

Present status of natural dyes

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The present status of natural dyes with reference to the stake holders of natural dyes, estimates of dye requirements, availability of natural dyes, technology for production, and some important natural dyes and mordants is critically discussed. Application techniques and fastness properties of natural dyes are also briefly discussed. It is suggested that the natural dyes are not substitutes of synthetic dyes. Some of the limitations of natural dyes such as use of banned metal salts as mordants, poor fastness properties and use of agricultural land for growing natural dye plants can be overcome through research and development.

Keywords: Environment protection, Mordants, Natural dyes

1 Introduction

Natural dyes find use in the colouration of textiles, food, drugs and cosmetics. Small quantities of dyes are also used in colouration of paper, leather, shoe polish, wood, cane, candles, etc. In the beginning, there were dyes derived only from natural sources. Some processing was required but essentially the dye itself was obtained from a plant, mineral or animal. After the accidental synthesis of mauveine by William Henry Perkin in 1856 and its subsequent commercialization, heralding the advent of coal tar dyes (now synthetic dyes), the use of natural dyes receded.

The limitations of the natural dyes that were responsible for their decline are:

- Availability,
- Colour yield,
- Complexity of dyeing process, and
- Reproducibility of shade.

Besides these, there are the following perceived technical drawbacks of natural dyes^{1,2}:

- Limited number of suitable dyes.
- Allow only wool, natural silk, linen and cotton to be dyed.
- Great difficulty in blending dyes.
- Non-standardized.
- Inadequate degree of fixation.
- Inadequate fastness properties.

- Water pollution by heavy metals and large amounts of organic substances.

The following properties are often considered to be the advantages of natural dyes²:

- They are obtained from renewable resources.
- No health hazards, sometimes they act as health cure.
- Practically no or mild chemical reactions are involved in their preparation
- No disposal problems.
- They are unsophisticated and harmonized with nature.
- Lot of creativity is required to use these dyes judiciously.

According to Hill³, the research effort devoted to natural dyes is negligible. If there had been significant research on the use of natural dyes, it is probable that they would have already been much more widely used than they currently are. As there is much catching up to do after 150 years of neglect, there is plenty of scope for rapid developments. This applies to the techniques of agricultural production, processing and dyeing.

2 Stake Holders of Natural Dyes

The use of natural dyes has increased substantially during the last couple of years. These dyes are being mainly used by:

- Hobby groups,
- Designers,

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- Traditional dyers and printers,
- Non-government organizations (NGO's),
- Museums,
- Academic institutes and research associations/laboratories, and
- Industry.

The use of natural dyes, particularly by women as a hobby, has continued in spite of the advent of synthetic dyes. Of late, this activity has increased considerably, particularly in US where many guilds have been formed to discuss about these dyes and organize workshops and training programmes on a regular basis. A quarterly journal '*Turkey Red Journal*' covers information about the workshops and the activities of various hobby groups. The easy accessibility of internet has also given fillip to this activity, where the various individuals exchange notes almost on daily basis. One such popular site is 'NaturalDyes@onelist.com' where one can get very useful tips from the most profound user Carolyn Lee and, of course, many other persons. Some schools have also introduced Natural Dyes as a co-curricular activity. Many companies have come out with hobby kits for beginners. In India, Alps Industries have come out with a large range of 'do-it-yourself' kits (Table 1).

Designers have very effectively utilized natural dyes as a design tool. The non-reproducibility and non-uniformity of shades make each creation a unique piece. Various kinds of design production methods, such as tie-and-dye or stitching (*shibori*), resist printing, stencilling, batik, Indian *Ajrakh*, *Kalamkari*, *Ikat*, etc. are being practised by the designers to create unique products. Weavers Studio, Calcutta (www.weaversstudio.com) is one unique set-up where Darshan Shah has very effectively combined many techniques to create visually attractive products. Jagada Rajapa is a weaver-designer who has been working with weavers in remote villages and helping them to look at their traditional designs and select

Table 1—US companies selling natural dyes through internet
 Jane's Fiber Works, <http://greene.xtn.net/~fibre/dyes.html>
 The Mannings Catalog, <http://the-mannings.com>
 Carol Leigh's Hillcreek Fiber Studio, <http://www.hillcreek.com>
 Louet Sales, <http://www.cybertap.com>
 Mawia Handprints, <http://www.maiwa.com>
 La Lana Wools, <http://www.taaosfiber.com>
 Misty Mountain Farm, <http://www.mistymountainfarm.com>
 The Spinnery, <http://www.thespinnery.com>
 Alps Industries, <http://www.alpind.com>
 Alexandria Textiles, <http://www.alextext.com>
 Earth Guild, <http://www.earthguild.com>

pleasing colour combinations. She has also been conducting workshops in natural dyeing and trying to rebuild the skills long lost (www.icr.com.au). While Himani Kapila is actively trying to promote the use of lac dye in Bihar, designing with indigo has been the main activity of Padmini Balaram. There are many more such creative designers in India and abroad. National Institute of Design is creating a data on natural dyes and products.

Kim Ji-hee of Catholic University in Taegu, apart from conducting research on traditional dyes, is also an accomplished textile artist. She uses traditional Korean dyes and textile production methods to produce contemporary artworks. In many of her works, she imitates the *pojagi* or traditional Korean wrapping cloth by piecing together natural dyed fabric using a traditional Korean stitching method. She then forms a collage by assembling these fabrics with handmade Korean mulberry paper, gold foil, stitchery and traditional folding techniques.

The handicraft industry in many countries has evolved around local talent in the art and craft of dyeing yarn with natural dyes and weaves them to produce speciality fabrics. Printing of natural dyes by direct, resist or dyed style is the speciality of printers of Rajasthan while *Kalamkari* with natural dyes is practised in Shi Kalahasti, Andhra Pradesh (www.icr.com.au).

Fine Turkish carpets recognized for their value and beauty are made with natural dyes obtained from plants, berries and trees (www.about-turkey.com). Perhaps, one of the most successful natural dyes project is the DOBAG (Dogal Boya Arastirma ve Gelistirme Projesi) of Anatolia (Turkey). The DOBAG project got underway in the autumn of 1981 in the district of Ayvacik. There are now two DOBAG co-operatives – one in the Ayvacik region with 220 families as members and other in the Yuntdag region with 130 members. Serife Atlihan from Marmara University, Istanbul, lives mainly in the DOBAG village and helps the weavers and does quality control on each carpet (www.dobag.com.au).

In India, we have ARANYA, a natural dyes project supported by Tata Tea and located in Pristine hills of Munnar in Kerala. It gives employment to the physically handicapped and family members of the employees of Tata Tea.

Another interesting project is the Akha Jim (Asian Tribal Handicrafts). Under this project, Akha tribes of Northern Thailand produce bedspreads, wall hangings and tribal jackets from hand-spun and hand-woven

cotton dyed with natural dyes. The production is supervised by American Jim Godman (www.bangkoknet.com/Goodman.html). Thailand is also the home of *Mat Mi Ikat*, made from natural dye-dyed yarns.

The Mexican Indians, also known as Zapotec Indians, living in the Central Valley of the state of Oaxaca have evolved their wool-weaving art, adapting and absorbing the ideas from other cultures through history. The Zapotecs use sheep's wool and natural dyes derived from the plants and insects of this rich region. Designs are varied. Some are traditional Zapotec designs while others are adopted from the Mayan and Aztec art (www.Southwestfurnishings.com). Natural dyes are also exclusively used for dyeing Porcupine quills by native Americans.

Ann Svenson has described the art of production of Kuba textiles⁴. The Kuba people of Zaire, formerly the Belgian Congo, live in the fertile lands of equatorial Africa between Kansai and Sankuru Rivers. Kuba cloth is woven from the fibres of the *Raphia Vinifera* Palm. Production of these textiles is a multiple - stage process that involves the participation of children, men and women of the same clan. The process includes gathering and preparing the raffia fibres for weaving and embroidery, weaving the basic cloth unit, dyeing the embroidery fibres, and embellishing the woven cloth with embroidery, appliqué and patchwork.

The township of Momostenango in Guatemala is known for its natural dye rugs. The rugs are produced from both cotton and wool. Solola is the only town in Guatemala where women wear natural dyed quilip (woman's shirt). Of course, Mayan women wear *traje*, a natural Mayan clothing.

Non-government organizations (NGOs) are also extensively engaged in promoting natural dyes in rural areas. Presently, Punjab Durrie Weavers (an NGO) is implementing a major project on the 'Development and Use of Natural Dyes in Textiles' in India. This two-year \$453,000 UNDP-funded project has very ambitious objectives of (a) establishment of a database of dye-yielding plants and traditional dyeing methods, (b) establishment of a bank of dye-yielding plant materials from Western India, (c) compilation of a short-list of plants with appropriate dye properties and suitable growth characteristics, (d) establishment of the veracity of traditional dyeing methods with regard to the dye-fastness with traditional dyeing methods, (e) economical production of high-quality indigo, (f) economic cultivation of dye

plants and cotton without the use of synthetic chemicals, and (g) evaluation of the potential of microbial pigments as textile dyes. The project is being co-ordinated by a textile historian, Ann Shankar. The main beneficiaries of this project shall be members of rural co-operatives and rural folk due to the equitable distribution of income by increased rural employment and increased crop variety.

A similar project funded by CEC on 'Cultivation and Extraction of Natural Dyes for Industrial Use in Natural Textiles Production', completed in 1997 by the collaborators from Jena, Germany (TLL), Wieren (LIVOS), University of Bristol, and IACR Long Ashton Research Station (GB), has led to the conclusion that natural dyes can provide a viable alternative to synthetic dyes in an industrial context (www.nf-200.org). This project studied the agronomy, biochemistry and dye production capacity of several species of dye plants. The project scientists were David Cooke (dave.cooke@bbsrc.ac.uk), David Hill and Kerry Stokers (kerry.gilbert@bbsrc.ac.uk).

As a consequence of this initial work, a three-year major project has been initiated through a LINK programme between the academic partners (University of Bristol and Silsoe Research Institute) and industry by the MAFF who have contributed almost £ 300,000, which has been matched by £ 400,000 from the private sector, viz. Willet International Ltd, Gortham and Bateson (Agriculture) Ltd, Express Separations Ltd and Agrifusion Ltd. The objectives of the work are to grow woad on an agricultural scale, using modern forming techniques, coupled to a breeding programme aimed at producing a greater yielding, stable variety of the crop. The woad will be harvested using the specially designed harvesters and the indigo precursor will be extracted using a process which will take 12 min to produce the dye against the old 12-week long process. At the instigation of the industry involved and based on the demands of the consumers for more environment-friendly materials, the end product will be used in the manufacture of water-based, ink-jet inks for computers (www.lars.bbsrc.ac.uk/plantsci/indink2.htm). A project for the cultivation and extraction of indigo from woad is in operation in southwest of France. This project, started in 1995, is being funded by Office National Interprofessionnel des Plantes à Parfum, Aromatique et Médicinales Midi-Pyrénées Regional Council. The project is being implemented by Laboratoire de Chimie Agro-Industrielle/Centre d'Application et de Yraitement des Agroressources.

Other major European projects are: (a) Oro Blu Project (Italy), and (b) Flax company project.

A process for better way of extracting and producing powdered form of natural indigo has also been developed by Guinean scientists working at the Quebec Centre for Textile Technology. As per this process, the leaves are fermented anaerobically for few hours, after which the liquor is filtered, decanted and dried in the sun to produce the powdered form of the dye (www.idrc.ca/aventure/eteintur.html).

There are many more examples of gainful collaboration between research institutes and user industries. For example, the DOBAG project mentioned above is administered by the Dean of the faculty of Fine Arts of Marmara University, Istanbul. Similarly in India, there is the Alps Industries-TIFAC-IIT (Delhi) project, being guided by the author and discussed elsewhere in this paper.

The agronomical research at the Department of Agronomy of Pisa University is aimed at the following issues of the production industrial chain (from raw material production to quality control) of *Reseda luteola*, *Anthemis tinctoria*, *Anthemis tinctoria*, *Genista tinctoria*, *Rubia tinctoria*, *Isatis tinctoria* and *Polygonum tinctorium*: (a) germplasm collection of several dye species and evaluation of their agronomic potential, (b) agronomic aspects of cultivation of madder, woad and weld, (c) seed production of madder, weld and woad, (d) chemical evaluation of pigments by HPLC, and (e) dyeing properties of natural dyes, colour measurement, and light and wash fastness.

Research work on the extraction, purification and characterization of the natural dyes by sophisticated techniques such as TLC, HPLC, UV-VIS and IR spectroscopy, mass spectroscopy and NMR is being carried out in many academic institutes all over the world. There are others working on the theory of dyeing by natural dyes and developing newer and easier methods of application as well as developing pretreatments to improve dye uptake and after-treatments to improve the fastness properties.

Research on the analysis and radiocarbon dating of the historical textiles is of interest to museums. Laboratory for Historical Colorants, housed in the Institute of Geophysics and Planetary Physics at UCLA, set up in 1974 is engaged in the analysis of historic and ethnographic colorants. It has analyzed samples for the Museum of International Folk Art, the Kunsthistorische Museum in Vienna, the School of American Research in Santa Fe, the Natural History

Museum of Los Angeles, etc. as well as for private collectors and dealers. In India, Kharbade of National Research Laboratory for Conservation of Cultural Property, Lucknow, is actively engaged in the analysis and characterization of natural dyes in historic textiles.

3 Estimates of Dye Requirements

The consumption of synthetic dyes has been estimated to be close to one million tonnes per year. As per the report of the German Ministry of Food and Agriculture and Forestry, about 90,000 tonnes of natural dyes can be produced every year⁵.

The production of natural dyes requires agricultural land. It is estimated that about 250-500 million acres of land will be required to produce about 100 million tonnes of plant material needed to produce one million tonnes of natural dyes. This land requirement corresponds to 10-20% of the area cultivated for grain throughout the world.

A market and technical survey on natural dyes has been conducted recently⁶. USA is one of the major importers of natural dyes. The total imports of these dyes which is about 3500 tonnes per year works out to be 0.4% of the synthetic dyes⁷. In terms of value, the US import market reached \$41 million in 1998 which was an increase of 70% from 1994 and an increase of 22% from 1997. Imports of natural dyes by EU countries were 5538 tonnes for the year 1998. This accounts for 0.55% of the synthetic dyes⁸. The EU imports market for natural dyes reached approximately 63 million ECUs (US\$70 million) in 1998, which was an increase of 46% from 1994 and 10% from 1997. The primary importers in Europe for natural dyes and colourants are Germany (32%), France (17%), Italy (14%) and the UK (10%). Besides this, in many countries the dyes are produced for local consumption which may also be about 1000 tonnes.

It is apparent from above that the present requirement of natural dyes is about 10,000 tonnes which is equivalent to 1% of the world synthetic dyes consumption.

4 Availability of Natural Dyes

From the information available on the internet, it is observed that there are over a dozen companies offering natural dyes, mostly in small packing. List of some of these companies is given in Table I. Mostly women dominate this activity. Some of the prominent among them are Michelle Wiplinger, Carol Todd, Carol Leigh and Trudy Van Stralen.

Alps Industries is one major natural dye producing company. The company has a production capacity of around 300 tonnes per year. Other Indian companies are: Satal Katha, Sam & Ram, Amma Herbal, D. Manohar Lal, etc.

Water extracts of natural dyes such as weld, chlorophyll, logwood and cochineal are also being produced by De la Robbia (Milan) since 1992. The dyes are sold in bulk as powders ready for use⁴.

Livos Pflanzenchemie Forschungs-und Ententwicklung GmbH has developed natural dyes in Germany. They are also marketing kits for use in a domestic washing machine to dye cloth⁴. Apart from these companies there are a large number of other manufacturers. Many of them produce only single dyes, namely indigo, lac, cochineal, catch, etc.

5 Technology for Production of Natural Dyes and Colourants

Technology for production could vary from simple aqueous to complicated solvent system to sophisticated supercritical fluid extraction techniques depending on the product and the purity being achieved. Purification may entail filtration or reverse osmosis or preparatory HPLC and drying of the product may be by spray or under vacuum or by a freeze drying technique. Analysis and characterization is another area of fundamental research, not only to identify new molecules of interest but also to authenticate valuable museum pieces. One can harness the catalytic ability of enzymes to hydrolyze the dye-cellulose bonds as is the case in the production of indigo, use microbes to generate anthraquinone-based colourants the way *Lusiffer Lacca* produces the lac dye or use biotechnological methods to increase the yield of colorants in plants.

6 Some Important Natural Dyes

Colouring matter could be obtained from all almost all vegetable matter. However, only a few of these sources yield colourants which can be extracted and work out to be commercially viable. Similar is the case of colourants obtained from animal origin.

Basically, three primary colours are required to get any given hue (or colour). This type of approach has been worked out for synthetic dyes. However, in the case of natural dyes, the dyeing procedures are different for different dyes and they cannot be blended to get the required colour easily. Nevertheless, while looking for different colours, it is better to

have a limited number of dyes with good fastness properties rather than having too many colours (sources) with limited fastness properties.

While selecting the proper palette of colours, one would like to have atleast one blue, one red and a yellow to start with. Due to the limited number of natural dyes available, the correct choice of the dyes is very important. Information on some important natural dyes is given bellow.

6.1 Blue Dyes

The Colour Index lists only three natural blue dyes; namely Natural Indigo, sulphonated Natural Indigo and the flowers of the Japanese 'Tsuykusa' used mainly for making awobana paper.

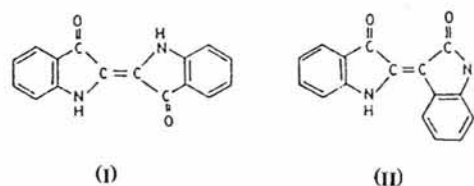
The only viable choice among the blue natural dyes is indigo. Natural indigo is obtained by fermenting the leaves of various species of *Indigofera*, running off the liquor and oxidizing it to precipitate the dye. Woad (*Isatis tinctoria* L.) is another important source of indigo. The plant is grown mostly in Northern Europe and the British Isles.

Until 1887, indigo was derived exclusively from plants. In that year more than 7,00,000 hectares of land in Bengal was cultivated with the indigo plant (*Indigofera tinctoria*). The annual production of pure dye was around 8,000 tonnes worth 100 million Marks (Rs. 240 crores, taking current value of DM = Rs. 24.00). Bengal produced 80% of the world production. Other growing regions were Java and Central America⁹.

With the synthesis of indigo in 1880 and its successful commercial exploitation in 1897 by BASF, the production of natural indigo decreased. The king of natural dyes went into oblivion. There are some signs of its revival.

The current demand of indigo in the country is estimated to be around 800 tonnes per year, priced at around \$ 20 million. This is equivalent to about 1/10 the production of natural indigo in the country in 1897.

The main ingredients of natural indigo are indigotin (I) and indirubin (II).



The same dyeing process is carried out with natural indigo as that used for the synthetic indigo. However, natural indigo has higher affinity and the dyed fabrics have better fastness.

6.2 Red Dyes

The Colour Index lists 32 red natural dyes. The prominent among them are madder (*Rubia tinctorum* L.), Manjeet (*Rubia cordifolia* L.), Brazil wood/Sappan wood (*Caesalpinia sappan* L.), Al or Morinda (*Morinda citrifolia* L.), Cochineal (*Coccus cacti* L.) and Lac dye (*Coccus laccae*). All these dyes are based on anthraquinone molecule except Brazil and Sappan wood based dyes. These dyes are prone to oxidation and hence are not suitable.

The most important colourants in madder are the anthraquinones, alizarin (III), purpuroxanthin (IV), rubiadin (V), manjistin (VI), purpurin (VII) and pseudopurpurin (VIII).

Madder has at least six identifiable components, all having different absorption maxima (i.e. different colour). Hence, the colour obtained from a given madder dye is the composite colour of all these compounds. Therefore, for getting consistent shade, dye should always be reformulated after extraction, purification, etc.

Madder has been used for many centuries and the cotton textiles dyed with it around 3000 BC are known from the Indus Civilisation. In the middle ages, madder became of great importance in Europe and was grown extensively in France and Germany. Between the sixteenth and eighteenth centuries, its production had become almost a Dutch monopoly and it was even exported to India for the expanding cotton industry¹⁰.

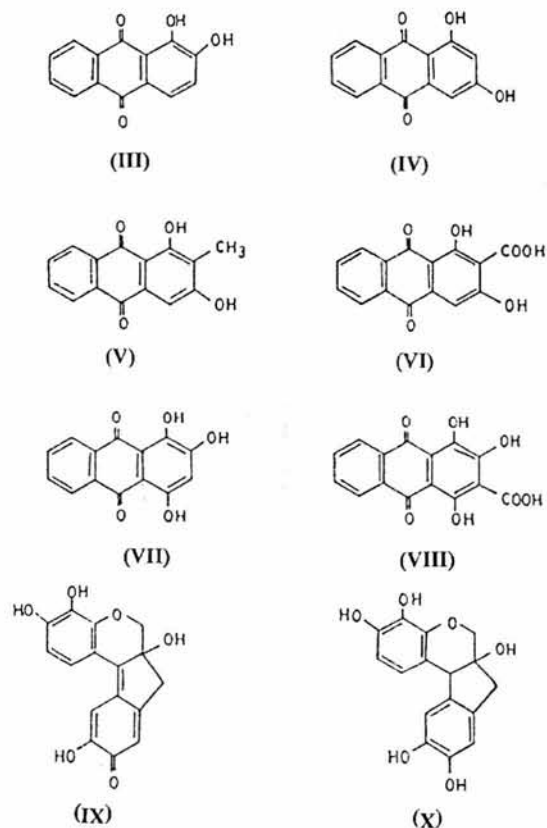
The strong and almost fadeless cotton dye known as turkey red was developed in India and spread from there to Turkey. It involved about twenty separate processes using wood, oil and rancid fat, charcoal, cow/sheep/dog dung, and liquid contents of animal stomach. Only the dyers and their families not surprisingly, occupied villages where the process was carried out. The use of madder declined abruptly following the development of synthetic alizarin in 1869.

Today, in India, most of the so called vegetable dye printed clothes of Rajasthan are printed with synthetic alizarin. Madder dye powder being produced in India costs about Rs 5000/kg. Good quality madder wood/root is priced at Rs 100 - 200/kg. It has about 3-4% dye, all of which is not recoverable.

Manjeet or Indian madder is another anthraquinone based red dye. The main colouring component of Manjeet is manjistin (VI). Other minor components found in Manjeet are purpurin (VII), pseudopurpurin (VIII) and pupuroxanthin (IV).

Manjeet was an important dye for the Asian cotton industry as the use of native plant was obviously much more economical than imported products. It is still used in Nepal in areas where interest in use of native dyes is being promoted. The whole plant, not just the roots, is dried and used to dye various fibres red and pinks.

Brazilin (C.I. Natural Red 24) is the main colouring component of *Caesalpinia echinata* Lam (Brazil wood) and *Caesalpinia Sappan* L. (Sappan wood). Brazilin (IX) gets oxidised to form the red Brasilein (X).



The use of Sappan wood is of great antiquity. It was exported from India to China as early as 900 BC. It is not known when the name was altered to Brazil wood. Brazil wood was known to Portuguese who first colonised South America in about 1500, where they found large number of similar trees growing and hence the named the country Brazil¹¹.

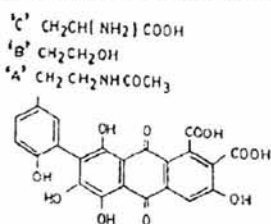
The dye is extracted from the wood by simply boiling it in water. The dye forms metal chelates with

alum, copper and chromium to give crimson black and purple shades respectively. These colours have poor light fastness.

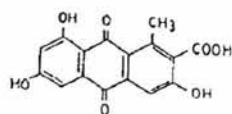
The most important red dyes of antiquity were all obtained from animal sources. Lac is perhaps one of the oldest of all known red dyes. However, cochineal and kermes were widely used in the western world for the production of bright purple and red colours.

The lac dye is extracted from lac, the resinous protective secretion of tiny insect, *Laccifer lacca*, which is a pest on a number of plants, both wild and cultivated. The secretions of the insect contain 1-2% dye.

There are four colouring compounds in lac, designated as laccaic acids A, B, C and D (XI, XII). Laccaic acid A is the most abundant. Laccaic acid is also called xanthokermesic acid and it closely resembles kermesic acid in structure.



(XI)



(XII)

Lac dye being an acid dye can be directly dyed on protein fibres such as wool and silk. It also produces very dark shades on nylon. The hues can be modified by post-mordanting treatment with metal salts. The dye has very good light and washing fastness.

Cochineal is another important natural red dye produced mostly as a food colour in Mexico and Peru (www.cochineal.cl/ingles.html). An International Congress on Cochineal and Natural Colours was held in Oaxaca, Mexico, last year to discuss the agronomical aspects, industrialization and uses, etc. (Source: IALC Online Newsletter).

6.3 Yellow Dyes

Yellow is the most common colour in the natural dyes. However, most of the yellow colourants are fugitive. The Colour Index lists 28 yellow dyes. Some of the important yellow dyes are obtained from Barberry (*Berberis aristata*), Tesu flowers (*Butea frondosa, monosperma*) and Kamala (*Mallotus philippensis*).

Other sources of yellow dyes are Black oak (*Quercus velutina*), Turmeric (*Curcuma longa*), Weld (*Reseda luteola*) and Himalayan rhubarb (*Rheum emodi*).

As a dye, barberry has been mentioned since the 14th century in the records of Christian monasteries. One of the most ancient centres of its use was the Mediterranean basin of North Africa and Turkey where this dye was used to dye carpets, tents, etc.

Wool and silk are kept, without boiling, in a dye bath composed of a decoction of the mashed plant until the desired intensity of colours is obtained. It turns brownish yellow on exposure to light. The roots, barks and stems are rich in alkaloids, essentially berberine (XIII)—the main colouring matter, accompanied by hydroxylated derivatives (XIV).

The main colouring pigment in Tesu flowers (*Butea monosperma*) is butein (XV), a calcone of orangish red colour. The dye from the flowers is extracted by boiling with dilute hydrochloric acid. The solution is then neutralized by sodium carbonate. To make colours more lively and fast, a decoction of lodh (*Symplocos racemosa*) or fruit of myrobolans (*Terminalia chebula*), both quite rich in tannins, is added to the dye bath by traditional dyers. Colours obtained range from orangish-yellow, ochre to brown depending on the mordant used. Colours have good fastness to washing and fair fastness to light.

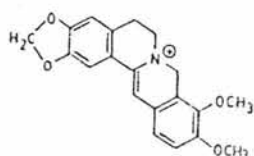
Kamala (*Mallotus philippensis*) is a small evergreen tree belonging to the Euphorbiaceae family, flowering in the forests of tropical Asia from India to Malaysia and Philippines, China and Australia. The tree bears fruits in the form of pods. The dye is an orange-red powder, which occurs as a glandular pubescence on these pods and is gathered by shaking the ripe capsules harvested in February - March.

The colouring matter of Kamala comprises several chalcones, such as rottlerin (XVI) and isorottlerin. The traditional method for dyeing with Kamala comprises single bath for mordanting and dyeing. The colour obtained is fast to soap, alkalis and acids but shows poor fastness to light. In combination with salts of tin, iron and copper, it gives a range of colours¹².

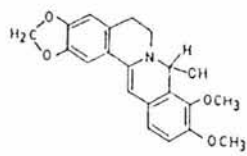
Another yellow natural dye of great importance is weld. It is grown throughout Europe, West Asia, North Africa and United States; however, it is not grown in India. The main colouring component of weld is luteolin (XVII). The yellow and olives produced by weld are light fast. In England, it was used with woad or indigo to produce the colour known as Lincoln or Kendal green. Weld has been gradually superseded by black oak which, weight for weight, produces a greater strength of colour.

An important anthraquinone-based yellow dye is extracted from Himalayan rhubarb (*Rheum emodi*). It

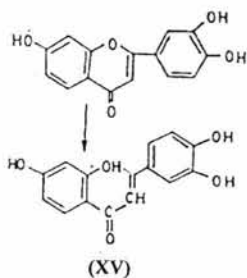
is a stout herb, grown mainly in the Himalayas from Kashmir to Sikkim. About 11,000 kg of rhizomes are collected annually from Kullu and Kangra valley of Himachal Pradesh. Rhizomes and roots are dug up in September from 3-10 year old plants, washed, cut into small pieces, dried and stored in airtight containers. Roots contain a number of anthraquinone derivatives the most prominent among them is chrysophanic acid (XVIII), the main source of the natural dye.



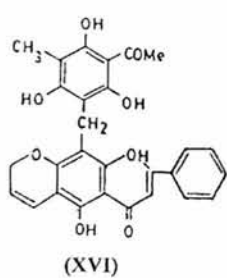
(XIII)



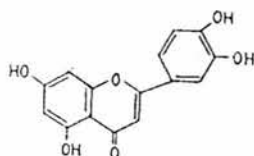
(XIV)



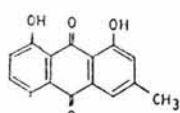
(XV)



(XVI)



(XVII)



(XVIII)

Wool and silk can be easily dyed in a range of colours with this dye. The colours obtained are yellow without any mordant, brown (Cu), olive green (Fe), red-violet (Cr) and bright yellow (Sn). Colours are very fast to light and washing.

7 Tannins

Tannins are the most important ingredients in the dyeing with natural dyes producing yellow, brown, grey and black colours. They also modify the affinity of fibres towards different dyes. A back tanning process improves the wash fastness of some dyes. However, the treatment with tannins makes dyeings dull.

Tannins are naturally occurring compounds of high molecular weight (about 500 – 3000) containing phenolic hydroxyl groups (1-2 per 100 Mw) to enable them to form effective crosslinks between proteins and other macromolecules. The term tannins was introduced by Seguin in 1796 to describe the substances present in number of vegetable extracts

which are responsible for converting putrescible animal skins into the stable product leather by tanning process.

In the dyeing of textiles, tannins form the basis of 'so called' natural mordant. As stated above, tannins are phenolic compounds, and those tannins, which have *o*-dihydroxy (catechol) groups, can form metal chelates, giving different colour with different metals. An after-treatment with metal salts not only alters the light sorption characteristics of tannins but also makes them insoluble in water. Hence, they are fixed on the textile substrate, giving good washing fastness.

Besides these reactions, it is postulated that tannins form following three types of bonds with proteins (e.g. wool and silk) and cellulose (e.g. cotton and viscose rayon):

- Hydrogen bonds between the phenolic hydroxyl groups of tannins and both the free amino and amido groups of protein, or the hydroxyl and carboxyl groups of other polymers.
- Ionic bonds between the suitably charged anionic groups on tannin and cationic groups on protein.
- Covalent bonds formed by the interaction of any quinone or semiquinone groups that may be present in the tannins and any other suitable reactive groups in the protein or other polymer.

The stability of the tannin-fibre bond depends on the pH, ionic strength and metal chelators.

The vegetable tannins may be divided structurally into two distinct classes depending on the type of phenolic nuclei involved and the way they are joined together.

7.1 Hydrolyzable Tannins

Tannins of this class are characterized by having as a core a polyhydric alcohol, such as glucose, the hydroxyl groups of which are esterified either partially or wholly by gallic acid or its congeners. Tannins having this structure can be readily hydrolyzed by acids, bases or enzymes to yield the carbohydrate and a number of isolable crystalline phenolic acids. Thus, they are called hydrolyzable tannins.

The other acid isolated from hydrolyzable tannins is ellagic acid. Therefore, sometimes the hydrolyzable tannins of vegetable origin are divided into two groups, namely gallotannins and ellagitannins. Some of the important raw materials for these tannins are: Myrobalan fruit (*Terminalia chebula*), Oak bark and

wood (*Quercus alibi* and other species), Sumac leaves (*Rheas typhoon*), Gall nuts (*Quercus infactoria*) and pomegranate rind (*Punica granatum*).

7.2 Condensed Tannins

Tannins of this class contain only phenolic nuclei. On treatment with hydrolytic reagents, the tannins of this class tend to polymerize, particularly in acid solution to yield insoluble amorphous often red coloured products known as phlobaphenes. Most tannins of this type are formed by the condensation of two or more molecules of flavan-3-ols, such as catechin.

Catechin was first isolated 140 years ago by Runge from the tannins of *Acacia catechu*. *Acacia catechu* is a deciduous tree of up to 25 m in height and is native to India, Burma and Sri Lanka. The colouring component obtained from this tree is popularly known as 'Cutch', which produces copper red colours on cotton, wool and silk of very good wash and light fastness.

8 Mordants

Mordants are considered as an integral part of the natural dyes or, to be more precise, the natural dyeing process by the most dyers of natural dyes. This is an anomaly, which continues to be perpetuated by different authors and practitioners of natural dyeing.

A close look at the chemical structures of natural dyes will show that these dyes, like synthetic dyes, also consist of vat dyes, acid dyes, basic dyes, disperse dyes, direct dyes and mordant dyes (i.e. dyes capable of forming a complex with metals). Many dyes can fall under more than one class of dyes. For instance, in the case of mordant dyes, there are dyes which have affinity for the fibre; however, their uptake as well as hue can be modified by pre-treatment or post-treatment with so called mordants. Hence, they can be placed in more than one class/category of dyes.

Tannins such as harda, tannic acid, etc. are considered natural mordants. By first dyeing, let us say cotton, with these compounds, one introduces additional hydroxyl and carboxyl groups in the fibre. These groups by themselves can only increase the dye uptake of basic dyes such as Barberine. A pre-treatment with tannic acid-tartar emetic combination was used for dyeing of, 'Mauviene', the first synthetic basic dye, on cotton as well as for dyeing of other synthetic basic dyes.

A subsequent treatment of the tannin-treated cotton with metal salts such as alum introduces aluminium ions in the fibre. The tannin-treated cotton at the

hydroxy or carboxy groups sorbs these ions, either by forming a metal-complex or metal salt. These metal ions then provide sites for the mordant dyes. Hence, introducing metal ions in the fibre, either directly or as tannin-metal complexes, can increase the affinity of cotton towards mordant dyes.

It is apparent from above that the tannins by themselves do not act as mordants but tannin-metal salt combination can only act as a mordant for the natural mordant dyes.

Alternatively, if one applies water-soluble salt such as alum to the cotton substrate and then insolubilizes this, say by treatment with alkali such as calcium carbonate or sodium carbonate, then an insoluble salt of aluminium is deposited in the material. The insoluble salt of aluminium provides the metal-chelating sites for the natural mordant dye. This kind of mordant treatment can form the basis to get bright shades of natural metal-complexing dyes. Allegro is perhaps the only natural dye manufacturing company that is marketing pre-dried aluminium hydroxide gels for use as mordant.

Since some of the natural dyes can form metal-complexes and thereby give different colours, there is a tendency to use all types of metal salt for this purpose. The restrictions to the use of metal salts have been put by the famous 'German Ban'. Accordingly, the indicative maximum permissible quantities of different metals in the ultimate product are as follows: As (1.0 ppm), Pb (1.0 ppm), Cd (2.0 ppm), Cr (2.0 ppm), Co (4.0 ppm), Cu (50 ppm), Ni (4.0 ppm), and Zn (20 ppm).

The upper limits of the presence of metals vary from product to product and are different for different Eco-Marks. However, there is no upper limit on aluminium, iron and tin. The upper limit on copper is also fairly high. Hence, the salts of these metals could be safely used for complexing and mordanting. However, their quantities should be optimized so as to minimize the pollution load.

Similarly, anionic and cationic sites can be created on the cotton fibre by pre-treatment with suitable chemicals/ polymeric compounds to modify its affinity for various natural dyes. Such pre-treatments can also qualify to be covered under the broad category of mordants.

9 Application of Natural Dyes

A classification of natural dyes on the basis of their application procedure has been given by Gulrajani¹³. As a guideline, the classification of some of the

common natural dyes is given in Table 2. It is apparent from the table that some of the dyes can be placed in more than one dye class.

The procedures of application of these dyes are similar to those followed in the case of synthetic dyes. For example, the natural indigo is dyed by the same procedure as the synthetic indigo. Both are vat dyes.

Madder, being a mordant dye for cotton, requires creation of dye-sites in the fibre before the dyeing is carried out. Conventionally, this was being done by first applying a water-soluble aluminium salt such as alum and then converting it into an insoluble salt by treating it with calcium hydroxide. The aluminium-calcium salts precipitated into the fibre acted as sites for the madder dye. This formed the basis of the famous Turkey Red colour.

The process at some stage got modified wherein the material was first treated with tannin-containing plant material which provided sites for aluminium to form complex as described above. Thus, the tannin-alum treated cotton became the base material for the dyeing of madder and other such dyes.

Since wool, silk and nylon have cationic groups in the form of protonated amino groups, these fibres can be dyed with natural acid dyes such as lac under acidic pH in the same manner as synthetic acid dyes. Lac can be post-mordanted to give dye-metal complexes. Hence, it is not only an acid dye but also a mordant dye (like chrome-mordant dyes among the synthetic dyes).

The chemical structures of many natural dyes are similar to those of synthetic disperse dyes in the sense that they do not have solubilizing groups and are only sparingly soluble in water. Hence, they can be dyed on hydrophobic fibres such as polyester and nylon.

Table 2—Classification of natural dyes on the basis of application properties

Botanical name/source	Common name	Dye class
<i>Indigofera tinctoria</i>	Indigo	Vat
<i>Rubia tinctorum</i>	Madder	Mordant/Disperse
<i>Rubia cardifolia</i>	Manjeet	Acid/Mordant/ Disperse
<i>Ceasalpinia sappan</i>	Sappanwood	Mordant/Disperse
<i>Laccifer lacca</i>	Lac dye	Acid/Mordant
<i>Berberis aritata</i>	Berberine	Basic
<i>Butea frondosa, monosperma</i>	Tesu	Mordant/Disperse
<i>Mallotus philippensis</i>	Kamala	Mordant/Disperse
<i>Rheum emodi</i>	Dolu	Mordant/Disperse
<i>Quercus infectoria</i>	Gall nuts	Acid/Mordant
<i>Acacia catechu</i>	Cutch	Acid/Mordant/ Disperse

Furthermore, these dyes can be directly dyed on wool and silk since these dyes also have some limited affinity for these fibres. However, these dyes can be fixed onto the fibres by post-mordanting treatment with metal salts.

For getting the compound shade wherein more than one dye is required to be used, the same principle as adopted for synthetic dyes works. That is the natural dyes, which can be dyed under identical condition, can be mixed and dyed together. However, a post-mordanting treatment may not work out successfully unless mastered carefully.

By scientifically understanding and analyzing the chemical structure of the natural dyes, a suitable method could be worked out for the application of these dyes on different substrates. A challenge an enlightened dyer has to face if he or she is planning to venture in this field.

10 Fastness of Natural Dyed Materials

Natural dyes are considered fugitive even though one finds many fabrics dyed with natural dyes in museums, wherein the cloth has retained its original colours throughout the centuries of exposure.

Poor light fastness of some of the natural dyes can be attributed to the inherent propensity of the dye chromophore to photochemical oxidation. The chromophore in some cases can be protected from photochemical oxidation by forming a complex with transition metal, whereby a six membered ring is formed. The photons sorbed by the chromophoric groups dissipate their energy by resonating within the ring and hence the dye is protected.

It is apparent from above that a post-treatment with a metal salt can result in an improvement in the light fastness of some natural dyes. However, a post-treatment with metal salt also results in change of the hue. Therefore, the post-treatment should be chosen carefully. This type of post-treatment with copper or chromium or combination of their salts is given to some synthetic dyes to improve their wash and light fastness.

The poor wash fastness of many natural dyes is mainly attributable to following factors:

- Weak dye-fibre bond between the natural dye and the fibre.
- Change in hue due to the breaking of the dye-metal complex during washing.
- Ionization of the natural dyes during alkaline washing. Since most of the natural dyes have hydroxyl groups which get ionized under alkaline

conditions, many fabrics dyed with natural dyes under acidic conditions change colour on washing with alkaline detergents or soap.

The wash fastness of some of the natural dyes could be improved by a post-treatment with alum or a dye-fixing agent, which results in the formation a dye-fibre complex or a crosslink between the dye and fibre respectively.

Tannins, being large molecular compounds, do not diffuse into the fibre easily. Hence, dyeings based on tannins show poor rub fastness on cotton. One can do very little about it except limiting the quantity of the tannin used.

To have a palette of colour with good fastness properties, one has to experiment and fill the knowledge gap.

11 Imperatives to the Use of Natural Dyes

- One of the major imperatives to the use of natural dyes is the knowledge gap. Very few serious attempts have been made to generate new information on the use of natural dyes. Most of the research in this area is carried away by the empirical information reported in literature that does not have any scientific reasoning or basis.
- Non-availability of the natural dyes in the standardized form, which may be powder, paste of solution. Using the raw material for dyeing has many limitations. Besides its being of unknown composition, it generates considerable amount of biomass that is cumbersome to handle in the dyehouse.
- Severe shortage of trained dyers. Most of the textile chemists in the country are trained to use synthetic dyes. Even the teachers have very poor appreciation for this centuries-old technology of dyeing. If this technology is to be used for generating revenue, employment and for creating

a strong base for renewable resources for the dye industry, a comprehensive training programme has to be launched, may be by making it a part of the syllabus.

- Dearth of books on the technology of dyeing with natural dyes providing the scientific basis to the subject.
- Adverse publicity being given to natural dyes, spearheaded by the synthetic dye manufacturing companies. Some of the points being overemphasized are discussed above. It must be kept in mind that natural dyes are not substitutes of synthetic dyes. They have their own market and any expansion in this market is not going to be at the cost of synthetic dyes. Some of the limitations of natural dyes, such as use of banned metal salts, poor fastness properties and use of agricultural land for growing natural dye-plants, being highlighted can be easily overcome by R&D.

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