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COMMERCIAL VIABILITY FOR COLOURATION OF NYLON SUBSTRATE WITH NATURAL VEGETABLE DYES

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Abstract: Natural colourants are unsophisticated and harmonised with a possibility of very little chemical reaction and consequently little health hazards. Due to the growing trend all over the world for natural colourants and in the present context of eco-preservation, these colourants are likely to develop a tremendous commercial potential. There is also a growing awareness of their non-hazardous nature which has led people all over the world to accept the fact that natural dyes are still much more traditional and hygienic. In the present work, a commercial approach has been undertaken to produce a variety of shades with different tones and hues on nylon substrate with natural vegetable dyes. The vegetable dyes selected for the work have been derived from Indigofera tinctoria, Mallotus phillipinesis, Curcuma tinctoria and Lawsonia inermis. These dyes are widely used in India for household purposes and other varied applications. These dyes are applied on nylon substrate by various dyeing methods, viz. exhaust, pad-dry-steam and pad-dry-cure dyeing methods. The dyeing results for substrates dyed with natural dyes have been analytically assessed by measuring the colour strength (K/S) values of dyed samples using UV spectrophotometer. From these values, the shade cards have been prepared for different percentages of shades. Various fastness properties (wash, light and rub) of the dyed samples have also been evaluated.

KEYWORDS: Nylon, *Indigofera tinctoria, Mallotus phillipinesis, Curcuma tinctoria, Lawsonia inermis*

1. Introduction

'Eco-friendliness', 'eco-conservation' and eco-protection' are the buzzwords today. Environmental related issues are freely debated and there is a growing concern over the depleting eco-system. Chemical processing involves use of about 800 different types of chemicals, apart from synthetic dyes, which are used for the colouration of textiles. These chemicals/dyes, etc. may be toxic/carcinogenic to human being as well as aquatic life/organism and may also disturb the ecological balance. At present, textile industry in many developing countries is facing a serious impact of the famous German ban on 118 specified azo dyes based on 20 carcinogenic aryl amines, including benzidine[1-5]. The banned dyes include 26 acid dyes and 6 disperse dyes used for colouration of textiles. The industry is, therefore, in a need of safe alternative. The above-mentioned factors have brightened the scope of the utilization of natural colourants, which could be considered as the best substitute for many hazardous synthetic dyes[6].

The present study deals with the replacement of synthetic dyes by natural dyes, derived from vegetable resources. Various natural dyes, viz. Indigo, Turmeric, Kamala and Henna – all obtained from natural vegetable resources were used for colouration purposes. Turmeric powder is generally used in kitchen and as a medicine for healing wounds, while Henna dye is used for dyeing hair and decoration of different body parts. Kamala dye is being used by Indian woman for application on forehead. Since most of these dyes are either used as eatables or for their application on body, they are supposed to have no carcinogenic effect. They are all considered to be bio-degradable. Dyeing of these dyes was done on synthetic proteinous textile substrate, viz. nylon, a polyamide fibre. Exhaustion, pad-dry-steam and pad-dry-cure techniques were used for application of natural dyes on nylon fabrics.

2. Materials and Experimental Methods

2.1 Materials

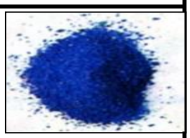
2.1.1 Fabric:

Plain-weave nylon fabric (weight: 47 g/m^2, 42 ends/inch and 38 picks/inch) was used for the study. The fabric was purified in the laboratory to remove the finish and minor impurities by giving a mild treatment with 2 gpl non-ionic detergent (Sandozin NIS) and 2 gpl soda ash solution at boil for 60 min. The fabric was then thoroughly washed and air-dried.

2.1.2 Natural dyestuffs:

The natural dyes, selected for the study, were obtained from various vegetable products used for various household activities. The various characteristic features of these dyes are mentioned in Table 1.

Table 1: *Various characteristics of vegetable dyes*

Common Indian name	**Botanical name**	**Colour Index number**	**Family**	**Colouring pigment**	**Photograph**
Indigo (Natural Indigo)	*Isatis tinctoria*	C.I. Vat Blue 1	*Fabaceae*	Indigotin	
Kamala or Kumkum	*Mallotus phillipinesis*	CI Natural Yellow 25	*Euphor-biaceae*	Rottlerin, iso-rottlerin (Chalcones)	
Turmeric	*Curcuma tinctoria*	CI Natural Yellow 3	*Lythraceae*	Curcumin	
Henna	*Lawsonia inermis*	CI Natural Orange 6	Bignoni-aceae	Lawsone	

2.1.3 Chemicals and auxiliaries:

The reducing agents used during the study were sodium hydrosulphite (Transpek Ltd., Baroda) and D-glucose (Sisco Research Laboratories, Mumbai) and were of Laboratory

Reagent Grade. All other chemicals and auxiliaries used for the experimental work were also of Laboratory Reagent grade.

2.2 Experimental methods

2.2.1 Application of Natural Indigo

Preparation of Indigo dye solution: Finely powdered indigo dye (1 g) was properly vatted and solubilised with requisite amount of glucose/sodium hydrosulphite (as reducing agent for vatting of indigo) in presence of caustic soda (alkali for solubilisation of reduced indigo) and the total volume of the liquor made 100 cc with water. Vatting was completed by gently heating the solution in a water bath at 50°C for 1 hour.

Dyeing Procedure: Conventional leuco vat reduction process was selected for conducting the dyeing of natural indigo. The nylon fabric was first impregnated in a charging bath followed by actual dyeing process as described below:

Charging bath: Well-wetted fabric was introduced in the charging bath containing caustic soda (1g) along with optimum amount (just sufficient for complete reduction of the dye) of reducing agent. The proportion of reducing agents used in the charging bath are-

Sodium hydrosulphite……………………1g
D-glucose………………………………..1.2g

The treatment in the charging bath was carried out at room temperature for 20 min.

Dyeing: The proportions of various dyebath additives are mentioned in Table 2. Glauber's salt was used for exhaustion of the dyebath.

***Table 2**: Dyebath recipes for dyeing natural indigo on nylon substrate*

Dyebath ingredients	Dyebath recipes for shades					
	Dyebath I			Dyebath II		
	1%	3%	5%	1%	3%	5%
Indigo dye (cc)	x	x	x	x	x	x
Caustic soda (g)	1	1.5	1.5	1	1.5	1.5
Glauber's Salt (%, *owf*)	5	10	10	5	10	10
Sodium hydrosulphite (g)	1	1.2	2.0	-	-	-
D-glucose (g)	-	-	-	1.2	1.5	2.5

Required amount of dye solution for 1%, 3% & 5% shade (*owf*) and required proportion of caustic soda and glauber's salt (*owf*) were added to the above charging bath and the fabric entered in the bath at room temperature. The impregnation was done for 15 min during which the amount of alkali and reducing agent were checked periodically to ensure the presence of sufficient amount of these agents in the dyebath. After 15 min, the impregnated sample was taken out of the bath, squeezed slightly and exposed to air for 5 min. The complete procedure of impregnation and exposure to air (for oxidation) was repeated for five times. The final exposure was being done for 15-20 min till desired shade develops on the nylon substrate.

After-treatments: After dyeing, all the dyed samples were rinsed, soaped at 60° C for 15 min using 2 gpl non-ionic detergent solutions, washed thoroughly and dried at ambient temperature.

2.2.2 Kamala, Turmeric and Henna dyes

Preparation of dye solution: 1 gm dye was treated with 100 cc water at room temperature and the solution was constantly stirred for few minutes and then kept in the dark overnight. The mixture was heated to boil for about 1 hour. After proper dilution the solution was directly used for dyeing purpose

Dyeing procedures: Exhaust, pad-dry-steam and pad-dry-cure dyeing techniques were utilized for the application of Turmeric and Kamala dye onto nylon substrate.

*** Exhaust dyeing process:** The dyeings were performed on a laboratory constant temperature water bath (Model: Paramount). The temperature in the water bath was maintained as per the dyestuff. The dye liquors were prepared as follows:

X%	Dye (owf)
10%	Acetic acid (owf)
20%	Glauber's salt (owf)
pH	4.5
Temperature	70° C (for Turmeric); At Boil (for Kamala and Henna)
MLR	1: 30
Total dyeing time	60 minutes

The dyeing temperature was kept at 70° C for Turmeric to prevent its decomposition at higher temperatures.

The fabric sample was entered in the above dyebath at room temperature and worked in cold for about 10 minutes. The temperature of the bath was gradually raised to desired end temperature and dyeing continued at this temperature for about 60 minutes. After dyeing, the samples were taken out from the dye baths.

*** Pad-dry-steam method:** The padding solution was prepared as follows –

X gpl	Dye
!00 gpl	Acetic acid

The solution was heated slightly to 40-45° C and the fabric was impregnated in this bath under warm condition. The fabric was then passed through a 2 bowl padding mangle to squeeze out excess dye solution, using 65% padding expression. The process was repeated thrice and then the fabric was dried at ambient temperature and steamed for 10 min at 102° C.

*** Pad-dry-cure method**

The padding process was kept same as mentioned above. After padding, the fabric sample was dried and then cured at 150° C for 5 minutes in a curing chamber.

After-treatments: After dyeing, all the dyed samples were rinsed, soaped at 60° C for 15 min using 2 gpl non-ionic detergent solutions, washed thoroughly and dried at ambient temperature.

2.3 Testing and Analysis

2.3.1 Evaluation of dyed samples: Dyeing performance of various dyed samples was assessed by measuring the relative colour strength (K/S value) spectrophotometrically. These values are computer calculated from reflectance data according to Kubelka-Munk equation[7].

2.3.2 Assessment of fastness properties: The washing, light and rubbing fastness properties of various dyed samples were evaluated according to standard methods[8, 9].

- **Fastness to washing:** Wash fastness of different dyed samples was assessed on Launder-0-meter using ISO standard test No. 3 The change in shade was visualized using Grey scale and graded from 1 to 5 – 1 indicates poor and 5 indicates excellent fastness to washing.
- **Fastness to Light:** Colour fastness to light was evaluated by exposing the dyed samples to sunlight according to AATCC test method 16B-1977. They were graded from 1 to 8 – 1 indicates poor and 8 indicates excellent fastness to light[9].
- **Fastness to Rubbing:** The rub fastness of dyed samples was tested on Crockmeter. The specimen to be tested was rubbed against perfectly scoured and bleached cloth of dimension not less than 22 cm x 5 cm. The white rubbing cloth was placed over the end of the finger of the testing device. In the dry rubbing test, the cloth to be tested was rubbed 10 times in 10 sec in dry state while in the wet rubbing test; the procedure was same, except that the rubbing cloth was wetted out and squeezed to 100% expression. The grading was given by taking into consideration the intensity of stain obtained on white fabric as well as lowering in the depth of the rubbed sample. The staining on the rubbing cloth was assessed with the Grey Scale and grades awarded from 1 to 5, where 1 stands for poor and 5 for excellent fastness to rubbing[8].

3 Results and Discussion

In this study, various natural dyes, viz. Indigo, Turmeric, Kamala, and Henna – all obtained from natural vegetable sources have been selected for the dyeing of polyamide fibre, nylon. In case of Indigo vat dye, conventional leuco vat reduction process has been utilized for the application, wherein the reduction of indigo is achieved with the help of either sodium hydroslphite or D-glucose. The alkali used for solubilisation of leuco (reduced) vat dye is caustic soda.

For natural dyes other than Indigo, acetic acid and soda ash were used to maintain the acidic and alkaline pH of the bath respectively. The alkaline conditions were utilized only during the application of Turmeric dye, where change in shade has been visualized. For other dyes, no change in shade was observed in alkaline conditions when compared with the acidic medium dyeing during the trial experimental work. Moreover, the brightness of the shades was hampered in the alkaline medium. Hence the application of Henna and Kamala dyes was preferably done in the acidic medium only. For Kamala, Turmeric, and Henna dyes, exhaustion, pad-dry-steam and pad-dry-cure techniques were used for application on nylon substrate.

3.1 Optimization of reducing agents concentration used in indigo dyeing

In the preliminary experimental work, dyeing has been carried out by using sodium hydrosulphite in amounts just sufficient to reduce indigo. For conventional reduction method, sodium hydrosulphite utilized in the charging bath was 1 g and that used for dyeing 1%, 3% and 5% shades was 1g, 1.2 g and 1.5 g respectively. Alternatively, a natural reducing agent, namely D-glucose was also utilized for reduction of indigo. Initially, the use of D-glucose has been done on the basis of amounts of sodium hydrosulphite used for charging and dyeing. A slight lower colour yield is being observed which may be due to less optimum reduction of indigo with glucose. Thus, it became necessary to optimize the concentration of glucose, particularly in the dyeing bath in order to achieve uniform dyeing results without any loss of colour value. The optimum amounts of glucose used in the charging as well as dyeing liquors are mentioned in Table 3.

Table 3: *Amounts of reducing agents used in charging/dyeing baths for dyeing 1% and 3% shades*

Reducing agents	**Proportion (g) of reducing agent in**								
	Charging bath			**Dyeing bath**			**Total**		
	1% shade	**3% shade**	**5% shade**	**1% shade**	**3% shade**	**5% shade**	**1% shade**	**3% shade**	**5% shade**
Sodium hydrosulphite	1.0	1.0	1.0	1.0	1.2	2.0	2.0	2.2	3.0
D-glucose	1.2	1.2	1.2	1.2	1.5	2.5	2.4	2.7	3.7

3.2 Concentration study of various natural dyes

For application of natural dyes, 1%, 3% and 5% shades of indigo, kamala, turmeric, and henna dyes were dyed in order to visualize their dyeing performance on nylon. It can be observed from the Tables 4 and 5 that the colour strength increases virtually with the increase in the concentration of the dye in the dye bath. This study may help, to some extent, to prepare the shade cards of these dyes for nylon fabric. Thus, light, medium and dark shades could be obtained by choosing appropriate concentration of the dye in the dyebath.

The turmeric dye exhibits an increase in depth of shade by exhaust dyeing process; henna and kamala dyes did gave extraordinary results on nylon; but there is not much effect of dye bath concentration when nylon has been dyed with henna dye. The depth of shade is drastically decreased when pad-dry-steam technique is utilized. The study is still under progress to explore the proper reasons for such unusual behaviour.

Table 4: *Colour strength (in terms of K/S value) of nylon dyed with natural indigo using various reducing agents*

Reducing agent	***K/S* values for natural indigo**		
	1% shade	**3 % shade**	**5 % shade**
Sodium hydrosulphite	7.53	14.55	21.85
D-Glucose	7.66	16.02	26.28

Table 5: *Colour strength (in terms of K/S values) of nylon dyed with kamala, turmeric and henna dyes*

Dye	**pH**	***K/S* values for**								
		Exhaustion			**Pad-dry-steam**			**Pad-dry-cure**		
		1%	**3%**	**5%**	**10 g/l**	**30 g/l**	**50 g/l**	**10 g/l**	**30 g/l**	**50 g/l**
Kamala	4.5	9.76	15.46	23.45	4.29	10.38	18.64	4.83	11.37	19.11
Turmeric	4.5	3.52	7.8	14.98	1.71	4.48	11.65	1.53	5.46	12.08
	10	11.74	17.78	26.22	7.56	12.48	18.95	6.99	13.11	19.07
Henna	4.5	8.93	9.05	11.23	12.35	13.55	14.67	16.66	17.54	18.88

3.3 Effect of reducing agent in dyeing of indigo on nylon

Table 4 indicates the colour strength (in terms of *K/S* values) of indigo dyed on nylon substrate by cold exhaust dyeing method. It can be seen from the table that as far as dyeing performance is concerned, better colour value is obtained when D-glucose has been used for the reduction of indigo. At lower depth of shade (i.e., 1%), the colour value obtained with either sodium hydrosulphite or D-glucose reducing agent for application of indigo on nylon is quite similar in terms of the colour yield, but for 3% and 5% shades, the respective K/S values were about 11% and 20 % for D-glucose (*K/S* = 16.02 for 3% shade and 26.28 for 5% shade) in comparison with sodium hydrosulphite (*K/S* = 14.55 for 3% shade and 21.85 for 5% shade). This may be due to possibly better reduction of indigo achieved with D-glucose reducing agent. It must be noted here that the amounts of any reducing agent used for charging as well as dyeing of nylon, have been kept similar in order to visualize their effect in the dyeing performance.

3.4 Effect of dyeing techniques on the performance of Kamala, Turmeric, and Henna dyes

Table 5 represents the comparison of dyeing performance of Kamala, Turmeric and Henna dyes applied on nylon by different dyeing techniques. These dyes gave excellent performance on nylon when exhaustion technique is being utilized for dyeing. Surprisingly, the dyeing performance for padding techniques gave somewhat inferior results, which are in contrast to otherwise the best performance exhibited by most synthetic dyes when applied on nylon by padding techniques, viz. pad-dry-steam and pad-dry-cure. Padding techniques, however, should be preferred for commercial application purpose because most of the dyeing liquor gets utilize during application and the effluent liquor is very less, thereby leading to minimal pollution load.

3.5 Production of various shades from the application of Indigo, Kamala, Turmeric and Henna dyes on nylon

Apart from various beautiful shades produced by the individual dyeing of these natural dyes on nylon substrates, it has also been observed that a wide variety of compound shades can be obtained dyeing kamala, turmeric and henna dyes in admixture with each other and also by over-dyeing each of these dyes with natural indigo. A brief list of shades produced by each of these natural dyes on nylon is mentioned below:

- Indigo – sky blue to deep blue
- Kamala – tomato red to brilliant red
- Turmeric – pale yellow to golden yellow to reddish yellow(acidic medium)
- Turmeric – reddish shades of different hues(alkaline medium)
- Henna – copper brown to dark brown
- Kamala + Turmeric – orange to reddish orange to red
- Turmeric + Henna – brown
- Kamala + Henna – deep yellow to reddish brown
- Turmeric + Kamala + Henna – light brown to reddish brown
- Kamala over-dyed with Indigo – dark brown to purple
- Turmeric over-dyed with Indigo – yellowish brown to blackish brown
- Henna over-dyed with Indigo – greenish black to brownish black
- Turmeric + Kamala over-dyed with Indigo – green to brown shades
- Turmeric + Henna over-dyed with Indigo – green to brown shades
- Kamala + Henna over-dyed with Indigo – black

- Turmeric + Kamala + Henna over-dyed with Indigo – deep olive green to dark brownish black

3.6 Fastness properties of natural colour dyed nylon substrate

Fastness to washing, light and rubbing (both dry as well as wet) of various samples dyed with various natural dyes have been examined and compared with each other.

Table 6: *Fastness characteristics of nylon dyed with natural indigo*

Reducing agent	**Fastness grades for natural indigo**							
	3% shade				**5% shade**			
	W	**L**	**R**		**W**	**L**	**R**	
			Dry	**Wet**			**Dry**	**Wet**
Sodium hydrosulphite	4-5	7	5	4-5	4	7	3-4	3
D-Glucose	5	6-7	4	4-5	5	6-7	4	4

W: Wash fastness; **L** : Light fastness; **R** : Rub fastness

Table 8: Fastness grades of nylon dyed with Kamala, Turmeric and Henna dyes

Dye	**pH of the bath**	**Exhaustion**						**Pad-dry-steam**						**Pad-dry-cure**					
		3%			**5%**			**30 g/l**			**30 g/l**			**30 g/l**			**50 g/l**		
		W	**L**	**R Dry**	**W**	**L**	**R Dry**	**W**	**L**	**R Dry**	**W**	**L**	**R Dry**	**W**	**L**	**R Dry**	**W**	**L**	**R Dry**
T	4.5	5	7	5	5	7	5	5	6	5	5	6	5	5	7	5	5	7	5
K	4.5	5	7	5	5	7	5	4	6	5	5	7	5	5	7	4	4	6	4
	10	4	6	4	4	5	4-5	4	6	3	3	5	4	3	6	3	2	3	3
H	4.5	5	7	4-5	5	7	5	5	6	4	5	7	5	5	7	5	5	7	5

Dye -- T: Turmeric; **K** : Kamala; **H:** Henna; **W** - Wash fastness; **L** - Light fastness; **R** - Rub fastness

Tables 6 represents various fastness grades of nylon substrates dyed with natural indigo using 3% shade. The overall wash fastness of natural indigo dyed onto nylon substrates by conventional dyeing method is found to be excellent which ensures proper penetration of the leuco form of indigo vat dyes inside the fibrous material followed by insolubilisation of the dye due to oxidation, whereby the dye particle gets perfectly entrapped in the fibrous material and is not removed on washing treatment. Nylon dyed with natural indigo does not follow oxidative fading and thereby exhibit good light fastness. Among rubbing fastness characteristics, it is found that both dry as well as wet rubbing fastness of nylon dyed material are better and it ranges from very good to excellent (table indicated values of dry rub fastness only).

It can be observed from the table 7 that for Kamala, Turmeric, and Henna dyes, the fastness properties of various dyed samples are adequate. Wash and dry rub fastness properties of dyed nylon samples ranges from very good to excellent. However, the light fastness is somewhat inferior indicating some sort of oxidative fading taking place exposure to light source.

4. Conclusions

Natural indigo can be successfully applied onto nylon using conventional leuco vat reduction process. Better results are obtained when D-glucose is used for the reduction of the dye as compared to the conventional sodium hydrosulphite used commercially for dyeing of anthraquinone vat dyes. Moreover, D-glucose is eco-friendly and can be successfully employed for the reduction of natural indigo. The application of other natural dyes, viz. Kamala, Turmeric and Henna on nylon fabrics also gave quite encouraging results. Turmeric dye gave yellowish shades in acidic medium and reddish shades in alkaline medium. Furthermore, a wide variety of simple as well as compound shades, ranging from yellow, blue, red, to purple, orange, violet, green and fast black were obtained by application of these dyes either individually or in admixture with each other and also by dyeing Indigo over the dyed samples of kamala, turmeric, and henna. The fastness characteristics of various dyed samples were quite adequate. Thus, it may be summarized that colouration of nylon can be very well done with the help of vegetable natural dyes.

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