
By the 1800's, Prussian blue and Sulphuric acid are available commercially. Prussian blue was formed from prussite of potash and iron salt, making it one of the earliest known chemical dyes (Gulrajani et al 1992).

In 1856, William Henry Perkin, while experimenting with coal tar in hopes of finding an artificial quinine as a cure for malaria, discovered the first synthetic dye stuff which he called "Mauve". The color quickly became a favorite of the royal family, and a new industry was begun (Gulrajani et al 1992). Later on after synthetic dyes came into vogue and were commercialized, still studies and researches were carried on for developing natural dyes (Gulrajani et al 1992).

2.2 NATURAL FIBRES

Natural fibers include those produced by plants, animals, and geological processes. They are biodegradable over time. They can be classified according their origin (Gupta et al 1998).

Vegetable fibers are generally based on arrangements of cellulose, often with lignin: examples include cotton, hemp, jute, flax, ramie, and sisal. Plant fibers are employed in the manufacture of paper and textile (cloth), and dietary fiber is an important component of human nutrition (Kumar et al 1998).

Wood fiber, distinguished from vegetable fiber, is from tree sources (Saxena et al 1997). Forms include groundwood, thermo mechanical pulp (TMP) and bleached or unbleached kraft or sulfite pulps. Kraft and sulfite, also called sulphite, refer to the type of pulping process used to remove the lignin bonding the original wood structure, thus freeing the fibers for use in paper and engineered wood products such as fibreboard (Padhyay et al 1990).
Animal fibers consist largely of particular proteins. Instances are spider silk, sinew, catgut, wool and hair such as cashmere, mohair and angora, fur such as sheepskin, rabbit, mink, fox, beaver etc (Gupta 1990).

Mineral fibers comprise asbestos. Asbestos is the only naturally occurring long mineral fiber. Short, fiber-like minerals include wollastonite, attapulgite and halloysite (Srivatsava 1992).

2.2.1 Cotton

Asiatic cottons first grew wild in East Africa. About 5000 years ago, the people in what is now Pakistan cultivated cotton (Singh et al 2005). The army of Alexander the Great first brought cotton goods into Europe in the 300s B.C. but the cloth was too expensive and only the rich could afford it (Eom Seong-il and Rhe Kyu-bong 1990).

The English began to weave cotton in the 1600s. They imported raw cotton from other countries bordering the Mediterranean Sea. Later, they imported cotton from southern colonies in America (Ratnagiriswaran and Venkatachalam 1942).

In the 1700s, English textile manufacturers developed machines that made it possible to spin thread and weave cloth into large quantities (Han and Yang 2005). Today, the United States, Russia, China and India are major producers of cotton.

2.2.1.1 Properties of cotton

- It is soft and comfortable.
- It wrinkles easily.
- It absorbs perspiration quickly.
• It has good color retention and is good to print on.
• Cotton is also strong and durable. (Daniel 2006).

2.2.1.2 Scope of cotton fiber / fabric

Cotton is the most important apparel fiber around the world. In the last year, U.S. cotton fiber production totaled approximately 8.5 billion pounds (Monthly Economic Letter 2004), which accounts for about 30% of the textile fiber consumption in the United States (Segal and Wakelyn 1998).

Cotton is a natural cellulosic fiber, comes from a renewable resource, and is intrinsically biodegradable. Therefore, many consumers believe it is an environmentally responsible product. In fact, cotton plants are very prone to attack by certain insects and fungi (Daniel et al 2006).

Although modern techniques can produce “transgenic cottons” with better insect and fungus resistance (Myers and Stolton 1999), the growth of conventional cottons demands heavy use of pesticides and fungicides; it is estimated that cotton uses only 3% of the world’s farmland, but about 25% of the world’s pesticides (Yates 1994) and the United States is the predominant user of these pesticides and insecticides (Myers and Stolton 1999). In addition, before the harvest of cotton, chemicals such as defoliants are also used to cause the leaves to fall off the plants so as not to stain the cotton fibers (Grayson 1984).

Recently, efforts have been made to find substitutes for toxic chemicals used in textile processing. Citric acid, for example, which causes no adverse effects to humans or the environment, has been introduced to replace formaldehyde, a possible carcinogen, for durable-press-finished cotton fabrics (Wei and Yang 2000). An effort made to improve cotton dyeing is the introduction of covalently bound cationic dye sites into the cotton fibers
so the affinity of the dyes for fibers is improved and the rinsing and after-washing steps of the conventional processes can be eliminated (Hauser 2000), thus reducing environmental pollution. In recent years, a few nonconventional strains of cottons have been grown under more environmentally responsible conditions and marketed as naturally colored cotton, organic cotton, and green cotton (Needles 1986).

Naturally colored cottons, available in various shades of green and brown, have been developed through selective breeding from natural mutants, and the fibers can be processed into colored or patterned fabrics without the use of dyes (Robbins 1994). Furthermore, naturally colored cotton plants have better resistance to pests and disease than conventional white cotton, which can reduce or eliminate the need for pesticides and fungicides (Abend 1994). Organic cotton is produced without the use of synthetic fertilizer, herbicides, and pesticides (Imhoff 1999).

The cotton is grown by using natural fertilizers (manure) and by replacing pesticides with beneficial insects to prey on insects harmful to the plants (Gupta et al 2005). Once it is harvested, certified organic cotton is stored without the use of rodenticides or fungicides (Rudie 1994). Green cotton is used to describe cotton fabric that has been washed with mild natural-based soap, and the fabric is not bleached or treated with any chemicals, except possibly natural dyes (Kadolph 2007). Despite the fact that a few types of environmentally responsible cottons have been introduced to the market, conventional white cotton still accounts for the majority of the cotton products (Duran 2002). Organic cotton, for instance, accounts for only about 2% of the total U.S. cotton production.
2.2.2 Silk

The Chinese has used silk since the 27th century B.C. Silk is mentioned by Aristotle and became a valuable commodity both in Greece and Rome (Suri Mona 1999). During the Roman Empire, silk was sold for its weight in gold. The Chinese domesticated silk worms and fed them with mulberry leaves (Taylor 1986, Schratz 1960).

Farm women in China at that period were supposed to raise such silkworms as one of their chores. Silk was used in China and exported along the Silk Road (the ancient trade route linking China and the Roman Empire) (Budavari 1996). This trade brought China great wealth, but the Chinese did not give away the secret on how silk was formed (Schwing-Weill and Wechsler 1986).

Christian monks finally broke China’s monopoly of the silk production by smuggling silkworm eggs out of the country, and soon other countries started to produce their own silk (Suri Mona et al 1999).

2.2.2.1 Properties of silk

- It is versatile and very comfortable.
- It absorbs moisture.
- It is cool to wear in the summer yet warm to wear in winter.
- It can be easily dyed.
- It retains its shape and is relatively smooth.
- It has a poor resistance to sunlight exposure.
- It is the strongest natural fiber and is lustrous (Daniel M et al 2006).
2.2.2.2  Scope of silk fiber / fabric

Cultivated silk is a beautiful luxurious fiber with a smooth luxurious hand. This type of silk can be dyed and printed in bright colors that are very pleasing to the eye (Bahl et al 1971). Wild silks are duller and have a more coarse hand and texture. Silk’s abrasion resistance is moderate. However, it is ranked high in strength for natural fibers. Silk fabrics have good absorbency.

Fabrics made from silk are comfortable in the summer and warm in the winter. Silk fabrics have only moderate resistance to wrinkling (Dimascio 1989). It is often recommended that silk garments be dry-cleaned. When hand or machine washing washable silk garments, test for water spotting in an obscure place because silk water-spots easily (Teli et al 2000). Perspiration and sunlight weakens and yellows silk fabrics (Frances 1982). Upholstery and drapery fabrics that contain silk should be protected from prolonged exposure to direct sunlight (Packer 1993).

Silk is considered to be more plastic than elastic because its very crystalline polymer system does not permit the amount of polymer movement which could occur in a more amorphous system (Stana-Kleinschek et al 1998). If the silk material is stretched excessively, the silk polymers, which are already in a stretched state (they have a beta-configuration) will slide past each other (Patnaik 1998).

The process of stretching ruptures a significant number of hydrogen bonds. When stretching ceases, the polymers do not return to their original position, but remain in their new positions (Takahashi 1982). This disorganises the polymer system of silk, which is seen as a distortion and wrinkling or creasing of the silk textile material. The handle of the silk is described as a medium, and its very crystalline polymer system imparts a
certain amount of stiffness to the filaments. This is often misinterpreted, in
that the handle is regarded as a soft, because of the smooth, even and regular
surface of silk filaments.

2.2.3 Wool

Wool was probably the first animal fiber to be made into cloth. The
art of spinning wool into yarn developed about 4000 B.C. and encouraged
trade among the nations in the region of the Mediterranean Sea (Tessier

The first wool factory in England was established in 50 A.D. in
Winchester by the Romans. In 1797, the British brought 13 Merino sheep to
Australia and started the country's Merino sheep industry (Van Rheede 1963).

There are 40 different breeds of sheep in the world producing a
rough estimate of 200 types of wool with varying standards (Burkinshaw and
Gotsopoulos 1996). The major wool producers in the world are Australia,
Argentina, China and South Africa (Wijnsma 1984).

2.2.3.1 Properties of wool

- It is hard wearing and absorbs moisture.
- It does not burn over a flame but smoulders instead.
- It is lightweight and versatile.
- Wool does not wrinkle easily.
- It is resistant to dirt and wear and tear (Daniel M et al 2006)
2.2.3.2 Scope of wool fiber / fabric

Wool is the most important animal fiber used in textiles (Bratt 1999). The fibers are the hair of animals, most often sheep. Although the production of wool does not involve the use of fertilizers or herbicides as in cotton production, wool cannot be produced without some negative impacts on the environment. For example, soil erosion can occur from overgrazing by sheep if not controlled properly. Also, excess sheep manure can create runoff contamination (Chiras 1993).

The processing of wool requires the use of soap and alkaline solutions to clean the fibers and to remove grease and impurities (Tortora and Collier 1997). Chemicals are also used on wool fabrics to prevent shrinkage, to ensure machine washability, and to provide resistance to moths and stains. Through selective breeding, colored wool can be obtained from sheep with natural pigmentation (Kloese 2005). The use of colored wool can eliminate the need for coloring the fibers. However, the amount of colored wool used still is minuscule compared to conventional wool (Donnell 1995).

2.3 SOURCES OF NATURAL DYES

The sources of natural dyes are broadly classified based on cultivation and collection. The natural sources cultivated are marigold, annatto, indigo etc. The collections of natural dyes are from cooperative stores and wholesale ayurvedic shops (Teli and Nayak 1994).

The importance of vegetable dyes has increased presently, with increased awareness about harmful effects of chemical dyes both in production and in its usage by human beings. In the light of these factors there is a very huge potential for vegetable dye and food colors, since all of them are extracted from natural sources and are having no harmful effects.
Different parts of plants, animal residues and some of the minerals are the sources of natural dyes. Vegetable source of natural dyes are renewable (Janhom and Watanesk 2006). Pigments extracted from the roots of vegetable sources are mostly used for red dyes (NCIB Pubmed 2002).

The organic cultivation of dye plants for the certified natural textile industry is as emerging and promising sector of organic farming (Anna Hartl and Vogl 2003). Henna or Egyptian privet is the source of an ancient and very important yellow dye (El-Shishtawy 2002). This dye has the rare distinction of being a dye whose use can be traced back to antiquity and which continues to be as commonly used all over the world today as it is in the ancient times (Christie et al 2006).

Turmeric is the most commonly used yellow dye followed by harshingar (nyctanthes arbor-tristis) and palash (butea frondosa). Weld has been the most commonly used natural yellow color in Europe countries (El Molla and Schneider 1995).

Coreopsis, goldenrod, onion skins give yellow color. Lilies, queen anne`s lace, rhododendrum give green color (Bechtold et al 2002). For purples or lavenders the sources are blackberries and grapes (Clipson 1989). Acrons, marigold, pomegranate give brown color (Traci Vandermar 2002). Lac is a unique dye material of animal origin being the secretion of tiny insect kema lacca (Kamel et al 2005).

Most of the plant materials used for the extraction of dyes are also credited with medicinal properties, and are rich in napthoquinones (Kamel et al 1998). Black walnut (juglans nigra), pecan (carya illinocnsis), shagbark hickory (carya ovata mill). Nut hulls can be used to make a dye to color the textiles to a brown color, pecan and a red/orange.
Indigo is the most important blue component in the class of natural
dyes for cellulosic and protein fibers (Janhom et al 2004). Brown from tengar,
bakau, obah, durina. Reddish brown from engkerbai psychutria viridiflora
reinu, megkudu angsana (Kamel et al 2005). Yellow from the wood of
asepang, bebaru, engkala burong, pedalai. Blue from tarum, indigofera.
Purple from the pods of jering (Dumitrescu and Varga 2006).

Teak plants are abundandy available in the forest of orissa, west
Bengal and in many other states (Mason 1999). Teak leaves are left as waste
which can be utilized to get dye for textile industry. It is reported that the teak
leaves contain 6% of tannin and also brownish red dye pigment in large

2.4 CLASSIFICATION OF NATURAL DYES

Natural dyes are obtained either from animal, vegetable or mineral
origin. Tyrine, kermes, cochineal are from animal sources. Roots, stems,
barks, leaves, berries, flowers are from vegetable sources (Suslick 1986). Iron
buffs, rust, copper belong to mineral sources (www.apparelsearch.com/dyes)
One other class which describes the role of natural dyes, rather than their
mode of use is the categrision of mordant dyes and vat dyes which are
basically anthroquinone and triphenyimethane constituents (Wikipedia 2006).

Natural dyes can be broadly classified as natural organic dyestuff or
vegetable, animal origin and mineral dyestuff or inorganic pigments. The
organic dyestuffs are obtained from roots, stems, leaves, berries and flowers
by various plants and from certain insects and shellfish, with a very elaborate
series of processes (Kamel MM 2003). The inorganic pigments are insoluable
salts precipitated on fiber by suitable double decomposition (Abraham and
Edelstein 1964).
Natural dyes are aesthetically appealing and to make the work less strenuous it has been traditionally divided into diverse groups and they are named accordingly to their specific function (El-Shishtawy et al. 2003). These categories were known as rangraj the dyers, chipper the printer, khatri tand bandhej for tie and die work, majithia or guldraj for merchants dealing with madder and vermillion. All these dyes concentrate on natural sourced dyes (Judd et al. 1975). Flavonoids which yield yellow dyes can be classified under flavones, flavonoids, iso-flavones, aurones and chalcones.

Based on the chemical nature it can be classified as:

**Groups** | **Examples**
---|---
Diarylolmethane dyes | turmeric etc
Carotenoid dyes | saffron, annatto etc
Alkaloid dyes | barberry
Quinonoid dyes | dolu, henna
Flavonoid dyes | French, marigold
Flame of forest dyes | kamala, kaiphal
Benzoquinone dyes | kamala, kaiphal
Anthroquinone dyes | manjit, chay root.

Natural dyes are classified into two groups namely substantive and adjective dyes. The substantive dyes require no pretreatment to the fabric (eg. Indigo, orchil, turmeric etc.) The adjective dyes can only dye the material mordanted with metallic salts or with the addition of a metallic salt to the dye bath (eg. Logwood, madder, cochineal etc.) The substantive dye can be further classified as direct, acid and basic dyes (Nalankilli 1997).

The direct class of dyes can be directly applied on cotton which they get absorbed without any pretreatment to the dye or the fiber. Many
natural dyes belong to this category (e.g., turmeric, safflower) (Brown B 1965). The mordant dyes require application of some mordant for fixing onto the fiber. It can be applied before dyeing, during dyeing and after dyeing (Frederick 1965). Now-a-days all those dyes which form a complex with mordants and have been included under this category. (e.g. Indian barberry, onion). Then indigo (neel)-indigo tinctoria which is a vat dye that produces all shades of blue (Iyer and Saxena 1999).

Some investigators classify natural dyeing tanning materials into two categories—hydrolysable and condensed tannins (Abramov OV 1998). The hydrolysable tanning extracts yield water soluble products upon hydrolysis with acid or enzymes while condensed tanning extracts from precipitates known as tanners red or phlobaphene under these conditions. This classification corresponds mainly to groups based on flavone related components. Condensed tannins do not have much textile use (Mohanty et al 1987).

2.4.1 Flavonol Dyes

Flavonols are the hydroxylated flavones, which contain hydroxyl group at position – 3 and are widely distributed in the plant kingdom usually in the form of glycosides. The pigments of this group give yellow colors which are deeper than those obtained from flavones but they are not so fast to light, undoubtedly due to their great sensitivity to oxidation (Adesogan 1973, Thomson 1971). Some common botanicals that come under flavonol group are weld, quercitron, fustic, osage, chamomile, tesu, dolo, marigold and cutch (Adon 1962).
2.4.2 Iso-quinoline Dyes

Isoquinoline is a heterocyclic aromatic organic compound. It is a structural isomer of quinoline. Isoquinoline and quinoline are benzopyridines, which are composed of a benzene ring fused to a pyridine ring. Common botanical that comes under iso-quinoline group is barberry (Gilchrist 1997, Harris and Pope 1922, Katritsky and Pozharskii 2000, Katritsky et al 1996, Nagatsu 1997, O'Neil and Maryadele 2001).

2.4.3 Chromene Dyes

A dye group that gives yellow dye that independently represents hydrogen, halogen, or an alkoxy group of 6 carbon atoms that independently represents cyano, esterified carboxyl, amide, a substituted or unsubstituted benzoxazole, or alkylsulfonyl; or may be taken together to form a pyrazolone, barbituric acid or Meldrum's acid residue (Anon 1996). Common botanical that come under chromene group is Kamala (Adon 1962).

2.4.4 Napthoquinone Dyes

The majority of naphthalene derivatives found in nature are quinones and most of these are plant products. Napthaquinones can exist in three isomeric forms and a group of closely related polyhydroxyl derivatives is found in certain species of sea urchin and a few others are elaborated by micro-organisms also (Berg et al 1974). Some common botanicals that come under napthaquinone group are henna, walnut, alkanet and pitti (Adon 1962).

2.4.5 Anthroquinone Dyes

Anthroquinone as such is not found in nature, although it had been prepared by laurent as early in 1835 by oxidation of anthracene with nitric
acid. The term ‘anthra’ refers to the greek word for coal from which anthracene was originally obtained. Anthraquinone is one of the most valuable intermediates in the manufacture of dyestuffs. It comprises of a greater number of dyes having outstanding fastness properties than any other group of dyes. Some common botanicals that come under napthaquinone group are lac, cochineal, and madder (Majithro) (Adon 1962).

2.4.6 Benzoquinone Dyes

The benzoquinone dye-carathamin is a red dye extracted from flowers of safflower (carathamus tinctorius). This group is isolated from the flowers that contain principally two matters, carathamin, which is scarlet red and insoluble in water and safflower yellow which is soluble in water. It gives cherry red color to cotton, silk and wool (Kamat and Alat 1999).

2.4.7 Indigoid Dyes

Chemically indican is indoxyl D-glucoside having molecular formula C_{14}H_{17}NO_{6}. It occurs in the leaves of indigofera tinctoria and isatis tinctoria. Indican hydrolyses easily to glucose and indoxyl when the leaves are macerated with water. The indoxyl oxidizes by atmospheric oxygen to give insoluble indigotin, which is also known as indigo blue (Daniel et al 2006). Natural indigo is a mixture of indigotin (indigo blue) and indirubin (indigo brown). The color of indigo is due to extended chromophore present in the indigotin structure. This dye has remarkable permanency and strength for its deep blue colors.
2.5 COLORS DERIVED FROM NATURAL DYES

The Color Index lists only three natural blue dyes that is Natural Indigo, sulphonated Natural Indigo and the flowers of Japanese used mainly for making awobana paper.

The prominent red dyes are madder (rubia tinctorum), manjeet (rubia cordifolia.L), brazil wood / sappan wood (caesalpina sappana), morinda (Morinda Citrifolia), cochineal (coccus aacti), lac dye (caccus / accae) (Clark et al 1993).

Yellow is the most common color in the natural dyes. However most of the yellow colorants are fugitive (Thakore 1990). Some of the important yellow dyes are obtained from barberry (berberis aristata), tesu flowers (butea frondosa, monoperma) and kamala (mallotus phillippensis).

Tannins are the most important ingredients in dyeing with Natural dyes producing yellow, brown, grey and black colors (Gulrajani and Gupta 1992)

Eupatorium odoratum is a plant herb and the colors obtained are bright yellow with alum, greenish yellow with blue vitriol, dark green with iron, brown with chrome (Delle 1985). Ageratum Condyzoides is a plant herb and the colors obtained are bright yellow with alum, bierge with blue vitriol, and grey with iron, brown with chrome (CSIR Publication 1985)

The color also changes according to the dyeing process and ingredients used (Roecker et al 1997). Starting from light shades to deep shades all could be dyed with varieties of mordants. India also yielded pink, purple, turquoise, green, olive and yellow shades from Indigo(Ali 1988)
Composite color or mixed color can be obtained by mixing dyestuff in the same bath, or different dyestuff or can be boiled separately and mixed in various proportions. The color can again be altered by the addition of small amount of mordant after dyeing. Some examples of composite colors are khaki, grey, bronze, maroon, chocolate brown, dark plum and shades of red. (ii) green color can be obtained by adding red yellow colors. (iii) blue-black colors can be prepared by combining blue and black grey. (iv) purple, violet, crimson, lilac, lavender can be prepared by red and blue (Sewekow 1988)

The wood from trees contain the colorless haematozylin which oxidize in air to red dye haematin and on using with iron mordant black color is got different colors. Madders are purplish red while combining alum, madder and logwood, brown from iron, madder and fustic. Reddish brown from chrome, madder, fustic and logwood. Also colors such as dull black from chrome, logwood, and fustic chips. Green black from alum, logwood, fustic in large extent. Lavender from chrome, logwood and madder (Frey 1997) Table 2.1 shows the colors derived from natural dyes.

**Table 2.1 Colors derived from natural dyes**

<table>
<thead>
<tr>
<th>Red</th>
<th>Yellow</th>
<th>Black</th>
<th>Brown</th>
<th>Green</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safflower</td>
<td>English oak</td>
<td>Alder</td>
<td>marigold</td>
<td>Lily</td>
</tr>
<tr>
<td>Caesilpinia</td>
<td>Parijatha</td>
<td>Rofbiamala</td>
<td>Sumach</td>
<td></td>
</tr>
<tr>
<td>Moninab</td>
<td>Marigold,</td>
<td>Custard</td>
<td>Balsam</td>
<td></td>
</tr>
<tr>
<td>citrifolia</td>
<td>Teak</td>
<td>Apple</td>
<td>Cutch</td>
<td></td>
</tr>
<tr>
<td>Beet root</td>
<td>Agrimony</td>
<td>babla</td>
<td>Ain bark</td>
<td></td>
</tr>
<tr>
<td>Anchusa</td>
<td>Chir</td>
<td>harda</td>
<td>Auch</td>
<td></td>
</tr>
<tr>
<td>Ladysbed</td>
<td>Pomegranate</td>
<td>Lodh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cochineal</td>
<td>Weld</td>
<td></td>
<td>Blackberry</td>
<td></td>
</tr>
</tbody>
</table>
2.6 \hspace{1cm} \textbf{TYPES OF NATURAL DYES}

There are three major types of natural dyes which are i) substantive dyes, that require no mordants, ii) vat dyes, iii) mordant dyes, that require auxiliary substances to become attached to the fiber. Less common forms of natural dyeing include rust dyeing, dye painting with earth oxides, and mud dyeing (Hill and Richter 1937).

2.6.1 \hspace{1cm} \textbf{Substantive Dyes}

Substantive dyes are used by simply combining the dyestuff, usually in a quantity equal to or twice that of the weight of the fiber, with the fiber (or fabric) and simmering for an extended period of time. An example is turmeric, the spice, which works on cotton as well as on wool; others include onion skins, walnut husks, and tea (Ismail 2002).

Substantive dyes, if made from edible materials, have the advantage of allowing the use of a regular cooking pot for dyeing in; most dyes, even natural dyes, and most mordants, require that a dye pot be devoted to their use, never to be used for cooking again. Another word for a substantive dye is direct; note that there are also a great many synthetic direct dyes (Hirosa 1968).

2.6.2 \hspace{1cm} \textbf{Vat Dyes}

The vat dyes work the same way on protein and cellulose, by being introduced into the surface of the fiber while in soluble form and then converted into an insoluble form (Karmat and Alat 1999).

The vat dyes include many synthetic dyes, but also the natural dye indigo, and the ancient Tyrian Purple dye extracted from shellfish. They are complex to use, requiring the establishment of an anaerobic (oxygen-free) fermentation. See Vat dyes for more information (Lloyd 1980).
2.6.3 **Mordant Dyes**

Most natural dyeing is done with the use of mordants, most commonly heavy metal ions, but sometimes tannins. (Tannins are particularly important in dyeing cotton and other cellulose fibers.) The mordant allows many natural dyes which would otherwise just wash out to attain acceptable wash fastness. A mordant remains in the fiber permanently, holding the dye. Each different metal used as a mordant produces a different range of colors for each dye (Perkin and Hummel 1893).

### 2.7 **NATURAL DYES FROM FRUIT SOURCE**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Botanical Name</th>
<th>Common Name</th>
<th>Family</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acacia nilotica</td>
<td>Sunt berry</td>
<td>Leguminoseae</td>
<td>Blue</td>
</tr>
<tr>
<td>2</td>
<td>Annona reticulate</td>
<td>Custard apple</td>
<td>Annonaceae</td>
<td>Black</td>
</tr>
<tr>
<td>3</td>
<td>Areca catechu</td>
<td>Areca nut</td>
<td>palmaceae</td>
<td>Red</td>
</tr>
<tr>
<td>4</td>
<td>Bixa orellana</td>
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<td>Pea</td>
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<td>Gab</td>
<td>Ebenaceae</td>
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<td>Kamala</td>
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<tr>
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<td>Kaiphal</td>
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<tr>
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<td>Harsingar</td>
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<td>Amrud</td>
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<td>Woodfordia fruticosa</td>
<td>Gulbhar</td>
<td>Lythraceae</td>
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2.8 STANDARD NATURAL DYEING

Standard natural dyes are made from dyestuffs comprised of plant material such as flowers, bark, and roots; minerals including alum, copper, and iron; cochineal and similar insects; and naturally occurring compounds such as ochre (Dean 2000).

Human and animal waste (Thirsk 1997) such as dung, guano, and urine were widely used in indigo dyeing (Balfour-Paul 1998) and to manufacture the dye known as Turkey Red (Liles 1990). Assists, fixatives, and mordants are all classified as dye additives (Dean 1994).

Mordant chemicals are essential in standard natural dyeing, but they and other additives are optional in alternative methods (Diadick Casselman 2001). The standard approach to the preparation of natural dyes among craft and textile practitioners is the immersion method. Immersion natural dyeing is a labor-intensive process. In this process the dyer selects and harvests the dyestuff, prepares it for processing, weighs the ingredients and extracts the dye by soaking the dyestuff in water for several hours and then dyed (Irwin 2000).

Another standard dyeing method is the immersion process where the dyer must weigh the goods to be dyed and then prepare them for dyeing, generally by pre-mordanting, thus adding several more steps to the immersion process. Then, the dyer must make the actual dyebath, immerse the goods to be dyed, and heat the bath. Careful record keeping is essential if the process is to be duplicated (Aycock 1996).

Immersion dyeing requires a large amount of water free of chlorine and similar additives that can react with mordants, dyes, and goods and adversely affect colors. Liquor ratios often exceed 50:1 (water to goods).
Significant mechanical and thermal energy is consumed as a result of the prolonged processing required with this method. A fully equipped dye studio, separated from living and food preparation areas of the home (Dean 2000), is essential for controlled dye research, large scale craft projects, and instructional dye workshops.

The primary advantages of immersion dyeing using traditional dyestuffs (Liles 1990) is level and predictable color that can be duplicated when using recorded recipes, thereby avoiding disappointing results. Mordants form a permanent bond between the textile goods and the dye (Crews 198, Crowell and Majtenji 1974) and generally improve dye performance.

2.9 NATURAL DYEING WITH MORDANTS

Mordants commonly used in natural dyeing are alum (aluminum potassium sulfate), chrome (potassium dichromate), copper (copper sulfate), iron (ferrous sulfate), and tin (stannous chloride) (Kadolph 1999). First described by Pliny the Elder (Plinius Secundus 1970), mordants used with adjective dyes help the dyer achieve a broad spectrum of fast colors (Liles 1990). In contrast, substantive dyes like onionskins, bark, and lichens require no mordants (Casselman 1993). Mordants are applied at various stages in the immersion dye process i.e the dyer can pre-mordant, mordant simultaneously during the actual dyeing, or mordant after dyeing (Casselman 1993). Mordants used alone or in combinations expand the palette and improve fastness; the primary advantage of mordanting is color diversity on a wide range of protein and cellulose fibers as well as many synthetic and manufactured fibers (Kim. et al 2001).

Most natural dyeing is done with the use of mordants, most commonly heavy metal ions, but sometimes tannins (Glover 1995). Tannins are particularly important in dyeing cotton and other cellulose fibers (Johns
The mordant allows many natural dyes which would otherwise just wash out to attain acceptable wash fastness (Lopez 1989). A mordant remains in the fiber permanently, holding the dye. Each different metal used as a mordant produces a different range of colors for each dye (Ong 2001).

Investigations about the possible use of natural dyes in textile dyeing processes have been performed by various research groups (Lee and Kim 2004). In general, to improve its fastness, most of the dyeing processes were conducted using metal salts (e.g., potassium dichromate, stannous chloride, ferrous sulfate, and copper sulfate) as mordants (Kashino et al 1993). The metal ions can act as electron acceptors to electron donor to form coordinate bonds with the dye molecules, which are insoluble in water (Trotman 1975).

2.10 NATURAL DYEING WITH ENZYMES

Enzymes are biological catalysts with polypeptide chains. They are well known in textile natural dyeing with selective and specific activity (Atkins and Paula 2001). Proteases are one of the major enzymes which have received much interest for their use in cotton, silk and wool processing (Heine and Hocker 1995).

A great many studies have been carried out on application of proteases, including antifelting and antishrink finishings, oxidative treatment followed by proteolysis, pilling performance, surface and appearance modification of wool fibers (Clark 1993). Makinson demonstrated that the hydrophobic properties and scaly structure of the fabric surface are the main factors that cause shrinkage while dyeing. Enzymes have been used for descaling process to improve shrink resistance (Makinson 1979 and Bishop et al 1998).
The majority of enzymatic processes in the last few years have been combined with chemical pretreatments (Cavaco-Paulo 1998 and Beynon et al 2001). In 1983, Kurashiki spinning Co. introduced a process for descaling the fibers using potassium permanganate as a pre-oxidising agent before dyeing treatment (Cegarra et al 1992). Another experiments described that proteolytic enzyme improves the dyeing behavior, the handle and luster of wool fabrics (Mazzucheti and Vineis 2005).

There have been relatively few papers studying the effect of enzymes on dyeing properties of wool with natural dyes. One study showed that protease produced a faster rate of dyeing with acid and premetalised dyestuffs and it decreased the apparent activation energy of dyes (Riva et al 2002).

Other experimental evidence indicated that enzymes can be used as auxiliary agents in dyeing and they attack the surface of the fiber resulting more acid dyes absorption (Riva et al 1999). Tsatsaroni et al. reported the dyeing properties are excellent in two natural yellow pigments on protease treated silk and cotton fibers (Galante et al 1998).

Protease enzyme also tends to improve natural dyes absorption on wool fibers (Tsatsaroni et al 1998). Certain limitation of enzyme dyeing is that the fiber swells and loses its strength after dyeing (Duran and Duran 2000). Even though it has the advantage of environmental friendly nature it cannot be combined while using naturally available mordants of potassium and sodium compounds that permit cross-likkage of dyeing activity (Nolte et al 1996).
2.11 PROPERTIES OF NATURAL DYES

Natural dyes are organic compounds, obtained from natural sources. In order for a colored compound to serve as a useful dye it should have (i) intense color (ii) solubility in water (iii) substantivity to the fiber (iv) durability to wet treatment (v) safe, easy to handle and reasonably priced (Gulrajani 1999)

Most Natural dyes become less soluble when they are purified, they are either in a soluble or dispersible form at the time of application. Some such as harda, catechu and punica granatum are water and yield clear solutions containing single molecules which are readily absorbed by fibers (Gulrajani 2001)

In contrast, some dyes, like the napthoquinone based lawsonite and juglone and anthroquinone munjistin and purpurin are only partially soluble in water. Since most of these dyes have hydroxyl groups (-OH), their solubility can be enhanced by adding an alkali such as sodium carbonate. Another “insoluble” natural dye is indigo (Deepti Bhal Gupta and Gulrajani 2001).

Dyes such as lac, munjistin and catechu will show good affinity for polyamide fibers (wool, silk and nylon) and basic dye berberin will have affinity for ionic fiber acrylic, nylon and polyester. These facts have already been substantiated experimentally. One of the most historic and popular dyes used on cotton namely madder has no inherent affinity for the fiber. Hence it follows that it is possible to create or modify affinity of a dye for a particular fiber by using certain auxiliaries (Deepti Bhal Gupta and Gulrajani 1994).

In natural dyes, the molar absorptivity would be on lower side, as the absorption spectrum in most cases is quite broad, that is why shades from 5-10% are common for natural dyes. Hence, the molar absorptivity should be
essential criteria for short listing dyes which can be commercially exploited (Deepali Rastogi et al 1999).

Most of the natural dyes show that they would acquire a negative charge when dissolved in water as the surface of cotton is anionic and this would lead to development of repulsive forces and the dye would not be absorbed (Seong-il Eom and Kyu-Bong Rhee 1999).

It has been observed that most natural dyes become less soluble when they are purified. Like their synthetic counter parts, they are either in a soluble or disposable form at the time of application (Deepti Bhal Gupta 2001).

### 2.12 ADVANTAGES OF NATURAL DYES

Natural dyes are procured from natural wealth like plants, minerals, and insects (excreta). These dyes are environmentally friendly and their production and composition will help in maintaining the ecological balance, since these dyes are biodegradable (Glover Brain 1995).

These dyes are non-toxic and health hazards like allergies can be avoided. Natural dyes are aesthetically appealing. Rural employment will be generated and it is cost effective too (John and Margaret Cannon 1994). When natural dyes are adopted the sludge disposal task becomes easier and easy in handling is met with these types of dyes (Rashmi Sanghi 2002).

As far as price is concerned, the natural dyes may be working out slightly costly, but if holistic view is taken the price difference is not so big that it cannot be adopted, given the value addition that vegetable dyes provide. Still the fact remains that only those natural dyes should be
used for commercial application, which are easily and regularly available at reasonable price (Deepti Bhal Gupta and Gulrajani 1999).

It provides an option to replace synthetic dye based dry colors by natural ones, which is safe, stain-free and eco-friendly, henna, walnut and alken nut are reported to exhibit anti-bacterial and anti-fungal activities (Tsatsaroni and Elifthieriadis 1994), many natural dye sources have been found and many colors are being derived, which has good health aspect to skin (Haylock and Rush 1976).

The dry colors have cosmetic effect on skin and it makes feel a bit soft too (Yoshida and Osawa 1965).

The natural dyes are obtained from renewable resources. They act as an advantage in health aspects of human beings. Partially no or mild chemical reactions are involved in their preparations and applications. No arrival of disposal problems. They are unsophisticated and harmonized with nature. They trigger the creativity of human beings on getting different colors by using the natural sources (Gulrajani 2000). Durability to wet treatments is an advantageous property of the chemical structure of natural dyes.

2.13 LIMITATIONS OF NATURAL DYES

Dyes which have a high substantivity are normally fast to washing. Most of these dyes are only sparingly soluble in water due to the absence of strong solubilising groups. Additional after treatments such as post mordanting with ferrous salt or black tanning often helps to improve the fastness of natural dyes by insolubilising the dye inside the fiber (Deepti Bhal Gupta and Gulrajani 1993).
Uniform dyeing of fabric in solid shades is more difficult. Special procedures need to be developed for each dye. Mordanting may be carried out before or after dyeing, depending upon the requirement. Other auxiliaries such as surfactants, penetrating agents or swelling agents should be employed. The temperature, pH and time profile have to be carefully monitored throughout the dyeing cycle for optimum result (Ministry of science and technology 1996).

Proper after treatment is necessary for good fastness properties. Thorough rinsing is required to remove all the superficially adhering dye from the fiber.

2.14 RECENT STUDIES / DEVELOPMENT OF NATURAL DYES

Recently, a revival interest in the use of natural dyes in textile coloration has been growing. This is a result of the stringent environmental standards imposed by many countries in a response to the toxic and allergic reactions associated with synthetic dyes (Deepti Bhal Gupta and Gulrajani 1994).

Trends which emerged were very favorable for natural dyes as many color shades are possible to achieve and the same applies to the color trends of fashion fields. Designers have the flexibility of dyeing variety of fancy yarns with natural dyes to create an eye-catching austerity. Designers from many countries, presented their latest line of casual and evening wear which were made of natural fabrics of natural dyes. India is focusing on different segments of natural dyes such as research, technical development, fashion trends and also natural dye bazaars, workshops etc, which could be on international scales (Lokhande et al 1998).
The traditional way of natural dyeing method is a time consuming laborious method and the reproduction of the same shade is difficult due to uneven extraction of dye pigments by crude method. The present study of extraction and dyeing procedure is economical, time and energy saving and easy to handle. And recently it is possible to obtain various intensities of color shades for variety of fabrics by using known quantity of dye source (Missouri 2000).

The yarn tie-dye, commonly known as ikat all over the world is a famous technique of India. Patan patolasare very well known all over the world for their accuracy in weaving combined ikat. In this case warp and weft yarns are both tie and dyed using many natural dyes as well as indigo to achieve a wide pallet of colors.

Natural dyeing using HDHP has been found to give better result as compared to open bath dyeing. Good awash fastness was obtained among natural dyes (Lokhande and Dorugade 1999).

The textile processing industry is currently being confronted with more and more inquiries on theme of dyeing with natural dyes and therefore, the subject of natural colors has once again become the matter of tropical interest (Lokhande et al 1998, Utlrich Sevekev and Leverkusen 1988).

2.15 CONCLUSION

Natural dyes have carved a unique place for themselves in the world of Textiles and have shown a slow but steady growth over the last ten years.
Nowadays the urge for pollution free environment is very well understood, and it is a fact to admit and agree that natural dyes are ecofriendly dyes. The thought of commercializing natural dyes exist among the textile people and to pave the way for it many new studies and researches to carry out the natural dyeing in an effect way should be found.

There are various methods on natural dyeing and it will vary accordingly to each and everybody who does the process. Each process differs with each other in its recipe and ratio of the ingredients used. Till now good results have been obtained with the adoption of new techniques.

Further the grade can be improved by adopting many new latest techniques such as microencapsulation, nano-technology. Innovations right from the initial stage of extraction till the application have to be welcomed.