Fundamentals of Natural Dyeing of Textiles: Pros and Cons

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Introduction

India is rich in natural wealth and there are ample scopes to explore and revive application of natural dyes on textiles for growing consciousness of eco friendliness. Hence around the world, there are more and more information are now made available [1,2] to understand the chemistry of natural dyes and interaction between metallic mordant, natural dyes and natural fibres, to get maximum depth of shade of natural colour ants with reproducible shades by optimizing extraction, mordanting method and dyeing conditions and also to improve colour fastness for such natural dyed textiles of natural fibres like cotton, silk, wool and jute etc.

In spite of the better performance of synthetic dyes, recently the use of natural dyes on textile materials has been attracting people more and more due to the following reasons [3]

- Wide availability of natural dyes in India and its subcontinent and their huge potential of producing wide range of shades with skin and eco-friendliness.
- Growing consciousness about allergic and toxic effects of some synthetic dyes, while understanding the non-toxic and non-allergic nature of natural dyes.
- To protect the ancient and traditional dyeing technology generating livelihood of poor artisan/dyers, with potential employment generation facility.
- To generate sustainable employment and income for the weaker section of population in rural and sub-urban areas both for dyeing as well as for non-food crop farming to produce plants for such natural dyes.
- Availability of some archaeological study for conservation and restoration of heritage of old textiles of India for natural dyed textiles.
- Availability more and more scientific study report on application methods for natural dyeing of specific textiles.

Production of synthetic dyes is dependent on petrochemical source, and some of the synthetic dyes contain toxic/carcinogenic amines which are not eco-friendly. The present global consumption of textiles is estimated at around 30 million tonnes, and such a huge amount of required textiles materials cannot be dyed with natural dye alone [2]. Hence, the use of eco-safe synthetic dyes is also essential. But a certain portion of coloured textiles can always be supplemented and managed by eco-safe natural dyes that too on natural fibres, assuring creating environment friendly measure of dyeing textiles, at least to a certain percentages.

Natural dyes consume 75% of 48,000 tonnes of dye stuff produced in the country [2]. The market for the natural dye stuffs is though very small but has a growing trend. Many textile manufacturers are not using these dyes regularly because these dyes are not easily available in ready form and finally the process of natural dyeing become more expensive than synthetic dyes. Researchers are however working to find out a cost effective way of dyeing with natural dyes, but at the same time efforts are on for obtaining reproducible shades with appreciable colour fastness properties.

U.S.A is one of the major importers of natural dyed textiles from India [4]. There is also very good demand in European countries. The primary importers in Europe are Germany, France, Italy and U.K. with demand for natural dyes is growing continuously due to awareness towards ecological and environmental problems related to the use of synthetic dyes. Use of synthetic dyes has cut down significantly due to toxic effluent resulting from the dyeing process of these dyes. Therefore, natural dyed products represent the good opportunity for value added manufacturing as the process is eco-friendly. These products are comfortable for the wearer as it has soothing colour and non-allergic properties [3]. The use of natural dyes will also generate more employment for rural people because natural dyes are originated in villages were the waste lands are used to grow the dye yielding plants [2].
The alchemy of colour has its origin deeply rooted thousands of years ago. From the epic age this colour has played a very important role in human life. This inspired us to explore the vast storehouse of the nature’s palette to initially paint ourselves then to dye the apparels we wore. Natural colorants are dyes and pigments that are obtained from plant, animal or mineral sources with or without any chemical treatments.

Today, when the world is facing threats of destruction from the synthetic toxic chemicals, eco-friendly awareness should be the major focus, else, it would be difficult to save this planet from compete extinction. Here lies the relevance of revival of this art of dyeing with ‘Natural Colorants’ or ‘Natural Dyes’ [4,5].

It is told earlier that in general introduction that the production of synthetic chemicals involves many chemical reactions requiring high energy. Moreover, there are many undesirable by-products generated during the reactions [4,5]. These toxic or environment un-friendly by-products have to be discharged in the rivers, ponds or into the atmosphere. These drawbacks of the synthetic dyes have prompted researcher to look for alternatives of producing eco-friendly products and technologies using natural dyes for dyeing. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process like dyeing of textiles with natural dyes.

Natural dyes many times lack in uniformity and reproducibility of colour. Also, the major problem encountered is their availability of natural dyes in bulk quantity. There is limited availability of scientific information on standardization of the methods application [5] of natural dyes. Sometimes natural dyes do not produce acceptable level of colour fastness. The question of cost is also a factor to reckon with. Antimicrobial and UV protection properties of natural dyes need to be explored after their application on textile fabrics. Hence, in the absence of any precise information of scientific analysis and technical knowledge on dying different natural fibre based textiles with natural dyes, there is a need to study the performance of various natural colorants on natural textiles including protein fibres and cellulosic/lignocellulosic fibres (having compositional differences) separately under different pre-treated/post treated conditions [5] varying different mordants and other additives.

Natural dyes have been used as a means to colour textiles for centuries. All the dyes until the later half of nineteenth century were made of different parts of plants and animals. For thousands of years people all over the world followed the same basic techniques using roots, stems, barks, leaves, hard wood, berries fruits, flowers of various dye plants and tree, as well as from certain insects and shell-fishes. Most natural dyes are non-substantive which means that they have little colouring power within themselves, and require the aid of mordant to penetrate the yarn/fibre.

In recent years, there has been an interest manifested towards natural dyes by both the consumers and producers of textile; the reasons being bio-degradability and eco-compatibility of natural dyes. Some other associated advantages include expected non-toxicity/lower toxicity [6,7] and anti-allergen [1] and some medicinal value as well as antimicrobial and UV protective character of some of the natural dyes.

Definition of natural dyes

The Society of Dyers & Colourist’s Colour Index (3rd edition) defines natural colouring matters as ‘the natural dyes and pigments comprise of all colours obtained from animal and vegetable matter with no or very little chemical treatments [1]. They are mainly mordant dyes [1,2], but they also include some vat, few disperse/solvent dyes, some pigment colour, a few direct, basic and acid dyes’ [1].

The term natural dye covers all the dyes derived from the natural sources like plants, animal and minerals i.e., derived from natural resources [8]. Natural dyes with very few exceptions are non-substantive, but must be used in consumption with mordants. A mordant usually a metallic salt has an affinity for both the colouring matter and the fibre and combining with the dye in the fibre it forms an insoluble precipitate or lake. Application wise, natural dyes include some vat dyes, a few solvent dyes, some pigments, and some direct and acid dyes. Only one natural basic dye is known but natural sulphur, disperse, azoic or ingrain dyes are still not available so far.

Classification of natural dyes as per application method

Natural dyes can be classified [1,5] in a number of ways. The earliest classification was according to alphabetical order or according to the botanical names. Later, it was classified in various ways, e.g. on the basis of hue, chemical constitution, application method. Most widely used classification is based on application method.

Classification of natural dyes on the basis of the method of application [1,5,9] as given below :

a. Mordant dyes: These are dyestuffs which require a mordant in their application as they have no affinity for the fiber being dyed. A mordant dye should have electron donating groups capable of forming a complex with the transition metal salt, e.g., madder, fustic, Persian, berries, kermes, cochineal etc.

b. Vat dyes: These are water insoluble dyes which are first converted to their water soluble form (reducing with Na-hydrosulphite and then solubilising it with alkali) and then applied to the fibres. The true colour is produced only on treatment with a hot soap solution. The soaping treatment completes the oxidation process, e.g., Indigo.

c. Direct dyes: Direct dyes are those dyes that have tremendous affinity for the cellulose fibres. They are dyed from a boiling dye bath. Turmeric, Harda, pomegranate rind etc. are a few of the direct natural dyes.
d. **Acid dyes**: These dyes are applied from an acidic medium. The dye molecules have either sulphonic or carboxylic group(s) which can form an electrovalent bond with amino groups of wool and silk. An after treatment with tannic acid and tartaric acid, known as back tanning improves the fastness of these types of dyes, e.g., Saffron.

e. **Disperse dyes**: Disperse dyes has a relatively low molecular mass, low solubility and no strong solubilizing groups. These dyes have hydroxyl and/or amino groups which impart same solubility to the dye molecule. Disperse dyes can be applied on to hydrophobic synthetic fibre from neutral to mildly acidic pH. They can also be applied to silk and wool. These dyes can be post-mordanted with chromium, copper, and tin salts, e.g., lawsone and many other flavone and anthraquinone dyes.

f. **Basic dyes**: Basic or cationic dyes on ionization give coloured cations and form an electrovalent bond with the -COOH group of wool and silk. These dyes are applied from neutral to mildly acidic pH. These dyes have poor light fastness, e.g., berberine.

**Methods of extraction of natural dyes**

The vegetable dyes can be taken from various sources like flowers, roots, bark, animal sources, mineral sources etc. The colour component present in these sources needs to be extracted so that it can be applied on the textile. Most vegetable dyes are extracted by pulverizing, grinding or soaking and boiling the herbs in water. The natural dyes can be extracted from dried solid raw material source of plant parts etc. using aqueous method [5] i.e., by using boiling/hot water for the extraction with or without addition of acid/alkali/alcohol in extraction bath [10] at specific pH, MLR, Temperature and time followed by distillation, evaporation and vacuum drying etc or by waterless supercritical carbon dioxide fluid extraction [11], or solvent extraction by using soxhlet apparatus extraction [12] by use of alcohol and benzene mixture and by using rotary vacuum pump/or doing the extraction under reduced pressure etc. Some water insoluble plant material like indigo leaves (i.e. Natural indigo being vat dye type) needs to be fermented and reduced to release the glucosides of the dye and this fermentation and reduction and solubilisation can be done with use of natural reducing agent and alkali combination (instead of Dithionite or disulphide and Caustic soda used for reding synthetic vat dyes) like combination of liquid jiggery and citric acid, use of paste of citrus fruits like tomato, lemons, ripened banana paste and Ash soaked water etc., in combination with use of lime in all cases and heating. Various studies have also been reported, where ultrasonic assisted extraction and enzyme assisted extraction have been also now being used to improve the yield of colour. The colour developed in natural dyeing on different textiles is sometimes pH dependant besides it is mainly dependant on type of mordant used besides dye concentration and mordant concentration as well. However combination of similar types of natural dyes in different proportion of compatible natural dyes are also another way for producing different shades for colour matching for combined shades.

**Methods and Steps for dyeing with natural dyes**

Prior to dyeing with natural dyes, the fabric is to be prepared by proper desizing, scouring and bleaching followed by usual pre-mordanting with single or double mordants applied in sequence. The colour much depend on the type of single or double mordants used by selecting a suitable mordant and natural dye-mixture combinations depending upon the colour needed and colour fastness level desired. Dyeing with natural dyes on textiles comprises of five to six steps:

1. **Mordanting**.
2. Preparation of Dye liquor from natural source or extraction and solubilisation of dye.
3. Exhaustion,
4. Diffusion and migration,
5. Fixation and
6. After-treatments (optional) for improving fastness or topping for tonal variation and final colour matching etc.

To facilitate completion of dyeing in the shortest possible time, most dyeing systems make use of different additives and auxiliaries such as pH controller, retarders or exhausting agents, levelling agents etc. For dyeing with natural dyes, depending on the type and nature of natural dyes taken, the dyeing procedure and conditions will vary. Natural dyes often show non-reproducible shades due to variation in conditions of dyeing or following non-optimised conditions of dyeing. Hence, standardisation/optimisation of dyeing methods for specific dye-fibre-mordant combinations is essential. Most of the natural dyes being mordantable; dyeing with such natural dyes is carried out using aqueous extracts of natural dyes in aqueous medium in normal/not aqueous dye-bath. Dyeing with natural dyes may be carried by pre-mordanting, post-mordanting, simultaneous mordanting, following standardised dyeing process at low temperature water bath or in boiling water bath [5], HTHP technique [13], with additives controlling the pH of aqueous medium i.e. (acidity or alkalinity) [14,15], or using ultrasonic dyeing technique [2,16-19], using single natural colours or mixture of natural colours [12,20] extracted appropriately and found compatible scientifically.

The major steps used in dyeing with natural dyes include the following:

a) **The application of the suitable metallic mordant (mordanting) or bio mordant**

b) **The application of the tannin substance e.g. tannic acid, myrobolan fruit (harda) having chebulinic acid, gallnut etc.** which is mainly done to increase the receptivity of the textile.
Advantages & disadvantages of natural dyes

In the recent years there has been an upsurge in the field of natural dyes. This is mainly because of the fact that although the synthetic colours are fast, durable and comparatively easy to apply, the natural dyestuffs have certain advantages over them. Some of these advantages are listed below:

a) Fairly non-polluting and have lower toxicity.

b) The naturally dyed shades are soft, lustrous and soothing to the human eye [1,5,21].

c) They produce a wide range of colours. A small variation in the dyeing technique or the use of different mordants with the same dye can create totally new colours, which are not possible with synthetic dyestuffs [1,5,22].

d) Natural dyestuffs produce rare colour ideas [1,5,23,24] and are automatically harmonizing.

e) Unlike the non-renewable which forms the basic raw materials for synthetic dyes, the vegetable based natural dyes are replaceable and at the same time biodegradable [1,2,5]. They save energy because the raw-materials are not from petroleum.

f) In some cases like indigo etc., the waste in the process becomes an ideal fertilizer for use in agricultural fields [1,5].

g) Many plants thrive on wastelands. Thus, wasteland utilization is an added merit of the natural dyes [1-2]. Dyes like madder grow as host in tea gardens. So there is no additional cost or effort required to grow it.

h) This is a labour intensive industry [1,5,21,23,24], thereby providing job opportunities for all those engaged in cultivation, extraction and application of these dyes.

i) It can increase the textile exports and thus help India in earning foreign exchange.

j) Some of its constituents are anti-allergens, hence prove safe for skin contact and are mostly non-hazardous to health [1,5,25].

k) Some of the natural dyes are enhanced with age, while synthetic dyes fade with time [9].

l) Natural dyes bleed but do not stain other fabrics [1,5,21,26], turmeric being an exception.

m) Naturally dyed materials have good resistance to moth and are anti-allergens; hence prove safe for body contact and are mostly non-toxic therefore non-hazardous to health [5].

n) Fabrics dyed with natural dyes can provide good protection against ultra violet rays without altering wear properties.

o) They are used in the conservation and repairs of historic textiles.

p) They can replace synthetic dyes in food-stuffs for safety [2,5].

Despite these advantages, they carry some inherent disadvantages [1,5], which were responsible for the decline of this art. Disadvantages of natural dyes:

a) There are lacks in sufficient scientific database and information on standardizing recipe and shade cards for the use of natural dyes [5,27] on different textiles. Hence, natural dyers are in complete uncertainty about dyeing shades and fastness results to obtained which vary from plant source to source, crop to crop and season to season (time to time and place to place and also from one crop to another) and even for mordant to mordant and their purity and extraction method. All these variations, if thus scientifically standardised, may be partially or completely avoided.

b) The extraction, preparation of textile materials requires and mordanting and natural dyeing need skilled craftsmanship and is thus expensive [5,28]. The use of expensive mordants, extraction of colouring component from raw material, low colour yield necessitating the use of more dyestuffs and long dyeing time sharply increase the cost of dying with natural dyeing considerably higher than synthetic dyes. However, if the natural dyeing of natural fibres is properly done maintaining eco-friendly processes, it has aspecitilyniche market for eco friendly natural dyed products of textiles particularly for expensive textiles and garments of cotton, silk and wool etc.
c) Poor scientific back up of a large part of this branch of science is still being explored [5,29] and to be explored for its commercial exploitation in industrial scale for both small, medium and large scale sector. Natural dyeing using Jigger machine or Continuous dyeing range etc are the present days’ need.

d) Lack of availability of precise scientific/technical knowledge on extraction and dyeing techniques [5,30] by optimizing dye wise and textile fibre wise process development for each natural dye type are essential to avoid the above said uncertainty for colour/shades and their colour fastness characters.

e) The natural dyed textile fabric may change colour when exposed to the sun (UV light), sweat (human perspiration) and air (oxygen) and moisture (water). This cannot be controlled if not scientific research are done in depth to understand the exact reasons of these effects and exact chemical interaction present in such cases for exposure to any particular agency at any particular time, which are not yet known [5,27].

f) Nearly all-natural dyes with a few exceptions require the use of metallic mordants to fix them on to the fabric substrate. While dyeing, a substantial portion of the metallic mordant remains unexhausted in the residual dye bath and these metals may pose some effluent disposal problem [5,23,24]. So, use of hazardous metallic mordants like Copper/chromium etc are to be avoided.

g) With a few exceptions, most of the natural dyes are fugitive [1,5] even when applied in conjunction with a mordant. Therefore, their colour fastness performances are generally not always adequate for modern textile usage. Use of acidic pH in dye bath or post treatment with natural or eco safe dye fixer is needed to improve colour fastness to wash, light, rubbing and perspiration etc.

h) The widespread use of natural dyes will result in a major shift in the land use pattern throughout the world [30]. In reality the area needed to satisfy the demand for the production of natural dyes is unavailable, because higher priorities are placed on the growing of food crops for the world’s burgeoning population. However, this may be noted that objective of promoting more and more natural dyeing is not to replace synthetic dyeing in totality or as majority, but objective of promoting natural dyeing is to promote eco-friendly dyed products of natural textiles for niche market for specific customers.

i) All natural products are not fully toxicity free. Very little work has been carried out to assess the toxicity of different natural dyes [23,24]. Although most of the natural dyes in use are known to have medicinal values and either antibacterial/ antimicrobial properties or UV protective properties and are eco safe, but there are reports on one or two natural dyes/colour source materials that have been identified as posing potential ecological or toxicity problems, e.g. quercetin is considered to be mutagenic. On the other hand, new synthetic dyes are fully tested for their levels of toxicity, and when introduced in the market, they have a full set of data on their toxicity test and eco-toxicity profiles. Such studies and database for each natural dyes are needed essentially.

j) There is severe shortage of trained dyers for application of natural dyes. Most of the so-called textile chemists in the country are trained to use synthetic dyes. If this technology is to be used for producing eco-friendly textiles, generating revenue, employment as well as for creating a strong base for renewable resources for the dye industry, a comprehensive training and interaction programme has to be launched.

k) Dearth of books and scientific literature on the technology of natural dyeing providing required the scientific basis for their application on different textiles.

l) Non-availability of the natural dyes in pure or standardised form, which may be powder, paste or in the solution form for easy and direct application in known shade percentage. Using source raw natural material directly for dyeing has many limitations, besides its being of unknown composition and colour yield, it generates considerable amount of biomass that is cumbersome to handle in the dye house.

Inspite of the aforementioned limitations associated with natural dyes, it is expected to have a separate good export market potential for fabrics from natural fibers dyed and printed with natural dyes, because of the rigid standards imposed by the advanced countries in combating toxicity, eco-hazards and pollution control problems.

Constraints for the uses of natural dyes on textiles

The major hurdles for using natural dyes are serious gap and lack/non-availability of scientific data base and knowledge base required for their successful application on textiles. Most of the researchers worked in this area generated very general information on types of shades/colour fastness properties and their dyeing related information reported in literature that does not have complete profile of its chemical nature, materials data specification sheet, standardized extraction and dyeing procedure and scientific reasoning for its nature of problems and solution and basis for nature of bonding between dye-mordant and fibre system, methods of improvement of colour fastness to wash, light, rubbing and perspiration and compatibility of different natural dyes to apply together as mixture of different proportions for obtaining compound shades and required matching etc. There are very limited information available on use of binary and ternary mixture of natural dyes and their interaction/compatibility etc, for which use of mixture of natural
dyes are still limited in traditional natural dyeing sector and have not advanced satisfactorily.

Unnecessary adverse talk and biased opinion are opinion of synthetic dye manufacturer/users against the use of natural dyes, where some of their logics are being over emphasised deliberately. One must keep in mind that natural dyes are NOT a substitute of synthetic dyes. They have their own market and any expansion in the market of natural dyed products is not going to be at the cost of losing synthetic dyes.

**Colour fastness of natural dyes**

Color fastness is the resistance of a material to change in any of its colour characteristics, to the transfer of its colourants to adjacent materials or both. Fading means that the change of colour strength (lightening or darkening) on washing or rubbing or in contact with human perspiration or on exposure to light. Cook [31] has described the use of post treatment with natural tannin related natural materials as after-treatment for improving the wash fastness and use of natural UV absorbers for improving the light fastness of mordant able natural dyes on cotton. There are many pre-treatments and post treatments known for improving either of wash-fastness, rub-fastness and light fastness of textiles dyed with synthetic dyes, but such treatments on textiles dyed with natural dyes are still very few. So, exploring such fastness improver from natural materials is essential.

The light fastness is the resistance of dyestuffs to the influence of UV-light energy [32], especially the ultraviolet (UV-A) part of the electromagnetic spectrum. UV light is subdivided into three category e.g UV-A (320-400nm), UV-B (280-320nm) and UV-C (100-280nm). The shorter is the wavelength (\(\lambda\)), the higher is the energy E and higher is the damage to dyestuff or human skin (as per Einstein’s rule: \(E= h\nu = [h X c/ \lambda]\)). Fortunately, UV-C is fully absorbed by ozone layer in the higher atmosphere (stratosphere), the usual content of UV-B in the total radiation intensity is less than 1% and is not that harmful, while to earth most common part of UV light reaches easily from Sunlight is UV-A part (320-400nm), which is about 5.6%. So, identifying of some UV absorbers from natural materials capable of absorbing UV -A part i.e in the region of 320-400nm and their application to dyed textiles are to be established.

The light fastness of the applied dyestuffs is sometimes also connected to the fading or inherent yellowing tendency of the fibre itself. Yellowing by UV Light exposure and associated damage to the fibre itself by exposure to UV light also accelerates fading of colour with or without photo-initiated fading of dyestuff [31]. Fading by UV light is generally promoted by moisture, heat, oxygen in air and other factors. The interactions of these influencing factors, including UV-absorbers photo-sensitizers, radical scavengers, singlet oxygen quenchers and their possible chemical reactions and interactions are quite complex. Moreover light fastness of natural dyes depends on its UV-absorption character of that dye [21,24,33]. Some natural dyes have inherent UV protective nature like anar peel/pomegranate rind.

Poor wash fastness of many natural dyes is mainly attributed because of weak dye-fibre bond formation between the natural dye-mordant and the fibre, change in hue due to breaking of dyemetallic mordant-fibre complex during washing for ionisation of the natural dyes during washing [12]. Since most of the natural dyes have hydroxyl groups which get ionised under alkaline conditions/acidic conditions and hence many fabrics dyed with natural dyes under acidic conditions change colour on washing with alkaline detergents or soap. Wash fastness of the natural dyes much depends on their chemical nature and type of bonds dye-mordant-fibre as a coordinating complex formed with specific dye-metal salt mordant-fibre combination. But as per expectations, many times there is less or limited very little or no such complex are formed actually and only H-bonding are formed causing poor wash fastness, which may be due to many reasons like stereo specific non fitting of physical structure/orientation of dye structure and fibre structure or any other problems.

Rubbing fastness is assessed by measuring change in colour on the rubbed textile surface or assessing the staining to the abrader white cloth after abrading in both dry and wet conditions (for wet rubbing fastness , additionaly the migration of colour to the abrading cloth by bleeding is also included). Depending on the kind of fibre, especially its tensile strength, small abraded coloured fibre particles may fuzz out showing loss of depth of colour on the rubbed textile surface. If the dyestuff involved is water soluble and not sufficiently fixed on the fibre surface, this can also be the reason for staining during rubbing. Rub-fastness ratings, according to the standard grey scales for both loss of depth (fading) and staining scale, range from 1 (poor rating) to 5 (best rating). Parameters that influence rubbing fastness of natural dyes include:

a. Molecular size and structure, chemical nature and fixation mode of Natural dyes used.

b. Type of mordants and Concentrations of mordants.

c. Concentration of natural dyestuff, shade%, and extent of diffusion of dyes.

d. Dyeing procedure, degree of fixation and extent of surface dyeing and ring dyeing.

e. After treatment with dye fixing agents, softeners, silicones and cross linking agents.

f. Types of fibre and its tensile strength and dry and wet abrasion resistance.

g. Type of textiles used as abrading cloth in contact: Its surface, kind of fibre and fabric.

h. Intensity of the contact: pressure, time, moisture and temperature.

The influence of the moisture is taken into account in the test methods (dry or wet crocking tests). Wet cellulosic fibres may be partly damaged by rubbing, leading to additional staining. The
rubbing force for the wet testing procedure is about double the rubbing force for dry rubbing. Therefore the wet rubbing ratings of the same sample are always poorer than the dry ones (up to two rating differences). For natural dye, if there are more unfixed dyes on the surface and when dyes are only bond by H-bonds without mordanting, both the dry and wet rubbing fastness may be inferior.

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