Synthesis and Application of Eco-Friendly Natural-Printing Paste for Textile Coloration

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Abstract: Both eco-friendly galactomannan gum and safety natural dye could be isolated simultaneously in one step process from Locust bean (carob) seeds. The obtained colored paste is regarded as natural-printing paste. It was assessed for rheological properties and evaluated in printing cotton, wool and silk in presence and absence of different mordants. The influence of chemical modification of cotton fabrics via: (a) cyanoethylation, (b) reaction with reactive cyclodextrin and (c) cationization on their printability was also investigated. The isolated paste was characterized by a non-Newtonian pseudoplastic behavior, its viscosity decreased by increasing the rate of shear. The colored printing paste isolated from carob seeds, could successfully be used in printing of cotton, wool and silk. Mordants enhance printing and create different colors. Chemical modification of cotton fabrics via: (a) cyanoethylation , (b) reaction with reactive cyclodextrin and (c) cationization, improved the printability of cotton fabrics with natural dye extracted from carob seeds, irrespective of the nature of modification. As the extent of modification increased the color strength (K/S) of the printed good increased. In all cases the overall color fastness properties was ranged from good to very good.

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1. Introduction

Locust been (Carob) gum is the refined endosperm of the seed of carob tree, evergreen the legume family, known botanically as *Ceretonia siliqua* L. The seeds are covered by a dark brown seed coat (natural dye), under which is the white endosperm (galactomannan gum); the yellow germ portion runs through the center. The ratio of D-galactose to D-mannose is 1:4 respectively [(1)]. It has been reported that galactomannan gum are more environmentally suitable among the other carbohydrate thickening agent[(2)].

Textile printing is one of the processes of textile industry that causes very high water pollution due to unfixed color, thickening agent, and other ingredients of printing paste which are washed off of the fabric into waste water [(2-4)].

Calls for the use of natural dyes on textiles has been just one of the consequences of increased environmental awareness [(5)]. It is believed that natural dyes are more friendly to the environment than synthetic dyes [(6-9)]. Since carob seeds contain natural colour and galactomannan gum, both of them are ecofriendly. The present work aims at isolating both the gum and natural dye from carob seeds simultaneously in a single step process. Utilization of the so obtained natural-printing paste for printing cotton, wool and silk in presence and absence of different mordants is also investigated. Furthermore, the impact of chemical modification of cotton fabrics via cyanoethylation, reaction with reactive cyclodextrin and cationization on their printability was reported.

2. Experimental

2.1. Materials

2.1.1 Locust bean (carob) seeds:

Dry clean carob seeds were obtained from carob pods. The latter was purchased from the Egyptian local market. The seeds are covered by a dark brown coat which contain a natural dye, under which is the white endosperm (the gum); the yellow germ portion runs through the center.

2.1.2. Substrate:

Cotton fabric:

Mill desized, scoured and bleached poplin cotton fabric (140g/m^2) manufactured by Misr/ Helwan for Spinning and Weaving Company was used throughout the present work.

Wool fabric:

Mill scoured pure wool fabric (270 g/m^2) was supplied by Misr Company for Spinning and Weaving, Mehalla El-Kubra, Egypt.

Natural silk fabric:

Mill scoured natural silk fabric (81 g/m^2) was supplied by Hussein El-Khatib Sons Company, Akhmim, Suhag Upper Egypt.

2.1.3. Mordants and other chemicals:

The mordants used were comprised alum, ferrous sulphate, cupper sulphate, potassium dichromate and tannic acid.

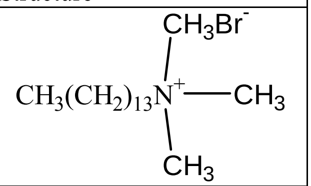
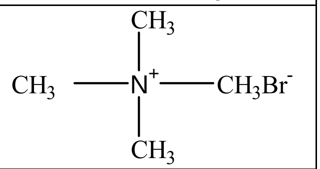
Sodium hydroxide, sodium carbonate, sodium bicarbonate, acetic acid, acrylonitrile as well as Reactive cyclodextrin were of laboratory grade chemicals.

Non-ionic detergent, under trade name, Hostapal CV-ET was used, prodused by Dystar, Germany.

High viscosity sodium alginate was used under the commercial name Daicothik RE.

2.1.4.Cationic agents:

The compound, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (65 wt. %) is a technical grade cationic agent and was kindly supplied under the commercial name (Quat-188) by Dow Chemical Company, USA. The second compound was dodecyl trimethyl ammonium bromide (DTAB). The third was hexadecyl trimethyl ammonium bromide (HTAB). The other compound two cationic agents are cleared in the following table and are of fine grade chemicals:

Symbol	Name	Structure
MTAB	Myristyl trimethyl ammonium bromide	
TMAH	Tetramethyl ammonium hydroxide	

2.2. **Methods:**

2.2.1. Isolation of natural-printing paste:

The hull of carob seeds contains natural color. That is why the seeds acquire a dark brown color. Several trials were carried out to isolate the natural colors along with the dissolved galactomannan gum with a view to obtain a natural-printing paste. Hence the experimental procedure adopted in the present work to isolate a natural-printing paste-based on galactomannan and natural dye – could be summarized as follows:

The seeds were crushed mechanically and sieved to remove the germ. The hull and endosperm were then soaked in 1% sodium hydroxide solution and left overnight to yield a colored viscous mass. The latter was purified through separation from other insoluble components of hull and endosperm by filtration using a mucilien fabric. The viscosity of the purified colored viscous mass so obtained was adjusted by adding 10 g sodium alginate/ Kg printing paste and used for printing.

2.2.2. Pretreatment by padding the fabrics with mordants:

Samples of silk, wool or cotton fabric were padded with 2 % aqueous solutions of the mordant to a wet pick up of 100 %, followed by drying at room temperature. The so mordanted fabric samples were screen printed using the natural-printing paste and the prints were realized through drying, steaming and washing.

2.2.3. Chemical modification:

Cyanoethylation:

Samples of cyanoethylated cotton fabric were prepared by padding the cotton samples in a solution of 100 g/l sodium hydroxide. After 2 hours of batching the samples were unrolled, padded in pure acrylonitrile, acrylonitrile: water (50:50 and 25:75 by volume) and batched for 4 hours. The treated samples were then washed with water, neutralized with diluted acetic acid, washed with water again and left to dry in air. Besides, a sample of cotton was treated with sodium hydroxide only and denoted as alkali treated sample [10].

Reaction with reactive cyclodextrin:

The conventional pad-dry-thermofixation method was applied. Thus pad bath containing R-CD and the catalyst (sodium bicarbonate) was prepared as follows. A small amount of water was added to R-CD and the resulting solution was warmed up until complete dissolution occurred. The solution was then cooled down to room temperature and the pad bath concentration was adjusted along with concurrent addition of the catalyst (sodium bicarbonate 20 g/l). Cotton fabric was padded in the bath twice to a wet pick up of 100 %. The treated fabric was dried in an oven for 13 min. at 60-70^{0}C and then subjected to heat treatment at 150^{o}C for 7 min. Different concentrations of R-CD viz. 25,50 and 100 g/l were used to obtain different extents of reaction [11].

Cationization of cotton fabric:

The cationization was carried out according to the Pad-Batch method [12]. The cationic reagent used at concentrations of 100g/L with corresponding sodium hydroxide concentrations of 43.6 g/L. The fabrics were padded through the cationization baths at aproximately100% wet pickup, and then padded fabrics were placed in plastic bags and stored at room temperature for different batching times. After the removal of the padded fabrics from the plastic bags, they were rinsed with warm water at 40 °C. To remove the unfixed and hydrolyzed cationic reagent, neutralized with 2 g/L acetic acid, rinsed with cold water and then dried at 100°C. Details of the procedure are mentioned elsewhere [12].

2.2.4. Printing:

Screen printing of cotton, wool and silk fabrics was carried out using the natural-printing paste .The so printed fabrics were then subjected to the following operations.(a) *Fixation*: Prints were fixed on the fabrics by steaming at 100°C for 15 minutes.(b) *Washing*: The fixed printed fabrics were thoroughly washed with cold running water followed by washing at 50°C with a solution containing Hostapal CV-ET (2 g/l) and sodium carbonate (3 g/l) for 15 minutes , then washed with water at 45° C for 5 minutes and finally rinsed with cold water and air dried.

2.3. Measurements and Analysis:

2.3.1. Determinations of the rheological properties:

The rheological properties were measured using a coaxial viscometer, "reheomat-15" Zurich, Switzerland. The apparent viscosity was calculated using the following formula.

$$\mu = \frac{\tau}{D}$$

(Where μ is the apparent viscosity in poise τ the shearing stress in dyne/cm^2, D the rate of sheer (sec^{-1})[12].

2.3.2. Nitrogen content:

The nitrogen content of the chemically modified and cationized fabric was determined by the Cole and Parks modification of the Semimicro Kjeldahl method [13].

2.3.3. Colour strength measurements:

The colour strength of the printed samples expressed as K/S was evaluated by light reflectance technique [14]. All the printed samples were measured using a Hunter Lab UltraScan PRO instrument.

2.3.4. Fastness and measurements:

The colour fastness properties to washing [15] to rubbing [16] and to perspiration [17] were carried out according to standard methods.

3. Results & Discussion:

It has been reported that galactomannan gums are more environmentally suitable than conventional thickeners [2]. Recently concern of the environment has also created an increasing interest in natural dyes. Conventional wisdom leads to the belief that natural dyes are more friendly to the environment than synthetic dyes [18,19]. As already stated the aim of current work is to prepare a natural-printing paste extracted from carob seeds and apply it in textile printing in presence or absence of mordants. Besides, the effect of chemical modification of cotton fabrics on their printability was investigated.

It is well known that carob gum is not easily soluble in cold water and it needs a complicated and long steps to extract the gum from the endosperm which is sticky well with the hull. To overcome this problem a warm water containing 1 % sodium hydroxide was used. The obtained paste was not viscous enough, hence a small amount of sodium alginate (10 g/Kg of the paste) was added to obtain the suitable viscosity as shown under.

3.1 Rheological properties:

Figure 1 represents the rheograms of the isolated printing paste before and after storing for 48 hours prior to commencing measurements.

As it is clear from figure 1 that the printing paste under investigation is characterized by a non-Newtonian pseudoplastic behavior since the up and down flow curves are coincident and curves are concaved towards the rate of shear axis. On comparing the rheograms before and after storing, we can easily conclude that the storing time has no remarkable effect on the rheological properties of the paste since it is still characterized by a non-Newtonian pseudoplastic behavior. Meanwhile the rheogram is shifted near to the rate of shear axis indicating that the viscosity of the paste undergoes gradual decrease, as shown in Table I.

It is clear from Table I that the apparent viscosity decreases as the rate of shear increases, for example it decreases from 85.71 to 12.18 poise by increasing the rate of shear from 2.18 to 137.1 sec^{-1}. Storing of the paste for 48 hours causes a slight decrease in the apparent viscosity where at a rate of shear 13.12 sec^{-1} it decrease from 48.91 to 43.89 poise. The decrease in the apparent viscosity by storing may be due to the hydrolysis of the galactomannan chains on storing.

3.2. Printing:

3.2.1. *Printing in presence and absence of mordant:*

In the proceeding section, an eco-friendly printing paste containing a natural dye and galactomannan gum could be obtained from carob seeds. The use of this printing paste in printing wool, silk and cotton fabrics was undertaken. Samples of the three fabrics were padded in a solution of some different mordants viz. tannic acid, ferrous sulphate, copper sulphate, potassium dichromate and alum at a concentration of 2% to a wet pick up of 80%, followed by drying and printing with the isolated printing paste. Color fixation of the prints by steaming was effected at 100°C for 15 minutes. Color strength (K/S) of the prints was measured and the results are given in figure 2.

It is clear from the data of figure 2, that in most cases the K/S of the protein fabrics, i.e. wool and silk is relatively higher than in case of cellulosic fabrics, i.e. cotton. This is expected since, it has been reported [20] that the tannins present in carob seeds are high molecular weight compounds containing phenolic hydroxyl groups which enable them to form effective crosslinks between proteins; where they form three types of bonds namely:

(a) Hydrogen bond: which is formed between phenolic hydroxyl groups of tannins and the free amino and amides groups of the proteins.
(b) Ionic bond: it is formed between suitable charged anionic groups of the tannin and cationic groups on the protein.
(c) Covalent bond: it is formed by interaction of any quinone or semi quinone group present in tannin with any suitable reactive groups in the protein.

However in case of cellulosic, exemplified by cotton, the tannins could form only two types of bonds as follows:

(a) Hydrogen bond: which is formed between phenolic hydroxyl groups of tannins and the hydroxyl groups of cellulose.
(b) Covalent bond which may be formed by the interaction of quinone or semi quinone groups present in tannins with suitable functional groups in the cellulose.

Table II represent the effect of mordanting on the K/S of cotton fabrics. As previously mentioned, cotton fabrics being a cellulosic fabrics have a small affinity to the natural dye compared with the protenic fabrics. But using different mordants can increase its affinity and hence increase the K/S values.

Results of table II reveal that the untreated cotton samples has the lowest K/S values, while the highest K/S was obtained on applying the tannic acid as a mordant. The K/S values of the prints in question can follow the order: samples mordanted using tannic acid (has the highest K/S) › ferrous sulfate › potassium dichromate › cupper sulfate › Allum › untreated samples.

The improvement in the K/S of cotton fabric samples on using tannic acid could be due to the formation of hydrogen bounding and covalent bounding as previously mentioned. While in case of metallic mordants (copper sulphate, potassium dichromate, ferrous sulphate) the K/S increase slightly compared with tannic acid. It is worthy to mention that in spite of the highest value of K/S obtained on using ferrous sulphate, it causes a degradation of cotton fabrics, since Fe^{2+} reacts with the atmospheric oxygen to form Fe^{3+} which, in turn, reacts with water to yield hydroxyl free radical (OH·). This hydroxyl free radical is responsible for the textile degradation[21]. For this reason it is not recommended due to its effect on cellulosic fabric.

Wool has a good affinity for natural dye, its chemical structure enables the fiber to unite chemically with a wide variety of dyestuffs [22]

Table III shows the K/S of the printed prepadded wool samples. Obviously the K/S values brings into focus the order: tannic acid › copper sulfate › potassium dichromate › ferrous sulphate › alum › non treated.

Wool being a protenic fabric has high affinity to the natural color. This is evidenced by comparing the K/S of table III and those of table II. The wool samples acquire high vales of K/S compared with that of cotton fabric irrespective of the kind of mordant used.

Also the highest K/S value is acquired when tannic acid was used as a mordant, some situation is encountered with the cotton fabric. But hear a remarkable observation is that tensile strength of wool fabrics is not affected by ferrous sulphate treatment as in the case of cotton fabric. This is expected since the wool fabric can resist the effect of the ferrous sulfate as a mordant compared with cotton fabrics.

Table IV discloses the K/S values when the natural-printing paste was applied to silk fabric. As is evident silk differs than wool and cotton. These differences can be realized from the following points:

(1) The lowest K/S value is obtained with the alum and not with the untreated fabric as in the cases of wool and cotton.
(2) The K/S values of silk fabric brings about the order: tannic acid › ferrous sulfate › cupper sulfate › potassium dichromate › untreated › alum.

Although silk fabric is categorized as a protenic fabric but it differs from wool in its weight, absorbance, resilience and reactivity. All these parameters may cause decreased K/S when alum was used as a mordant.

The metallic mordants used specially copper and ferrous sulfate are well known for their ability to form coordination complexes. In this study both readily chelated with the dye. As the coordination numbers of copper II and iron II are 4 and 6 respectively, some coordination sites remained unoccupied when they interacted with the fiber. Functional groups such as amino and carboxylic acid groups on the fiber can occupy these sites. Thus, these metals can form a ternary complex on one site with the fiber and on the other site with the dye. Such a strong coordination tendency can enhance the interaction between the fiber and the dye, resulting in high dye uptake. Furthermore, since copper complexes are normally much stronger than those of iron, fabric- mordant –dye interactions are stronger when using copper mordants, resulting in higher K/S values.

It can thus be concluded that the K/S depends on both (a) nature of the fiber, and (b) nature of the mordant used.

Tables II, III IV comprise the overall color fastness properties, i.e. color fastness to washing, to rubbing and to perspiration for cotton, wool and silk fabrics printed using the printing paste isolated from carob seeds. It is clear from the data that in all cases the color fastness properties are quite satisfactory for practical purposes where, it ranges between good to very good.

3.2.2. Chemical modification of cotton:

Chemical modification of polymers with the aim of imparting specific desirable properties is one of the main directions of development in modern macromolecular chemistry. As previously mentioned the aim of the present work is to carry out some chemical modification on cotton fabrics to improve its printability with natural color extracted along with the galactomannan gum from carob seeds.

With the above in mind, cotton cellulose in the fabric form was chemically modified via (a) cyanoethylation, (b) reaction with reactive cyclodextrin, and (c) cationization. For every modification different extents of reaction expressed as %N were made available.

Samples of cotton fabrics before and after chemical modification were printed with the natural-printing paste extracted from carob seeds via screen, i.e. screen printing. After printing, the samples were fixed via steaming, washed, air dried and then assessed for K/S and over all fastness properties. The results obtained are given in tables V and VI.

Cyanoethylation:

The reaction of cellulose with acrylonitrile may be expressed as suggested by scheme (1):

$$\text{Cell-OH} + \underset{\text{Acrylonitrile}}{CH_2=CH\text{-}CN} \xrightarrow{\text{NaOH}} \underset{\text{cyanoethylated cellulose}}{\text{Cell-O-}CH_2\text{-}CH_2\text{-}CN} \qquad \text{scheme (1)}$$

Table V shows the effect of cyanoethylation of cotton fabrics on their K/S and overall fastness properties when printed using the printing paste isolated from carob seeds. The results obtained with prints developed from untreated and alkali-treated cotton fabrics are also given in the same table for comparison.

It is clear from the data of table III that irrespective of the degree of cyanoethylation the K/S of the printed goods follows the order: Cyanoethylated cotton › alkali treated › untreated cotton. It is also clear that, as the degree of cyanoethylation, expressed as % N increases, the K/S increases, where it increases from 2.18 to 2.83 as the % N increases from 0.39 to 0.78.

This indicates that the introduction of cyanoethyl group in the molecular structure of cotton cellulose enhances the printability of the latter by the natural dye extracted from carob seeds.

It is also clear that, treatment of cotton with alkali prior to printing enhances the printability of the fabric. Hence the combined effects the alkali and cyanoethylation reaction on increasing the susceptibility of cotton to printing are responsible for the higher values of K/S observed with cyanoethylated cotton. That is during cyanoethylation, cotton cellulose undergo changes in the physical and chemical structure. Changes in the physical structure, inevitably occurring during the chemical modification via cyanoethylation comprise: (a) opening up the cellulose structure due to the presence of cyanoethyl groups and groups created thereof under the effect of alkali, (b) enhancing the accessibility of cotton by the alkali and, therefore its swellability. On the other hand, the chemical changes results in introduction of cyanoethyl groups which offered additional sites for dye adsorption.

Table V reveal that the overall color fastness properties of both cyanoethylated and alkali-treated cotton fabrics printed with natural color of carob seeds are comparable with those obtained for prints developed from the untreated cotton fabrics.

Reaction with reactive cyclodextrin (R-CD):

As an electrophilic compound, R-CD reacts in the presence of alkali with nucleophilic groups such as the hydroxyl groups of cellulose (cell) , as shown in scheme (2).

$$\text{Cell-OH} + \text{R-CD} \xrightarrow{\text{Alkali}} \text{Cell–O–CD} \qquad \text{scheme (2)}$$

The reaction involves covalent bonding to the cellulose and therefore can be categorized in the reactions that induce chemical modification of cellulose.

The influence of the presence of reactive cyclodextrin (R-CD) in the molecular structure of cellulose on behavior of the latter towards printing with the extracted paste was also investigated, where; samples of cotton fabrics were allowed to react with different concentrations of R-CD according to the procedure described in the experimental section. After treatment and fixation the treated fabrics were washed to remove the unfixed R-CD followed by drying. The results of the nitrogen content, K/S and overall fastness properties are given in table V. It is clear that the K/S of the R-CD modified cotton fabric samples is relatively higher than the untreated cotton sample irrespective of the nitrogen content of the modified fabrics. It is also clear that as the % N increases, the K/S of the printed fabric increases, where; it increases from 2.19 to 2.45 by increasing the % N from 0.15 to 0.5.

The increase in the K/S by modification of cotton with R-CD may be due to: (a) the inclusion of the dye molecules in the cone-shaped of cyclodextrin molecules and/or: (b) the physicochemical changes of R-CD modified cotton fabrics.

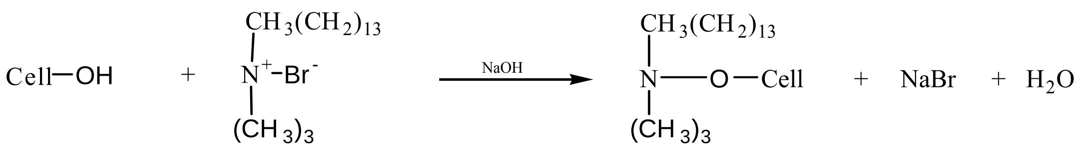
Table V reveal that the color fastness properties for rubbing, washing and perspiration of R-CD modified cotton fabric samples are nearly comparable with those obtained in case of the unmodified cotton sample.

Cationization:

In other approach, the effect of cationization of cotton fabrics using different cationic reagents on printing with the aforementioned printing paste was also investigated. Different cationized samples were subjected to screen printing using the paste in question, then the printed samples were adjusted to measurement of % N as well as K/S and overall fastness properties, and the results are summarized in Table VI.

It is clear from Table VI that the %N as well as the K/S values were affected by the kind of the cationic reagent. It can be easily observed that the highest %N and the K/S were obtained when using MTAB as a cationic reagent while when using Quat 188, HTAB, TMAH and DTAB the % N decreases respectively.

MTAB (Merstyl trimethyl ammonium bromide) at which the highest K/S was obtained can easily react with the hydroxide groups of the cellulosic fabric under the catalytic action of sodium hydroxyl by forming ether linkages cellulosic fabrics according to the following scheme (3)



Scheme 3

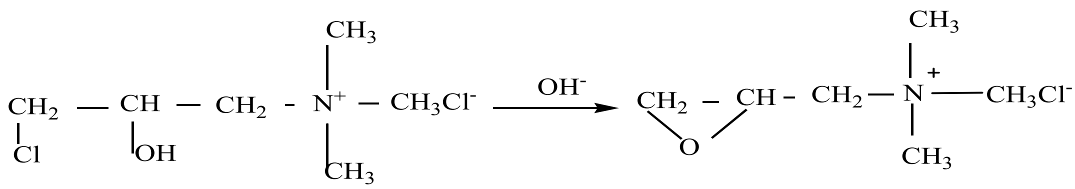
Hence treating cotton fabric with MTAB result in substitution of the hydrogen group of the cellulose hydroxyl by the MTAB molecule and hence increase the % N.

The increase in K/S value due to the treatment with MTAB may be due to the following reasons:

(a) First, MTAB reacts with the free hydroxyl group of cellulosic fabric and results in substitution of the hydrogen atom with the MTAB molecule with its high bulky form compared by that of hydrogen atom, results in opening up the cellulosic structure with this molecule, increasing spacing which enable the dye to jump and diffuse over the fabric ending in high K/S value.

(b) Second reason may be due to the +ve charge of MTAB moiety, which causes high affinity of the so formed cationized cotton to absorb the dye. i.e. to create high affinity of the cellulosic fabric to resemble the high affinity of the protenic fabrics.

On the other hand, Quat also aquires high % N by virtue of its structure, which is 2,3- epoxy propyl trimethyl ammonium chloride (I) [22] . This reactive material is prepared in situ by reaction of the reaction of 3- chloro – 2- hydroxypropyl-trimethyl ammonium chloride (II)(Quat-188) with alkali according to the scheme4.



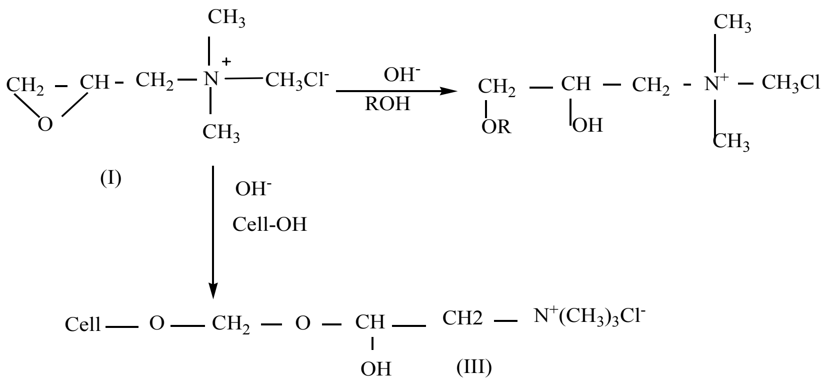
(II) Scheme 4 (I)

Compound (I) will react with alcohols under alkaline conditions to form ethers (Scheme 5) and will thus produce a modified fiber when it reacts with cotton to form the structure (III)[23].

Based on the above, it is obvious that introduction of the + ve charge compounds into the cellulose structure as well as introduction of this bulky compound into the vicinity of cotton fabric cause an increase in the K/S values of the printed samples.

We can conclude, therefore, that the cationization of cotton samples can improve its printability behavior towards the natural dye extracted from the carob seeds and such improvement depends on the kind of cationized reagent used.

Fastness properties of the samples in question range from good to excellent, indicating great fastness properties to washing, rubbing and perspiration, which could be achieved with such innovative natural-printing paste extracted from carob seeds.



Scheme 5

Table I: Apparent viscosity for self printing paste isolated from carob seeds before and after storing for 48 hours:

Rate of shear (Sec $^{-1}$)	Apparent viscosity in poise for self printing paste	
	Before storing	After storing for 48 hours
2.180	85.71	66.92
2.927	82.29	63.51
3.851	76.22	61.99
5.139	67.25	56.59
6.779	62.69	54.39
9.771	53.34	45.64
13.12	48.91	43.89
17.26	40.59	40.91
23.03	36.94	36.54
30.38	31.81	31.54
44.10	25.94	23.91
59.22	22.09	20.85
77.92	18.91	17.35
103.9	15.65	15.01
137.1	12.18	11.92

Table II: K/S and overall fastness properties of cotton fabric samples printed with self printing paste in presence and absence of different mordants

Mordant Used	K/S values	Rubbing fastness		Washing fastness		Perspiration fastness			
						Acidic		Alkaline	
		Wet	Dry	Alt.	St.	Alt.	St.	Alt.	St.
Blank	2.02	3-4	4	3	3-4	4	3-4	3-4	4
Allum	2.32	4	4-5	3-4	3-4	4	4-5	3-4	4-5
Ferrous sulphate	8.87	4	4-5	4	4	4-5	4	4	4-5
Copper sulphate	2.98	3-4	4	4	4	4-5	4	4	4
Potassium dichromate	4.15	4	4-5	3-4	4	4	4-5	4	4
Tannic acid	10.68	4	4-5	4	4	4	4	4-5	4

St. = Staining Alt.= Alteration

Table III: K/S and overall fastness properties of Wool fabric samples printed with self printing paste in presence and absence of different mordants

Type of mordant	K/S values	Rubbing fastness		Washing fastness		Perspiration fastness			
						Acidic		Alkaline	
		Wet	Dry	Alt.	St.	Alt.	St.	Alt.	St.
Blank	2.39	4	4	4	3-4	3-4	4	4	4
Allum	3.12	4	4-5	4	4	4	4	4-5	4
Ferrous sulphate	4.02	4	4	4-5	4	4	4-5	4	4
Copper sulphate	6.90	3-4	4-5	4-5	4-5	4	4	4	4-5
Potassium dichromate	6.79	4	4	4	4-5	3-4	4	4-5	4
Tannic acid	9.88	4	4	4-5	4	4	4-5	4	4

St. = Staining Alt.= Alteration

Table IV: K/S and overall fastness properties of Silk fabric samples printed with self printing paste in presence and absence of different mordants

Type of mordant	K/S values	Rubbing fastness		Washing fastness		Perspiration fastness			
						Acidic		Alkaline	
		Wet	Dry	Alt.	St.	Alt.	St.	Alt.	St.
Blank	2.11	3-4	4	3-4	4	4	3-4	4	4
Allum	2.87	4	4	4	4-5	4	4	4-5	4
Ferrous sulphate	8.83	4	4-5	4-5	4	4-5	4	3-4	4
Copper sulphate	7.36	3-4	4	4	4	3-4	4	4	4-5
Potassium dichromate	**5.62**	4	4	4-5	4	4	4	4	4-5
Tannic acid	10.23	4	4	4	4-5	4	3-4	4-5	4

St. = Staining Alt.= Alteration

Table V: Effect of chemical modification of cotton fabrics on its printability on using self printing paste isolated from Carob seeds

Type of chemical modification		% N	K/S	Rubbing fastness		Washing fastness		Perspiration fastness			
								Acidic		Alkaline	
				Wet	Dry	Alt.	St.	Alt.	St.	Alt.	St.
Untreated(Blank)		-	2.02	3-4	4	3-4	3-4	3	3-4	3-4	4
Alkali treated		0.00	2.13	4	4	4	4	3-4	4	4	3-4
Cyano Ethylated	I	0.39	2.18	4	4	4-5	4	4	4	4-5	4
	II	0.62	2.35	4	4-5	4-5	4	3-4	4	4	4-5
	III	0.78	2.63	4-5	4	4	4	4	4-5	4	4
Reacted with reactive Cyclodextrin	I	0.15	2.19	4	4	4	4	4	4	4-5	4
	II	0.30	2.23	4-5	4-5	4	4-5	4	4-5	4	4-5
	III	0.50	2.45	4	4	4-5	4	4-5	4	4	4

St. = Staining Alt. = Alteration

Table VI: Effect of cationization of cotton fabrics on its printability on using self printing paste isolated from Carob seeds

Cat ionizing agent	% N	K/S	Rubbing fastness		Washing fastness		Perspiration fastness			
							Acidic		Alkaline	
			Wet	Dry	Alt.	St.	Alt.	St.	Alt.	St.
Untreated (Blank)	-	2.02	3-4	4	3-4	3-4	4	3-4	4	3-4
MTAB	0.27	2.99	4	4	4	3-4	4	4	4	3-4
DTAB	0.09	2.49	4	3-4	4	4	4-5	4	4	4
HTAB	0.13	2.54	4-5	4	3-4	4	4-5	4	4	3-4
TMAH	0.10	2.52	4	4-5	4	3-4	4	4-5	4	4
Quat	0.18	2.82	4-5	4	4-5	4	4-5	4	4	4

St. = Staining Alt. = Alteration

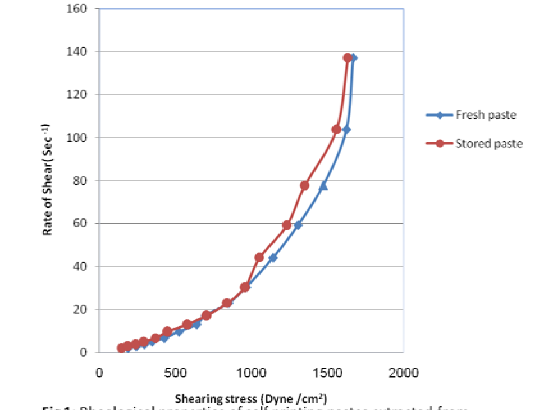


Fig 1: Rheological properties of self printing pastes extracted from carob seeds before and after storing for 24 hours

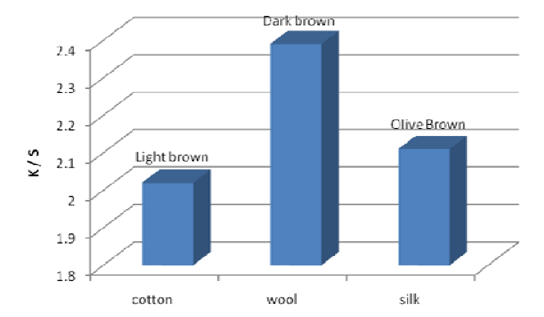


Figure 2: Different shades occurred when applying the natural-printing paste on natural fabrics.

Conclusion:

A natural printing paste comprising a natural dye and galactomannan gum was successfully extracted from carob seeds. The paste is characterized by a non-Newtonian pseudoplastic behavior, and its apparent viscosity decreases by increasing the rate of shear. The use of this printing paste in printing cotton, wool and silk fabrics was undertaken and results obtained conclude the following:

(1) The K/S of the unmodified fabrics follows the order: Wool fabric › silk fabric › cotton fabric. Treatment of cotton and wool fabrics with mordants enhance the K/S and overall fastness properties and create different colors. The highest K/S was obtained when tannic acid as was applied as a mordant followed by › ferrous sulfate › potassium dichromate › cupper sulfate › Alum › untreated samples. In case of silk fabric the alum has no effect on the K/S values.

(2) Chemical modification of cotton fabrics via cyanoethylation and reaction with R-CD enhance its printability. The K/S increases as the extent of reaction expressed as % N increases.

(3) Cationization improves the printability of cotton fabrics where the K/S depends on the nature of the cationizing agent and follows the order: MTAB › Quat 188 › HTAB › TMAH and DTAB.

(4) The overall fastness properties, viz. color fastness to rubbing, washing and to perspiration of cyanoethylated, modified with reactive cyclodextrin or cationized cotton fabrics are quite satisfactory for practical purposes where, they range between good and very good.

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