Isolation and its Purification of Laccaic Acid Dye from Stick Lac and study of its (Colour Fastness) Properties and Reflactance on Silk Fabric Dyed with Heavy Metal Mordants

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Abstract-Dye from stick lac was extracted, isolated and purified to remove wax and shellac which were removed as by products. Dye extracted was purified and applied on silk fabric using four different heavy metal mordants (Potash alum, potash Chrome alum, copper sulfate and ferrous sulfate) by using Metamordanting method of dyeing. Colour fastness properties (fastness to washing, rubbing. light and heat) were studied with the aid of grey scale for metamordanted and control silk fabrics. Reflactance of all the dyed fabrics was also noted. ʎmax and absorbance of dye were determined by spectrophotometer. Results showed that mordant dyeing increased the uptake of dye on silk fabrics. The results of colour fastness properties were from best to excellent.

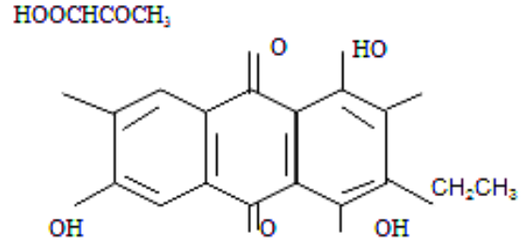
Keywords-Mordant. Reflectance, Isolation, Wax, Shellac.

I. Introduction

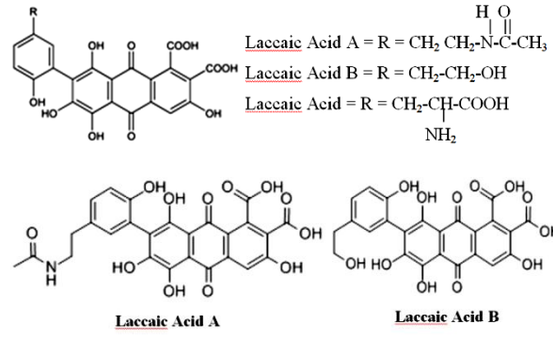
A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. It adheres to the fabrics like cotton, silk, linen, woolen, leather and many other materials. Dyes are of two types i) synthetic dyes and ii) natural dyes. As synthetic dyes cause environmental problems in textile and leather processing industries being major environmental polluters in the World. Many of synthetic dyes are carcinogenic and allergenic. It is the need of hour to use dyes and chemicals which are environment friendly and are less polluting [1], [2], [3]. Natural dyes have been known for a long time. These dyes not only come from flowering plants and vegetables but also from animal and insect sources like fungi, lichens and insects like shellfish [4], [5]. Lac dye is also one of the animal dyes. Natural dyes produce different subtle and soft colours on the yarn and fabrics and are gaining momentum day by day [6], [7].

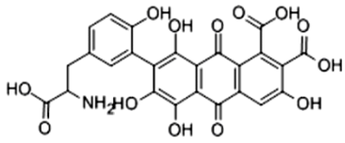
Insect dyes are obtained from the body of the insects. They live on different plants to get food colour and produce dye in the abdomen of the insect. The ancient dye stuff (lac) is obtained from the dried bodies of an insect coccuslaccae (LacciferLacca) found on twigs of certain trees of South Asian countries, which secretes Lac resin [6], [8], [9]("Lac,").

Lac is chemically very similar to carmine, carminicacidkernes or kermesic acid based partially on these findings, the following structural formula for laccaic acid has been proposed.

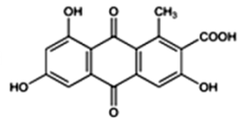


This formula was studied by Schmidt in 1887 who investigated the colouring matter of the lac dye and gave it the name of Laccaic acid. Latter on it was found that there are four compounds found in lac designated as A, B,C and D [8]. Laccaic acid A is most abundant *and* the major compound [10], [11], [12].Laccaic acid A, B, and C are very similar but differ at a single point that is illustrated in the following formulas. Laccaic acid D is also called Xamhokermesic acid *and* closely resembles kermcsic acid in structure:





Laccaic Acid C



Laccaic Acid D

It may be noticed that structures A, B, and C differ at a single point only.

Lac dye and Shellac has many applications in different fields. Lac dye is natural food pigment because of its approval from FDA. Shellac is used to coat apples and other fruits to make them shinner to improve its shelf life. It is used in cosmetics for making lipsticks and eye brow pencils and in sunscreen emulsions [13]. Lac dye is used for dyeing the fabrics usually wool and silk [14], [15], [16].

Shellac is also used in varnishes, extensively in food finishing, coating of candies and pharmaceutical tablets to protect against moisture and to seal off active ingredients. It is used to some extent as a leveling resin in some formulations& printing inks. It is used in vilons and other varnishes and is soluble in alcohol ("Lac,").

Use of natural dyes particularly insect dyes is gaining interest for dyeing and application in biological staining [14]. Pure insect dyes are highly valuable. Pakistan policy makers should show interest in propagation and applications of these dyes as these are environment friendly and create source of income for people living in rural areas.

Present work includes the extraction and purification of laccaic acid, study of its application on silk fabrics and colour fastness properties [17], [18], [19]. Most natural red colour dyes are highly soluble in water. So colour fastness to washing of lac dye was found quite low. In order to improve its colour fastness properties heavy metal mordant method was conducted. In which metal ions can act as acceptors to electron donors to form coordinate bonds with dye molecule which is insoluble in water [10], [3].

Most of the colour of the plant origin is anthrocyanides, flavonoid and carotenoids.

II. MATERIALS & METHODS

2.1 Instrumentation

IR spectrometer model "bruket OPUSTUM Nicolet IR 200 200 (USA).D400 IR dyeing machine (SDL Atlas England). Launderometer (Roaches). Oven Ci 3000 – Xenon. Weatherometer, (Atlas Enland). Water bath. Grey scales for staining (ISO 105 A03). Grey scale for change in shade (ISO 105 A02.). Crockmeter (SDL Atlas England). Multifiber (DW). Twiglac.

2.2 Chemicals & Reagents

Potash alum, Potash chrome alum, copper sulfate, ferrous sulphate, detergent, SDC standard soap (without optical brightener), distilled water, sodium carbonate, sodium chloride (AR Grade).

2.3 METHOD

2.3.1 Isolation of Lac Dye

Source: Fresh twig lac was plucked and collected in the month of June from the branches ofberri (Zizzyphous) tree which were found to grow in campus of PCSIR Phase-1, Housing Society, Canal Road, Lahore. Many branches were infected with insect laceiferlacca.

Lac (Shellac) was separated from the twigs and branches manually with the help of spatula. Fibrous material of branches, twigs, debris and infected sects were sorted out. 500 gms of natural shellac thus obtained was coarsely ground in mortar and added 5000 ml of water. Stirred it well for 3 to 4 hours. It was then filtered through coarse mesh sieve washing the residual lac on the sieve with 100 ml water. The dark red filterate solution was filtered through Buckner funnel, covered with filter cloth. The dye solution was finally centrifuged till clear solution of red dye was obtained. The clear solution was decanted carefully into conical flask [6], [18], [10], [20], [21]. The clear red filtrate was acidified with conc. hydrochloric acid to pH 1-2 till red dye was precipitated. It was stirred for 2-3 hours by magnetic stirrer then centrifuged. The precipitated dye was separated from supernatant liquor. The precipitated dye was removed and transferred to petri dish for drying. The dried dye had still waxy touch, so finally it was extracted with hexane to remove any waxy material. Laccaic acid dye 3.4% was obtained by applying above mentioned process.

2.3.2 Isolation of Wax, Aleuritic Acid

Dye free lac (residual lac) was extracted with hexane in the Soxhlet apparatus. Hexane soluble material containing wax and aleuritic acid was made free from hexane by distillation. The hexane free solid material was taken in diethyl ether and added ethanol drop wise, Wax was precipitated and separated from the solvent mixture. The solvent was distilled off and white fluffy material aleuritic acid was obtained.

2.3.3 Dyeing with Lac Dye

Dyeing is the process of colouring textile fibres and other materials, in such a way that the colouring matter becomes an integral part of materials (fabrics etc.) rather than a surface coating. Dyeing was completed with 2% lac dye solution without and with mordant (metamordanting technique). The liquor

ratio of (fabric and water) during dyeing was 1:20. Before dyeing silk fabric was wetted with wetting agent. Temperature was maintained at 100°C. Dyeing was completed in 1 hour. After dyeing silk fabrics were washed, squeezed and dried at room temperature.

2.3.4 Dyeing with Mordants

The processing agent which can make link between cloth and dye is known asmordant which is derived from a Latin word 'mordate' means to bite [22]. Mordant may be added in three different ways (I) Premordanting when fabric is treated with mordant before dyeing (2) Metamordanting in which mordant is added during dyeing of fabric and (3) Postmordanting when fabric is treated with mordant solution after dyeing. Metamordanting technique was used during this study using heavy metal mordants (Potash alum, potash chrome alum, copper sulphate and ferrous sulphate) [23], [24].Wet fabrics were dipped into 2% lac dye solution. The liquor ratio during dyeing was 1:20. The temperature of dye bath was maintained at 100°C and total time for dyeing was 1 hour. After 45 minutes of dyeing different mordants of 0.1M strength were added to the dyeing bath for fifteen minute, then fabrics were rinsed, washed and squeezed and dried at room temperature.

2.3.5 Colour Fatness to Washing

Dyed silk fabrics and multifibre DW were cut into 4 X 10 cm size pieces and sewed with each other from one side in such a way that their faces were adjacent to each other. Soap solution made by adding 5gm soap per liter of water, under specified conditions of time and temperature, were added to different steel containers fixed in launderometer having liquor ratio 50:1. Change in colour or the specimen and staining of adjacent fabrics (DW multifibre) was assessed with the help of grey scale. Results of colour fastness to washing are shown in Table I (1006, 1990).

2.3.6 Colour Fastness to Dry and Wet Rubbing

Colour fastness to dry and wet rubbing of metamordanted dyed silk, fabrics were performed with the help of crockmeter instrument. For this test different silk fabrics of 5 cm x 14 cm were fastened by means of clamps to base board of the testing device. The standard cloth was first rubbed in dry condition and then in wet condition in to and fro motion in a straight line along a track 10 cm long on surface of fabrics 10 times in 10 seconds with a downward force on 9 N. Fabrics were, dried at room temperature. Change in shade of the dyed fabrics and staining of the rubbing cloth was assessed with the help of grey scale. The results of colour fastness to rubbing are given in Table II (1006, 1990).

2.3.7 Colour Fastness to Light

Colour fastness to light was carried out with instrument weatherometer by Atlas according to ISO 105 standard procedure B02, in which Xenon arc lamp was used as an artificial light source, representative of natural day light D65. Silk fabrics of measurement 7 cm x 12 cm were exposed to D65 light and result of colour fastness to light against blue wool were noted with the help of grey scale. Change in shade was noted. Results obtained are tabulated in Table II.

2.3.8 Colour Fastness to Heat

Colour fastness to dry heat fastness for all silk fabrics was performed by hand iron. Silk fabrics were pressed for five minutes at specific temperature with and without mordants. Results are shown in Table II.

2.3.9 Reflectance of Silk Fabrics

IR spectrometer, model–Bruker OPUSTM Nicolet IR 200 (USA) was used for recording reflectance in the infra region for silk cloths dyed with Iac dye with and without mordants. The spectrum of laccaic acid dyed fabrics was recorded on the above mentioned IR spectrometer [25].

2.3.10 Procedure

Silk fabrics were put on the lens of IR spectrometer and noted the reflectance peaks of the dyed silk fabrics. Results & discussion are given in Table III.

III. RESULTS & DISCUSSION

The grey scale results of the silk fabrics dyed with lac dye (control) and dyed with different heavy metal mordants are given in Table I & II for colour fastness to washing, dry and wet rubbing fastness, light and heat.

TABLE I
COLOUR FASTNESS TO WASHING FOR SILK FABRIC DYED WITH HEAVY METAL MORDANT AND WITHOUT MORDANTS (CONTROL)

Sr. No.	Observed dyed	Diacetate	Cotton	Nylon	Polyester	Polyacrylic	Wool	Change in shade
1.	Control	4	3-4	5	4-5	4-5	4	2-3
2.	Potash alum	4-5	4	5	5	5	4-5	3-4
3.	Potash chrom alum	5	4-5	5	5	5	4-5	3
4.	Ferrous sulfate	4-5	4	5	5	5	4-5	3
5.	Cooper sulfate	4-5	4	5	5	5	4-5	2-3

Colour fastness to washing was observed for control silk fabric (dyed with lac dye on silk) and silk fabrics dyed with four heavy metal mordants using metamordanting method respectively. For control fabrics the values for colour fastness to washing did

not gave good results, because dyeing on fabric does not adhere on the fabric, resulting light colour shades with different concentration of dye. Application of different heavy metal mordants not only increase the depth of shade on fabrics but also change the colour of the dye. Potash alum gave move (purplish) colour. $CuSO_4$ gave grayish move colour while potash chrome alum gave dark pinkish move colour. Reason is that heavy metal mordants increase the binding capacity of the dye to the fabric.

So in metamordanting process of dying the dye is absorbed on the fiber followed by the formation of an insoluble complex with metal ions showing bathochromic shift. So some of the dye is lost became of formation of this insoluble complex in the dye bath itself. So this phenomena bring about a decrease in the effective dye concentration in the dye bath.

For washing tests all the values for change in stain and change in shades were noted and are shown in Table I.

3.1 Change in Staining

On diacetate staining strip of multifibre, (DW) lac dye control gave good 4 rating, while potash alum, ferrous sulfate and copper sulfatemordanted silk fabrics gave best 4-5 rating while excellent results rating 5 were observed with potash chrome alum. On cloth staining strip of multifiber gave rating 3-4 satisfactory results for control (fabric dyed with lac dye) where no mordant was used. Potash alum, potash chrom alum, ferrous sulfate and copper sulfate gave good 4 rating on grey scale. On Nylon strip of multifiber all the five silk fabric dyed with Iac dye and silk fabrics mordanted with potash alum, potash chrom alum, ferrous sulfate and copper sulfategave excellent rating i.e. 5. Polyester strip ofmultifiber showed 4-5 best rating with control fabrics and 5 excellent rating with potash alum, potash chrom alum, ferroussulfate and copper sulfatemordants silk fabrics. Polyacrylic strip showed same results as for polyester stip, while wool strip gave 4 good rating with control silk fabric and 4-5 best rating with other four metamordanted silk fabrics.

3.2 Change in Shade

When change in shade of original dyed fabrics (control) and mordant treated fabric, was observed, it was found that control fabric (dyed with lac dye) gave 2-3 i.e. poor rating potash alum mordanted silk fabric gave 3-4 i.e. satisfactory rating. Potash chrom alum and ferrous sulfate mordanted silk fabrics gave 3 rating while copper sulfate mordantedsilk fabric also gave 2-3 poor rating.

3.3 Results of Grey Scale for Rubbing Fastness, Light Fastness and Heat Fastness

Rubbing fastness was performed according to ISO 105 X 12 by ISO method with instrument crockmeter. Roth dry and wet rubbing along warp and weft were noted with standard cloth fabric. Similarly light fastness was performed according to ISO 105 standard procedure B02 while heat fastness with hand iron.

TABLE II
RESULTS OF RUBBING FASTNESS, LIGHT FASTNESS AND HEAT FASTNESS ON SILK FABRICS DYED WITH AND WITHOUT HEAVY METALS MORDANTS

Sr. No.	Name of Fabric	Rubbing Fastness				Light Fastness	Heat Fastness (Dry)
		Dry Rubbing		Wet Rubbing			
		Warp	Weft	Warp	Weft		
1.	Control	4-5	4-5	4	3-4	4	4
2.	Potash alum	5	5	4-5	5	4-5	4-5
3.	Potash chrom alum	5	5	4	4-5	4-5	4-5
4.	Ferrous sulfate	5	5	4	4	4	4-5
5.	Cooper sulfate	4-5	5	4-5	4	4-5	4-5

3.4 Results of Dry Rubbing Fastness

Dry rubbing fastness of lac dye gave best 4-5 results along warp and weft while with potash alum, potash chrom alum and ferrous sulfate mordanted silk fabrics gave excellent 5 results on grey scale along warp as well as weft. With CuSO4 mordant, dry rubbing gave best 4-5 results along warp and excellent 5 results along weftside of the silk fabrics. In all the cases where rubbing was performed with control fabric gave low grey scale rating and low quality level of dyeing as compared to rubbing performed by the application of metal mordants.

3.5 Wet Rubbing Fastness

Wet rubbing fastness of control fabric gave better 4 rating along warp and satisfactory 3-4 rating along weft. Potash alum gave best 4-5 rating along warp and excellent rating 5 along weft potash chrom alum and ferrous sulfate both gave good 4 rating along Warp and 4-5 best, (good) 4 along weft respectively. Copper Sulfate gave 4-5 best results along warp and 4 (good) along left side of the silk fabric.

3.6 Result of Colour Fastness Light

According to Table II colour fastness to light with control fabric gave 4 (good) results. Potash chrom alum and copper sulfate dyes silk fabrics gave 4-5 best, rating for colour fastness to light.

3.7 Results of Colour Fastness to Light

Colour fastness to heat have 4 better rating for control fabric (dyed with lac dye soln.) and best results for potash alum, potash chrom alum, ferrous sulfate and copper sulfate mordanted silk fabrics. Results of washing fastness light fastness and colour fastness showed low

grey scale rating with control silk fabrics dyed with lac dye.

3.8 Results of Reflective Peaks

IR reflectance peaks of spectra of dyed fabrics with and without mordants are given in Table III.

TABLE III
RESULTS OF REFLECTANCE PEAKS OF DYED SILK FABRICS WITH AND WITHOUT MORDANTS

Dye	Frequency cm^{-1} Dyed silk with mordant				Dyed silk mordant	Intensity	Assignment
	A	B	C	D			
550	640	665	520	700	724.41	Var	4
1000	1000	1000	1040	1000	1016	Wk	Amine
-	1090	1100	1100	1110	1094	-	-
1260	1240	1240	1210	1280	1238	Med	Carboxylic acid
1400	1400	1410	1430	1410	1408	Str	C=O
1630	1690	1690	1590	1520	1505	Med	Arene
-	-	2430	-	-	2360	-	-
2850	2700	-	2890	2890	-	-	-
2950	-	-	2950	2950	-	-	-
330	-	3000	-	-	-	-	-

A=Chrom alum, B=Copper sulphate, C=Ferrous sulfate and D=Potash alum.

IV. CONCLUSION

The use of natural dyes, particularly insect dyes is gaining interest again for natural dyeing of fabrics and other applications in food, pharmaceuticals and cosmetics industries. The results show that mordanted dyeing with lac is more applicable because colour uptake on silk fabrics increases and results are best to excellent. Lac dye is environment friendly and creates source of income for people living in rural areas. Researchers, policy makers and industrialist should make efforts to popularize the use of lac dye fabrics among the masses.

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