World Skill Development Institute

Natural Dyes Technology

Course Duration – 1 Year

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources. Dyeing is the process of imparting colors to a textile material. Different classes of dyes are used for different types of fiber and at different stages of the textile production process, from loose fibers through yarn and cloth to completed garments. There are technologies that manufacture the pigments for plastics, rubber and cosmetics. Therefore; dyes and pigments have a vast area of applications and have a huge demand in industry. Contrary to popular opinion, natural dyes are often neither safer nor more ecologically sound than synthetic dyes. They are less permanent, more difficult to apply, wash out more easily, and often involve the use of highly toxic mordant. Of course, the colour possibilities are far more limited; the color of any natural dye may be easily copied by mixing synthetic dyes, but many other colors are not easily obtained with natural dyes. However, some mordant are not very toxic, and the idea of natural dyestuffs is aesthetically pleasing. Applying natural dyes in your fabric production using enzymes will reduce your production cost and improve control. There are various kind of natural dyes; quinonoid dyes, cyanine dyes, azo dyes, biflvonyl dyes, omochromes, anthraquinone, coprosma gesus etc. The use of natural dyes in cloth making can be seen as a necessary luxury to trigger off a change in habits. Dyes which stand out for their beauty and ecological attributes would never be employed on just any material but on noble fabrics such as wool, silk, linen or cotton, made to last more than one season. Market value will benefit from consumer preferences for environmentally friendly products, which will support consumption of high performance dyes and organic pigments.

This course basically deals with the use of carotenoids as food colours , bianthraquinones and related compounds, intermediate degradation products of biflavonyls, dyestuffs containing nuclear sulphonic and carboxylic acid groups, quinonoid dyes, cyanine dyes, optical whitening agents, natural dyes for food, stability of natural colourants in foods effect of additives, pyrimidine pigments, the total synthesis of the polyene pigments, red pigment from geniposidic acid and amino compound, effect of acid and amine on the formation of red pigment from

geniposidic acid, effect of the substituted position of amino group and chain length of amino compound etc.

Natural dyes comprises of those colourants (dyes and pigments) that are obtained from animal or vegetable matter without chemical processing. They are mainly mordant dyes although some vat, solvent, pigment, and acid types are known. Natural dyes fall into three categories on the basis of their origin; plant/vegetable origin, Insect/ animal origin and mineral origin. Some of the examples of plants used for producing natural dyes are; Al, Alkanet, Balsam, Bougainvillea, Canna, Tulsi, Terminalia Arjuna, etc. India has a very rich tradition of using natural dyes. The art and craft of producing natural dyed textile has been practiced since ages in many villages by traditional expert crafts persons in the country. Natural dyes, when used by themselves have many limitations of fastness and brilliancy of shade. However, when used along with metallic mordants they produce bright and fast colours. The use of metallic mordants is not always eco friendly, but the pollution problems created by metallic mordants are of very low order and can be easily overcome. Therefore, instead of using unsustainable technology for producing colours one can use mild chemistry to achieve almost similar results. There is a growing demand for eco friendly/non toxic colorants, specifically for health sensitive applications such as coloration of food and dyeing of child textile/leather garments. Recently, dyes derived from natural sources for these applications have emerged as an important alternative to potentially harmful synthetic dyes and pose need for suitable effective extraction methodologies. Natural dyes also referred as mordant dyes; do not readily adhere to cotton so mordants are used. Mordants are needed to set the colour when using natural dyes. It is thus a chemical agent which allows a reaction to occur between the dye and fabric. Some of the important natural dyes are blue dyes, red dyes, yellow dyes, etc. Natural dyes can produce special aesthetic qualities, which, combined with the ethical significance of a product that is environmentally friendly, gives added value to textile production as craftwork and as an industry.

Some of the fundamentals of the course are history of natural dyes, promotion of natural dyes, sources of natural dyes, constitutional aspects, requisites of a true dye, types of dye, chemical entities responsible for colors, classification based on chemical nature, classification based on colors, basics of natural dyeing, advantages of natural colors/vegetable dyes, natural dyeing principles, nature of material to be dyed, measurements of mordants and dyestuffs, temperature, mordanting the textiles for natural dyeing, standardization of vegetable dyes, quality standards for vegetable dyes, methods of dye extraction etc.

Due to pollution problems in synthetic dyes and pigments industry, the whole world is shifting towards the manufacturing of natural dyes and pigments. The course describes the step wise methodology of extraction, mordanting, dyeing with pictures of the actual plants part used for extraction of Natural dye. This course contains techniques of producing different natural dyes

and pigments, which has huge demand in domestic as well as in foreign market. It is hoped that entrepreneurs, technocrats, existing units, institutional libraries will find this course very useful.

Part - 1

1. HISTORY OF NATURAL DYES

Promotion of Natural Dyes

Sources of Natural Dyes

Constitutional Aspects

Requisites of a True Dye

Types of Dye

Chemical Entities Responsible for Colors

Classification Based on Chemical Nature

Classification Based on Colors

Classification Based on Colors

2. BASICS OF NATURAL DYEING

Advantages of Natural Colors/Vegetable Dyes

Natural Dyeing Principles

1. Nature of Material to be Dyed

2. Measurements of Mordants and Dyestuffs

3. Temperature

4. Agitation

5. Natural Dyes are Unpredictable

6. Wet Fibers Look Darker

7. Rinsing

8. Using Natural Dyes

Mordanting

Mordants

Mordanting of Cotton

Preparation of Fabric for Dyeing

Modifier

pH

Safety Measures Required in Natural Dyeing

Disposal of Mordants and Dyes

Vat Dye

Overdyeing

3. MORDANTING THE TEXTILES FOR NATURAL DYEING

Treatment of Fabric Before Dyeing

Methods of Mordanting

Common Mordants used in Natural Dyeing

4. STANDARDIZATION OF VEGETABLE DYES

Quality Standards for Vegetable Dyes

5. METHODS OF DYE EXTRACTION

Methodology

Subcritical Water Extraction

Al

Alkanet

Balsam

Bougainvillea

Canna

Carthamus

Cassia Fistula

Cineraria

Cosmos

Eucalyptus Bark

Osbeckia Chinensis

Parkia Javanica

Pomegranate

Sappan Wood

Tectona Grandis

Terminalia Arjuna

Tulsi

6. DYEING METHODOLOGY

Materials

Selection of Plant Sources for Dye Extraction

Extraction of Colorants

Aqueous Extraction

Solvent Extraction

Equipment used for Dyeing and Analysis of Dyed Fabric and their Principle

Sonicator

Ultraviolet and Visible Spectrophoto-meter

Fourier Transform Infra Red Spectroscopy

Gas Chromatograph Mass Spectrometer

Inductively Coupled Plasma Optical Emission Spectrometer

Gas Chromatograph

Xenoster

Wash Wheel

Perspirometer

Crock Meter

Material to be Dyed

Specification of the Fabric

Physical Characteristic of Cotton

Chemical Composition of Cotton Fiber

Chemicals and Reagents Used

Methodology

Preparation of Cloth For Dyeing

Desizing

Scouring

Bleaching

Treatment of Fabric Before Dyeing

Pre Mordanting

Post Mordanting

Dyeing

Assesments Of Eco Friendliness

Assessment Of Antimicrobial Properties

7.CHEMISTRY OF DYE

Basic Concept of Dyes Color

Relation Between Color and Constitution

Characterization of Natural Dyes

Solubility Studies

1. Thin Layer & Column Chromatographic Studies

2. Ultra Violet-visible Spectrophoto-metric Studies

3. Fourier Transform Infra-red Studies

4. High Performance Liquid Chromato-graphic Studies

5. Gas Chromatography Mass Spectro-photometric Studies

Mordants used in Dyeing

Mordant

Tannins and Tannic Acid

Metal Salts or Metallic Mordants

Oil Mordants

Techniques used for Dyeing

Mechanism of Dyeing

Fastness Properties

Fastness Properties of Dyed Materials

Evaluation of Eco-friendliness

Companies Selling through Natural Dyes through Internet

Estimates of Dye Requirements

Some Important Natural Dyes

Blue Dyes

Red Dyes

Yellow Dyes

8. SOME RECENT PUBLICATIONS ON NATURAL DYES

1. Dyeing Cotton, Silk and Wool with Brassica Oleracea or Purple Cabbage

Introduction

Vegetable Chosen

Studies on Cotton, Silk and Wool

Chemicals Used

Nature of the Colorant

Extraction of Colorant

Optimization of Extraction Condition

Extraction Amount and Time Required

Extraction Temperature

pH of Extraction Medium

Mass to Liquor Ratio

Determination of pKa

Chemical Characterization of the Colorants

Treatment of Fabric before Dyeing

Dyeing

9. Commercial Viability of Dyeing Cotton with Aqueous Extract of Lawsonia (Heena) Using Eco friendly Mordants

Introduction

Materials and Methods

Fastness Testing

Dyeing Cost

Results and Discussion

For Eco-friendliness

Pesticides

Characterisation of Eco-Friendliness

Conclusion

References

Part - 2

1.Ommochromes

Distribution

A. Ommatins

B. Ommins

Isolation and Purification

A. Ommatins

B. Ommins

Structure of the Ommochromes*

Xanthommatin

Ommatin D

Rhodommatin

Ommin A X

Biogennesis

2.Bisdehydrocanthaxanthin

3.Carotenoids Field

Carotenoid Biogenesis

Carotenoid Total Syntheses

The use of Carotenoids as Food Colours

4.Black pigments

Animal Pigments

Melanins

Sclerotization

Plant Pigments

Humic acids

1,8-Dihydroxynaphthalene polymers

5.Anthraquinone

Plant Pigments

Insect Pigments

6.Coprosma genus

7.Bianthraquinones and related compounds

Skyrin

Oxyskyrin

Skyrinol

Iridoskyrin

Rugulosin

Luteoskyrin and Rubroskyrin

Lumiluteoskyrin

Flavoskyrin

Biogenesis

8.The Biflavonyl Pigments

The First Investigations

The Work of Nakazawa on Ginkgeting

The Work of the Bristol Group

On Ginkgetin and Isoginkgetin

The Work of Kariyone and Kawano on

Sciadopitysin, 1956

Further Work of Brispol Group on

Ginkgetin and Sciadopitysin

The Work of Kawano on Sciadopitysin and GINKGETIN, 1959

The Synthesis of Ginkgetin Tetramethyl ether, Nakazawa, 1959

The Structure of Ginkgeting

The Structure of Isoginkgetin

The Structure of Kayafyavone

The Structure of Sotetsuflavone

Summary of Biflavonyl Structures

Intermediate Degradation Products of Biflavonyls

Optical Inactivity of the Biflavonyls

The Structure of Hinokiflavone

Natural Occurence of Biflavonyls

9.Azo dyes

10.Dyestuffs

Introduction

Primary Products for VS-Dyestuffs

1. Methods of preparation

2. Reactions

Processes for the Manufacture of VS-Dyestuffs

Fastness and Dyeing Properties of VS-Dyestuffs

1. VS-Dyestuffs free from nuclear sulphonic and carboxylic acid groups

2. Dyestuffs containing nuclear sulphonic and carboxylic acid groups

Summary

11.Disperse dyes

Light Fastness

Gas Fastness

Sublimation Fastness

Wash Fastness

Structural Modifications Leading to All-Round Fastness

12.Quinonoid dyes

13.Cyanine dyes

Chemistry of 2, 3-Dichloro-1,4-Naphthoquininone (I)

Chemistry of Chloranil (II)

Vat Dyes from Chloranil

Benzodipyrrocolinequinones Pyrrocolinequinones,

Unsymmetrical Dipyrrocolinequinones and Naphth of Uranopyrrocolinequinones

2-alkylamino-(arylamino)-3-chloro-1,

4-naphthoquinones And Di-3-(2-chloro-1,

4-naphthoquinonyl)-alkylamines And Arylamines

Cellulose Acetate Dyes From (i) And (ii)

Sinthesis Of Non-coplanar Quinonoid Dyes

14.Fluorescent brightening agents

15.Optical whitening agents

Introduction

Physical Considerations of Fluorescence and Optical Whitening

Chemical constitution of Optical Whitening Agents

1. Stilbene derivatives
2. Benzidine derivatives
3. Benzthiazole, benzoxazole and benziminazole derivatives
4. Coumarins
5. Pyrazolines
6. Other types

Some Specific Applications of Optical

Whitening Agents

1. Soaps and detergents
2. Textile applications

16.Natural dyes for Food

Complex formation

Copigmentation

Condensation

Chemical modifications

Porphyrins

Others

17.Pyran Pigments : I. Flavones and Flavonols

Flavones

Chrysin (IV)

General Methods of Synthesis of Flavones

A. From Aromatic Diketones

B. From o-Hydroxyacetophenones

C. From o-Hydroxychalkones

D. From Phenols

Flavonols

The Wessely-moser and Related

Rearrangements of Flavones

The Formation of Salts by Flavones and Flavonols

The Reduction of Flavones

Isoflavones

The Synthesis of Isoflavones

18.Pyran Pigments : II. Anthocyanins and Anthocyanidins

Cyanidin (III)

The Synthesis of Anthocyanidins

The Synthesis of Anthocyanins

Color Reactions of The Anthocyanidins and Anthocyanins

Anhydrobases

Carajurin (XCIX)

Dracorubin (CXXV)

19.Pyran Pigments : III. Xanthones

Ravenelin (II)

Mangostin (XI)

Pyran Pigments : IV. Rottlerin

Pyran Pigments : V. Brazilin and Mematoxylin

Brazilin (XXXII)

Hematoxylin (XL)

Trimethylbrazilone (XLI)

Brazilein (LXXIX, R - H)

The Synthesis Of Brazilin

Pyrrole Pigments : I. The Porphyrins

Hemin (cxxxvii)

The Synthesis of Dipyrrylmethenes

The Synthesis of Porphyrins

The Structure of Hemin

Pyrrole Pigments : II. Chlorophylls

Pheoporphyrin, Chloroporphyrin, and Phylloerythrin

The Vinyl Group in Chlorophyll

The Structure of Chlorophyll

Position of the Phytyl Group in Chlorophyll

The Phase Test

Allomerization

Approaches to the Synthesis of Chlorophyll

Chlorophyll-b

Bacteriochlorophyll

20.Pyrrole Pigments : III. The Bile Pigments

Bilirubin (XXXII)

Verdins

Violins

Bilenes

Bilanes

Stereochemistry and Tautomerism

Complex Salts of the Bile Pigments

Pyrrole Pigments : IV. Prodigiosin

21.Pyrimidine Pigments : The pterins

The Gmelin Reaction

Pterorhodin

22.Quinonoid Pigments

Benzoquinonoid Pigments

Perezone (XII)

Polyporic Acid (XIV)

Astromentin (XXVIII)

Phoenicin (LXI)

Napthaquinonoid Pigments

Lapachol (LXXI)

Eleutherin (CXXI)

Alkannin and Shikonin (CXLIX)

Anthraquinonoid Pigments

Helminthosporin (CLVIII)

Kermesic Acid (CLXI)

Skyrin (CLXXVIII)

Extended Quinone Pigments

The Aphin Pigments

Erythroaphin-fb (CCXVI) or (CCXVII)

Hypericin (CCXXV)

23.Polyene Pigments

Bixin (X) and Croceting (XI) the Carotenes

b-Carotene (LV)

Lycopene (LXXIII)

The Total Synthesis of the Polyene Pigments

Combination of Units in the Order C19 + C2 + C19

Combination of Units in the Order C16 + C8 + C16

Combination of units in the Order C14 + C12 + C14

Combination of Units in the Order C10 + C20 + C10

The Dehydro - Retrodehydrocarotenoids Epoxides

and Furanoid Oxides

24.Anthocyanins from Indian varieties of Grapes

Material and Methods

Extraction

Purification

Total anthocyanins

Separation

Partial hydrolysis of anthocyanin

Aglycone and sugar

Acyl moieties

Spectral measurements

Thin layer chromatography

Results and Discussion

Recovery of anthocyanin

Separation of pignnents by paper chromatography

Absorption spectra of pigments

Partial hydrolysis of anthocyanins

Aglycones

Sugar identification

Acyl moieties

25.Red pigment from Geniposidic Acid and Amino Compound

Materials and Methods

Preparation of geniposide (GS) and GSA solution

Preparation of other iridoid compounds

Enzyme and reagents

General method of preparation of pigment

Evaluation of pigment

Identification and quantification of carbon dioxide

HPLC and NMR measurement

Structural relationship of iridoids to red pigment production

Acidity and evolution of carbon dioxide

Time course of enzymic reaction

Acidity and atmosphere on the reaction

HPLC monitoring of the pigment formation from GAA and a-alanine

NMR monitoring of the pigment formation from GAA and methylamine

Results and Discussion

The relationship between the evolution of carbon dioxide and reaction pH

The process of formation of red pigment

Molecular mass and colour evaluation of red pigment derived from GAA and a-alanine

NMR spectroscopy of red pigment formed from GAA and methylamine

Monitoring of the reaction by NMR

The formation mechanism of red pigment

26.Effect of Acid and Amine on the formation of Red Pigment from Geniposidic Acid

Materials and Methods

Preparation of geniposide (GS)

Preparation of geniposidic acid (GSA) solution

Enzyme and reagents

General procedure for the red pigment formation

Evaluation of pigment

Kind of acid

The concentration of organic acid

The substituted position of amino group and chain length of amino compound

Kind of amino compound

Results and Discussion

Effect of acidz

Effect of the substituted position of amino group and chain length of amino compound

Kind of amino compound