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Application of natural mordants on textile

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ABSTRACT

Dyes do not interact directly with the materials they are intended to colour. Natural dyes are substantive and require a mordant to fix to the fabric, and prevent the colour from either fading with exposure to light or washing out. These compounds bind the natural dyes to the fabrics. A mordant is an element which aids the chemical reaction that takes place between the dye and the fibre, so that the dye is absorbed. Use of metal salts mordants in naturally dyed textile products make them not fully environmental friendly. Some plant based natural mordants are being used as a mordant. This study forms an important basis on which many more natural materials can be developed to be used as mordants when dyeing not only cotton but other textile products made from other fibers.

Key Words : Natural dye, Natural mordant, Fastness property, Eco-dyeing

INTRODUCTION

The word “mordant” comes from the French word “Mord” or “to bite” and mordants can be described as metallic salts with affinity for both fiber and dyes stuffs and that improves the colour fastness. Even some of the fugitive dyes have been used successfully with the help of mordants. (Vankar, 2007). It helps in absorption and fixation of natural dyes and also prevents bleeding and fading of colours *i.e.*, improves the fastness properties of the dyed fabrics. The majority of natural dyes, whether chemical dyes or natural dyes, adhere to the fiber through a chemical bond. With straight dye and fiber, this bond is easy to degrade and break. However, some compounds can cause the dye to adhere to the fiber. These compounds are called mordants, and are usually metal salts. Some of the important mordants used are alum, potassium dichromate, ferrous sulphate, copper sulphate, zinc sulphate, tannin, and tannic acid. Although these metal mordants contribute to developing wide gamut of hues after complexing with the natural colouring compounds, most of these metals are toxic in nature and only in trace quantity their presence is found to be safe for the wearer.

Limitation on colour yield and poor fastness properties prompted a search for ideal mordants, the chemicals which increase natural dye uptake by textile fibers. Different types of mordants yield different colours even for the same natural dye. Therefore, final colour, their brilliance and colour fastness properties are not only dependant on the dye itself but are also determined by varying concentration and skillful manipulation of the mordants.

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Improving the quality of natural dyes :

The term mordant is used for chemicals which usually have a metal with a valency of at least two or more, they can also be other types of compound as well. Natural dyes also referred as mordant dyes; do not readily adhere to cotton so mordants are used. Mordants are needed to set the color when using natural dyes. Different mordants will give different hue color with the same dye. A mordant is thus a chemical agent which allows a reaction to occur between the dye and the fabric. In textiles, mordants are used to fix the color in dyeing or fabric printing, especially for fabrics of plant origin (cotton).

Poor light fastness of some of the natural dyes is attributable to photooxidation of the chromophore. We have tried to prevent!, minimize such photooxidation by forming complex of the dye with transition metal. We have improved the washing fastness of natural dyes by treatment with eco-friendly mordants such as alum, stannic chloride, stannous chloride and ferrous sulphate. We have also used tannins with mordants. Treatment with metal salts alters the light absorption characteristics of tannins in addition to making them insoluble in water with the fabric acquiring washing fastness.

Types of mordant :

A mordant is more important than the dye itself. Moreover, the ideal mordant for bulk use should produce appreciable colour yield in practicable dyeing conditions at low cost, without seriously affecting physical properties of fibre or fastness properties of the dyes. Also, It should not cause any noxious effect during processing and the dyed textile material should not have any carcinogenic effect during use. Mordants can be broadly classified into three types:

Metallic mordants:

They are generally metal salts of aluminum, chromium, iron, copper andtin. The metallic mordants are of two types.

Brightening mordants:

a) Potash alum, b) Chrome (potassium dichromate), c) Tin (stannous chloride)

Dulling mordants :

a) Copper (cupric sulphate), b) Iron (ferrous sulphate)

Tannins :

Tannins are polyphenolic compounds having capacity of gelling under certain conditions. Among the tannins, myrobalan (harda) and galls/sumach are most important. Tannic acid is available in its natural form and can be extracted from number of vegetables. Oak galls, sumach, cutch and some barks are all rich in tannic acid. Dyestuffs that contain tannin such as black oak, pomegranate, cutch, fustic, etc. do not need an additional tannin mordant. Some of these tannic acid rich sources may also contain dyes, and so this may affect the resultant colour after dyeing has taken place, resulting in darker and less brilliant colour (Bohmer, 2002).

Certain plant materials contain high concentrations of tannic acid, or tannin, which works well as a mordant to bond color to plant-based fiber. Tannin as a mordant, especially in combination with alum, can provide a greater color range with more successful results on most vegetable fibers. Certain tannin-bearing plant materials work especially well as mordants, such as horse chestnuts,

pine bark, certain roots, some leaves, acorns, oak galls, pomegranate rind, and some fruits. Among the plant-based mordants, oak galls contain the highest amount of tannic acid. Some tannin substances will bind to the fiber and stay clear, allowing the true color of the dye source to saturate the fiber. But some tannins can alter the color by making it dull, especially if the dyes are yellow, pink, or brown tones.

Table 1 : Tannin producing plants and their tannin content

Sr. No.	Botanical name	Common name	Parts Tannin content	(%)
1.	*Acacia catechu*	Khair	Wood	57-60
2.	*Acacia mollissima*	Mimosa	Bark	35-36
3.	*A. mearnsil*	Black Wattle	Bark	35
4.	*A. nilotica*	Babool	Bark	12-18
5.	*Anogeissus latifolia*	Dhawada	Leaves	16-18
6.	*Anacardium occidentale*	Cashew	Leaves	20-25
7.	*Astroniumbalansal*	Urun day	Wood	10
8.	*Casealpinia brevifolia*	Algarbilla	Pods	50
9.	*C. coriaria*	Dividiv	Pods	35-50
10.	*Cassia auriculata*	Avaram	Bark	15-20
11.	*C. fistula*	Amaltas	Bark	9-12
12.	*Castanea* spp	chestnut	Wood	30
13.	*Casuarina equisetifolia*	Casuarina	Bark	7-8
14.	*Ceriops roxburghiana*	Goran	Bark	20-40
15.	*C. Tagal*	Goran	Bark	20-40
16.	*Cleistanthus collinus*	Karad	Bark	23-27
17.	*Emblica officinails*	Amala	Stem Bark, Fruit, leaves	8-9,21-24
18.	*Ecualyptus occidentalis*	Mallet	Bark	40
19.	*Eucalyptus* spp.	*Eucalyptus*	Bark and wood	55
20.	*Eugenia jambolana*	Jamun	Bark	13-19
21.	*Hopea parviflora*	Hopea	Bark	21
22.	*Larix* spp.	Larch	Bark	10
23.	*Mangifera indica*	Mango	Bark	17
24.	*Peltophorum ferrugineum*	Peltophorum	Bark	20-22
25.	*Pithecelobium dulce*	JungliJalebi	Bark	30-35
26.	*Punica granatum*	Pomegranate	Fruit and Rind	26
27.	*Quebracho colorado*	_	Heart Wood	20-27
28.	*Quercus aegilops*	Oak	Bark	30
29.	*Q. marolepis*	Valonia	Cup and Bread	25-30
30.	*Q. montana*	Chestnut oak	Bark	6-15
31.	*Rhizophora mucronata*	Mangrove	Bark	30
32.	*Rhus.* spp.	Sumach	Leaves	20-35
33.	*Rhus pentaphylla*	Tizrah	Roots and Wood	30
34.	*Shorea robusta*	Sal	Bark	7-9
35.	*Terminalia alata*	Saja,Laurd	Bark	15
36.	*T. arjuna*	Arjun	Bark	23
37.	*T. bellirica*	Beheda	Nut	12
38.	*T. chebula*	Myrobalan	Nut	30-55
39.	*T. tormentosa*	_	Fruit	10-23
40.	*T. suga*	Hemlock	Bark	25
41.	*T. heteropkylla*	West.hemlock	Bark	25
42.	*Tamarindus indica*	Tamarind	Fruit	20
43.	*Uncaria gambir*	Gambier	Leaves	35-40

Oil type mordants :

Vegetable oils or Turkey red oil are such type of mordants. Turkey red oil as mordant is mainly used in the dyeing of deep red colour from madder. The main function of turkey red oil as oil mordant is to form a complex with alum when used as a main mordant. Sulphonated oil possess better binding-capacity than the natural oils. Oil mordanted samples exhibit superior fastness and hue.

Plant-based mordants :

Acorns : Acorns can be collected under oak trees in autumn, or you can buy acorn powder from specialty herbal or grocery stores. Grind foraged acorns to a powder, removing the shells, and soak the acorn material in water for several days to get the full color intensity. Acorns create colors from light beiges to grays and teal blues.

Oak galls : Oak galls are formed where wasps have laid their eggs on oak tree branches. The galls look like balls sticking to the branch. Galls make an excellent mordant, especially for vegetable fibers, and can be collected from many kinds of trees, especially oak trees (*Quercus* species). Oak galls have extremely high tannin content, which is also found in plant sources like bark and leaves, and is a natural mordant. It enhances the dye color as well as improving colorfastness. Alum can be used to treat fiber with tannin in one or two dye baths to achieve even stronger color results.

Pomegranate rind : The powdered rind, or skin, of the pomegranate (*Punica granatum*) can be used as a tannin mordant, as well as a dye to obtain peachy yellow with alum mordant, and to get gray to moss green with iron mordant. Pomegranate rind was also used as a color source for painting medieval illuminated manuscripts. The age of the fruit affects the color of the dye: the less ripe the fruit, the greener the yellow.

Juniper needles : A natural mordant can be made from the needles of the juniper tree (*Juniperus communis*). Gather the dry branches and burn them over a wide container. Catch only the needle ashes, and add 1 cup of ashes to 2 cups of boiling water. Stir and strain. The liquid is the mordant. Using juniper needles as a mordant comes from the Navajo tradition. Juniper ashes can be a substitute for alum as a mordant, making the dyes more colorfast and creating brighter shades. Caution: Be careful with this homemade mordant. Since the ashes and water can form a type of lye, which is highly alkaline and can cause burns, use protective measures when working with it.

Sumac leaves : The leaves of sumac (*Rhus* species) are rich in tannin, making them a good natural mordant. When dried, sumac leaves can contain up to 35 per cent tannin per weight. Sumac as a mordant brightens and extends colorfastness for most vegetable- based fibers. The leaves of sumac contain tannin which can be used in the process of mordanting cotton. Sumac is also used in treating leather. Some people have an allergic reaction to sumac.

Rhubarb (Rheumspp) as a mordant : Tibetans use the liquor from boiled rhubarb leaves as natural mordant that works best with animal fibres. Apparently, a pound of rhubarb leaves can mordant several pounds of fibre. Boil the leaves for an hour to extract the tannin. Make sure you boil the leaves in a well-ventilated area, as the fumes can cause problems, and note that rhubarb leaves contain oxalic acid, which is a poison, and should not be eaten.

Aloe vera :

The aloe vera plant which is about 1-2 feet tall hold leaves that contain a slushy translucent gel and known around the world for incredible healing properties. The gel composed of near 96%

water, few organic and inorganic compounds, Different vitamins and eighteen types of amino acids. It has both antiviral and antibacterial quality and can treat almost every thin from diabetes to constipation. Hence, the application of aloe vera in ayurvedic textiles can have a synergistic effect to reach a high achieving point. In fact, the prospect of aloevera as a mordant is not only a possibility now but also the reality.

Uncaria Gambir :

Gambier is a kind of sap that comes from compressed extract of leaves and twigs of gambier plants (*Uncaria gambir* Roxb.). The use of gambier is being developed for natural dye of textile products such as weaving yarn. Previous research showed that solution of gambier 5% had been good enough to be used as a textile dye. Gambier residual dyeing solution is liquid waste that still contains active ingredients namely tannins and catechins which still can be reused.

Tamarind :

Tamarind seed coat tannin was extracted and its tannin class was determined. The extracted tannin was employed as a natural mordant alone and in combination with metal mordant namely copper sulphate for cotton, wool and silk fabrics and dyed using natural dyes namely turmeric and pomegranate rind. The mordanted and dyed fabrics resulted in good antibacterial activity up to 20 washes, when natural mordant was used along with 0.5% and 1% copper sulphate mordant and dyed with natural dyes.

Hemlock bark :

Eastern Hemlock, *Tsuga canadensis*, had been the main domestic source of tannin in the United States from the beginning of the industry. The pressure on the forests was so great as to practically eliminate the species. Hemlock bark has 8-14 per cent tannin. It was used for sheepskins and for sole and other leathers, either by itself or in combination with oak. Later extracts with 28-30 per cent tanning became available. Some attention was also given to the Western Hemlock, *Tsuga heterophylla*.

Mangrove :

Mangrove is a good source of tannin and gradually became more important as other sources diminished. The Red Mangrove, Rhizophora mangle, has been the main source. It is abundant in tropical swamps of both hemispheres. The bark is very hard and heavy and contains 22-33 per cent tannin. The leaves may also be used and the extract has been the least expensive of tanning substances. However, it causes the leather to darken and is therefore rarely used alone.

Wattle :

This source is used mainly in Great Britain. It is obtained from several species of acacia, mainly Acacia decurrens and its varieties dealbata and mollis, and *Acacia pycnantha*. These are small trees native to Australia but have become cultivated in Africa, Ceylon, Brazil and other countries. The bark may have tannin content of 40-50 per cent.

Other bark sources:

Other barks that are occasionally used for tanning are the European larch, Larix decidua, Norway Spruce, Piceaabies and some birches and willows. Birch bark is favored in Russia and the

fragrance of Russian leather is due to the presence of an essential oil in the bark. Willow bark gives light-colored, soft pliable leather favored for tanning gloves. Some tropical barks are of minor importance. Mallet bark is obtained from Eucalyptus occidentalis of Western Australia, with tannin content of 35-50 per cent. Avaram bark is from Cassia auriculata, important in India. Tanekaha bark from *Phyllocladus trichomanoides*, a New Zealand tree is used for gloves because it contains an orange-yellow dye.

Chestnut wood:

Castanea dentata and *Castanea sativa* contain tannin that is extracted at high temperatures from wood chips. The final product is 30-40 per cent tannin. Chestnut is used for heavy leathers.

Quebracho wood :

This wood of several South American trees is a very important source of tannin. *Schinopsis lorentzii* and *S. balansae* are the main species. The wood from these trees is some of the very hardest known with a specific gravity of 1.3-1.4. Argentina and Paraguay are the main producers. Extracts are made in factories located near the sources. The logs are chipped and cooked with steam in copper extractors until the liquor is very concentrated. This has tannin content of 40-60 per cent. It is very quick in its tanning action and is used either by itself or in combination for all kinds of leather, especially sole leather because it imparts extra durable qualities.

Myrobalan fruits :

Myrobalan nuts are the unripe fruits of two trees of India, *Terminalia chebula* and *T. bellerica*. These trees are grown in India for both fruit and timber. The nuts have tannin content of 30-40 per cent. When they are used by alone they yield spongy, light yellow leather, but in combination they are preferred. They are used to tan leather of goats, calves, and sheep and are best suited for soles and harnesses.

Mango bark :

Mango bark extract possibility of being used as a mordant. The natural dye used was extracted from bitter leaves and pre or post mordanted with mango bark extract, the amount of dye in the sample after dyeing and after washing was tested using CIELAB equipment, UV-Vis absorption spectroscopy and wash fastness test. Comparing the mango bark mordanted sample with control samples which included; un-mordanted sample and samples mordanted with copper IIsulphate, significant mordanting effect was confirmed which was even better than the conventional mordant used.

Divi-divi fruit :

The tannin is obtained from the dried twisted seedpods of a small leguminous tree, *Caesalpinia coriaria*, of the West Indies and South America. The tannin content is 40-50 per cent.

Tara fruit :

A stocky shrub or small tree Tara, *Caesalpinia spinosa* is widely distributed in tropical America. The fruits are 43-51 per cent tannin. The plant is cultivated in Peru and North Africa. It is used for producing a high grade of leather as it changes the color only slightly. The fruits are also used for ink and black dye.

Algarobilla fruit :

Caesalpinia brevifolia from Chile has pods with high tannin content. It is usually used in combination with other materials.

Canaigre roots:

Rumex hymenosepalus is a species native to the southern United States and Mexico. It is widely cultivated. The roots are sliced and the tannin extracted. The tannin content is about 30 per cent and yields a bright orange firm and heavy leather.

Palmetto roots:

Sabal palmetto has been used somewhat as a source of tannin, but the content is only 10 per cent.

Mordanting methods :

There are three types of methods for application of mordants based on the time of their usage. They are:

1. Premordanting
2. Postmordanting
3. Metamordanting or simultaneous mordanting.

Premordanting : As suggested by the name, in premordanting, the mordants are applied to the fabric prior to dyeing. It is most common for cotton and cellulosic as in the unmordanted state they do not have affinity for many natural dyes. Even for animal fibers, some natural dyes such as cochineal require this type of mordanting process for producing good shades. Various famous traditional printing styles with natural dyes from India such as ''Kalamkari'' in Andhra Pradesh and ''Sanganeri'' in Rajasthan use this mordanting method.

Postmordanting : In the postmordanting method, the fabric after dyeing is treated with mordant in a separate bath. The final color is developed during the last phase. Iron salts are very often applied in this manner for producing grey and black colors.

Simultaneous mordanting : In the metamordanting or simultaneous mordanting method, both dyeing and mordanting processes are carried out in the same bath itself. Usually for cotton and cellulosics, mordant is also added to the dye bath at the start of dyeing so that both dyeing and mordanting processes take place simultaneously in the same bath. For animal fibers such as wool, mordant may sometimes be introduced into the dye bath towards the end of the dyeing process when much dye has already been exhausted onto the textile. The dyeing duration is reduced in this method due to a reduction in the number of steps. This method produces darker shades for some dyes whereas for others, color yield may reduce due to the loss of some dye and mordant to dye–mordant complex formation in the dye bath which may also cause uneven dyeing. As the mordant cannot be reused, this process is more useful for small lots.

Application of mordants and process of dyeing :

A dye comprises of two principal groups: the chromophore and auxochromes. Chromophore (usually an aromatic ring) is associated with the coloring property and has unsaturated bonds, whose numbers decides the intensity of color. The auxochrome helps the dye molecule to combine with the substrate, thus imparting colour to the latter. Although some fabrics such as silk and wool can be colored simply by dipping in the dye, others such as cotton require a mordant. Some natural

dyes, such as indigo will give good color when used alone, these dyes are called direct dyes or substantive dyes. The majority of plant dyes, however, require a mordant or a chemical used to "fix" the color to the textile fabric, and prevent the color from either fading with exposure to light or washing out. These dyes are called adjective dyes such as logwood. By using different mordants, dyers can often obtain a variety of colors and shades from the same dye. Fibers or cloth may be pre-treated with mordants, or the mordant may be incorporated in the dye bath.). The final colour, lustre and colour fastness properties of the dyed fabric are dependant not only on the dye but are also determined by the concentration and type of mordants used. Common mordants are alum (usually used with cream of tartar, which helps evenness and brightness lightly); iron (or copper) (which saddens or darken colors, bringing out green shades); tin (usually used with cream of tartar, which blooms or brightens colors, Textile fibers, especially cellulosics, do not have much affinity for the majority of the natural dyes; hence these are subjected to an additional step known as mordanting.

Mordants are the substances that have affinity for both textile fibers and dyes, thus they act as a link between the fiber and dyestuff. Those dyes that do not have affinity for a fiber can be applied by using mordants. In the case of dyes having affinity for the fiber, the use of mordants increases the fastness properties by forming an insoluble complex of the dye and the mordant within the fibers, which also improves the color. Unlike animal fibers, vegetable fibers such as linen and cotton do not readily hold the mordants resulting in duller color compared to the bright colors obtained on wool and silk. Mordanting is very important for cotton as it is more difficult to dye than wool or silk due to the absence of amino and carboxyl groups that provide attachment sites to dye molecules (Arora *et al.,* 2017).

Use of non-eco-friendly metallic mordants :

The use of metallic mordants during natural dyeing often puts a question mark on the eco-friendliness of natural dyes. Only a small amount of these metal salts gets fixed onto the textiles and the rest is discharged as effluent which leads to the contamination of land and water resources. However, it has been observed that out of the five metallic mordants traditionally being used for natural dyes, alum andiron are environmentally safe and these have not been restricted by any ecoregulations. In fact they are used for effluent treatment of synthetic dyes. Out of the remaining three mordants, chromium as Cr VI is very toxic, hence should not be used. Tin should also be avoided; copper may, however, be used judiciously as it has a higher tolerance limit in various eco-regulations. Of course the effluent should contain as low an amount of the mordant as possible to avoid pollution problems. Creation of awareness about this aspect among traditional dyers using natural dyes is important to make the naturally dyed textiles eco-friendly. Use of standing baths for these mordants can minimize the pollution problems but it would require working out the exact amount exhausted onto the fibers so as to facilitate replenishment. Traditional recipes need to be reworked for maximizing the mordanting bath exhaustion so that lower quantities can be used and there is less mordant to be discharged as effluent. Use of some auxiliaries such as formic acid or cream of tartar can improve the uptake of metal ions by the animal fibers and a pretreatment with tannin substances can improve the metal ions pick-up by cellulosic materials. At the same time, it should also be ensured that the amount of restricted metals on the fabric is within the prescribed eco limit. Extensive reworking of mordanting and dyeing recipes is also needed so that the required level of fastness properties could be achieved while maintaining heavy metal mordant content within the limits suggested by eco-regulations. In order to make natural dye sustainable, it would be very important if metallic-salt–based mordant scan be replaced with natural mordants. Several

research studies have attempted to use tannin-based natural substances such as myrobolan, tannic acid, and pomegranate rind as natural mordants in place of metallic mordants and these were found to be effective in improving the fastness properties. Thorough research and transfer of research results to actual users is necessary to stop the usage of non-ecofriendly mordants.

Mordanting technique tip:

The safest mordanting method is to do a normal alum or plant based mordant. Then dye your fabric, and use the other metal mordants in a mild after-bath solution so that they can change the color. This helps protect your fibers, and also your health when working with mordants, so that you can make sustainable clothing. For some fiber reactive dyes, vinegar is used as a fixative. Vinegar is not a mordant, but it changes the pH to enable the fiber and dye molecules to bond. Vinegar can be helpful with natural dyes, since some dyes do not reveal their full color unless their pH changes to acid. Specific instances include some yellow natural dyes, and some woad dye baths that I have done. Always follow safe disposal methods with metal salt mordants. Also, some metals in natural tap water can change the brightness and tone of natural dyes.

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