

Research Article



A Benign Strategy For Synthesizing Environment-Friendly Textile Prints Using Guar Acetate and Natural Dye

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Accepted on: 05-07-2016; Finalized on: 31-08-2016.

ABSTRACT

Herein we present a benign strategy for synthesizing environment-friendly prints on wool, silk and cotton. The strategy is based on utilization of cheap renewable resources in preparation of environment-friendly printing pastes. As known, the latter are the essential reasons for pollution caused by textile printing industry. The strategy involves mechanical isolation of galactomannan gum from the seeds of Guar Followed by thorough purification. Thus obtained gum is a yellowish white powder that was used to thicken the printing paste along with the natural dye. This dye was extracted from alkanet roots to yield alkanine natural dye with beautiful pink colour. In another route, galactomannan gum was submitted to acetylation and the acetylated gum (DS= 0.463) was also used to thicken the printing paste in comparison with the gum before acetylation. Rheological studies disclose that the apparent viscosity decreases by increasing the rate of shear and storing time before commencing the measurement. It also decreases after acetylation. The as-prepared non polluting printing pastes produce varieties of colours on wool, silk and cotton fabrics printed with concomitant mordanting using chitosan or tannic acid; Metallic salts were also used for comparison. Colour shade is a manifestation of type of fabric, thickening agent and type and kind of mordant used. Colour fastness to washing and to light of fabrics printed using Guar gum and its acetate derivative are comparable and satisfactory for industrial application.

Keywords: Guar, Alkanet, acetylation, printing, mordant.

INTRODUCTION

The increasing concerns of environmental pollution world-wide arises the interest in natural resources to come back.¹⁻⁴ Pollution prevention occupies pivotal position in the efforts being paid to remedy the environment. It can be defined in terms of green chemistry as the use of materials, processes or practices that eliminate or at least reduce hazardous and noxious substances.⁵⁻⁷ Textile printing industry pollutes the environment seriously because of the unfixed dye, excess thickener and printing paste additives washed from the printed fabrics to waste water.⁸⁻¹⁰ This is, indeed, an important work field where pollution prevention can be practiced.

Guar gum is a unique outstanding example of green eco-friendly biopolymers by virtue of its non toxicity, biodegradability and water solubility. It is a polysaccharide constituting the endosperm of the seeds of Guar plant (*Cyamopsis tetra gonolobus*) that belongs to the legume family. Native to India and Pakistan, and is grown in southern regions of Saudi Arabia.^{8,11-14}

Guar gum has many industrial applications in the textile industry.^{8,10,11,14-16} Guaran, the functional polysaccharide in Guar gum, is a galactomannan of a chain of (1-4)- β -D-mannopyranose backbone with branch points from their 6-positions linked to α -galactose [(1-6)- α -D-galactopyranose]. Ratio of mannose to galactose units is about 2. Chemical modification of Guar gum involves replacement of free hydroxyl groups of Guar backbone by different cationic, anionic, amphoteric, and nonionic

groups which improve its applications and features.^{8,10,11,14-16}

Concerns of the environmental pollution have also created a growing interest in natural dyes utilization instead of synthetic dyes. Dyes extracted from plants are interesting because of their environmental compatibility.^{17,19}

Alkanet (*Alkanna Tinctoria*) belongs to the family Boraginaceae. Alkanet is known to be both antiseptic and anti-inflammatory.²⁰⁻²² The roots produce a red dye [Colour index: Natural Red 20]. The colouring pigment in alkanet root is Alkanine (Anchusin). Alkanine is soluble in fat/oil and various organic solvents producing a red solution. It is insoluble in water. However it can be extracted with alkaline solution producing a bluish- violet solution, the colour of which can fade with washing or overexposure to sunlight.

In the era of textile printing, our previous research efforts were mainly devoted to development of new thickeners for reactive printing to replace sodium alginate which is universally recognized as the best thickener for relative printing.²³ Thus, research was designed to cover all factors affecting reactions with starch as well as carboxymethyl cellulose (CMC) to make both polymeric materials suitable for reactive printing. CMC was subjected to oxidation, cyanoethylation and vinyl graft copolymerization using acrylic acid, methacrylic acid and acrylamide. The copolymerization products were used as thickeners for reactive printing in the form of composite which represents all the copolymerization products on in



the form of graft copolymer where the homopolymer was removed from the products of the copolymerization reaction.

Similarly, starch and oxidized starches were subjected to same reactions and its modified form or its composites or copolymers were used successfully to prepare pastes for reactive printing. Particularly notable is the success of using starch-polyacrylamide composites on industrial scale.

A part from our previous research efforts, current work presents a benign strategy for green printing of three biopolymers in the fabrics form, namely, wool, silk and cotton fabrics. Green pre cursors for printing, viz. the thickeners and the dye are used. The thickeners comprise galactomannan gum extracted from guar seeds as well as the acetate derivative of galactomannan gum.

On the other hand, the natural dye is extracted from the locally available alkanet roots, to yield the alkanine pigment which is converted to water soluble through extraction with alkaline solution.

The work is further extended to include characterization and analysis of the said thickener and their feasibility along with the natural dye under investigation to effect green printing on wool, silk, and cotton.

MATERIALS AND METHODS

Materials

Plant seeds

Dry clean Guar seeds were obtained from Crops Center, Ministry of Agriculture, Egypt.

Fabrics

- Mill scoured pure wool fabric (220 g/m², 24 yarn/cm warp & 22 yarn/cm weft) supplied by Misr Co. for Spinning and Weaving; Mehalla El-Kubra, Egypt, was used through this study.

- Mill scoured natural silk fabric (140 g/m², 32 yarn/cm warp & 30 yarn/cm weft) supplied by Hussein M. El-Khatieb Sons Co., Suhag, Egypt, was also used.

- Cotton fabric (165 g/m², 40 yarn/cm warp & 36 yarn/cm weft) used in this study have been produced by Misr/Helwan Co. for Spinning & Weaving, Cairo, Egypt.

Chemicals

Sodium bicarbonate, potassium hydroxide, copper sulphate, potassium dichromate, tannic acid, chitosan, acetic anhydride, ethyl alcohol, and hydrochloric acid were of laboratory grade chemicals.

Natural Dye

Dry alkanet roots were purchased from the market in Jazan, Saudi Arabia Kingdom. It was soaked in Castor oil at a concentration of 150 g. plant/L. to extract the beautiful pink colour. Then the extract was filtered and used as the liquid dye under the name alkanine.

Methods

Isolation of the gum from the seeds

To separate the endosperm (Guar gum), the pods of the Guar plant were peeled off to separate the seeds. The dried seeds were crushed mechanically and sieved to remove the germ. After heat treatment, the husk was easy to separate by crushing. At this end, the endosperm was recovered, and milled. The purified gum was obtained by dissolution in hot water followed by precipitation in ethanol.

Acetylation of the gum

Acetylation of the gum was performed according to a previously reported method:²⁴ Thus the finely ground gum sample (5g) and solid NaHCO₃ (5g) wetted with ethanol (5 ml) were mixed well. Acetic anhydride (10 ml) was added gradually till homogeneous slurry was obtained. The slurry was left at 50°C for 2 h, and then mixed with 50% ethanol (10 ml). The as prepared mixture was neutralized with 0.1N sodium hydroxide solution to pH 7, then precipitated with ethanol, and finally dried at ambient conditions.

The prepared Guar acetate derivative was characterized by IR spectra (KBr, cm⁻¹) using Thermo-scientific Spectrophotometer.

Preparation of printing paste

Recipe of the printing paste was formulated as follows:

Natural Dye -----	40 g
Thickener * -----	940 g
Mordant -----	Xg
Balance -----	Yg
<hr/>	
Total -----	1000g

*The stock thickener paste of Guar gum was prepared using 2% of Guar powder.

Printing and Fixation

Fabrics were printed using the silk screen printing technique and fixation of the prints was carried out by ironing of the printed fabrics on their back face at the degree appropriate for each fabric.

Washing

After ironing, the printed fabrics were washed as follows:

Rinsing with tap water, washing with hot water and treatment with non-ionic detergent solution at 45°C, then rewashing with hot then cold water, and drying.

Analysis and Measurements

Determination of the degree of substitution (D.S.)

0.1 g of the acetate derivative of guar was added to 50 ml of 75/25 (v/v) ethanol-water solution. The latter was



stirred at 50°C for 30 min. Then cooled down 40 ml of 0.5N potassium hydroxide solution was added and excess alkali was back-titrated after 72 hours with 0.5 N HCl using phenolphthalein indicators.

The same analysis was carried out with respect to native dried guar as a blank sample.

The percentage acetyl content (% Acetyl), and degree of substitution (DS) were calculated from the following equations:²⁴

$$\% \text{ Acetyl} = \frac{(V_b - V_a) \times 0.043 \times \text{Molarity of HCl}}{\text{Sample weight}} \times 100$$

Degree of substitution (DS) represents the average number of substituted hydroxyl groups per galactopyranose unit.

$$DS = \frac{162 \times \% \text{ acetyl}}{(ME \times 100) - [\% \text{ acetyl} \times (ME - 1)]}$$

Where; V_b is the volume of HCl (ml) for blank, V_a is the volume of HCl (ml) for the prepared acetate derivative, ME is the molecular weight of acetate groups. ($\text{CH}_3\text{CO} = 43 \text{ g/mol}$).

Determination of the rheological properties

The rheological properties of the printing pastes were measured using Rheomat-15 at 25°C and the apparent viscosity (η) at various rates of shear was calculated from the shearing stress (τ) and rates of shear (D) as follows:

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

Colour measurements

- Absorbance properties of the dye solution were measured using JENWAY 6800 UV/Vis. Spectrophotometer.

- The colour strength (K/S) was measured by reflection spectroscopy with a Hunter Lab Ultra Scan PRO spectrophotometer.

Colour fastness measurements to washing and to light were conducted as per standard methods.²⁶

RESULTS AND DISCUSSION

As already stated, the present work aims at establishing a benign strategy for green synthesis of prints on wool, silk and cotton fabrics using a cost-effective, eco-friendly printing pastes of alkanine natural dye.

The latter is thickened with galactomannan gum isolated from Guar gum before and after being submitted to acetylation.

Isolation of the gum

Previous reports^{8,10,11} disclosed that, Guar gum is the main constituent in the endosperm of Guar seeds.

The seed consists of the hull, the endosperm (gum), and the germ. Chemical structure of Guar galactomannan gum and the proportional constituents of Guar seeds are

shown in Figure 1.

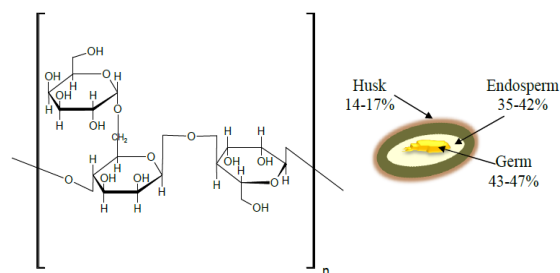


Figure 1: Proportional composition of Guar seed, and chemical structure of Guar galactomannan gum

In common practice Guar galactomannan gum is isolated mechanically from Guar plant seeds. Figure 2 represents schematically the steps of Guar galactomannan gum separation. The purified Guar galactomannan gum obtained is a yellowish white powder that swells in water yielding viscous solution.

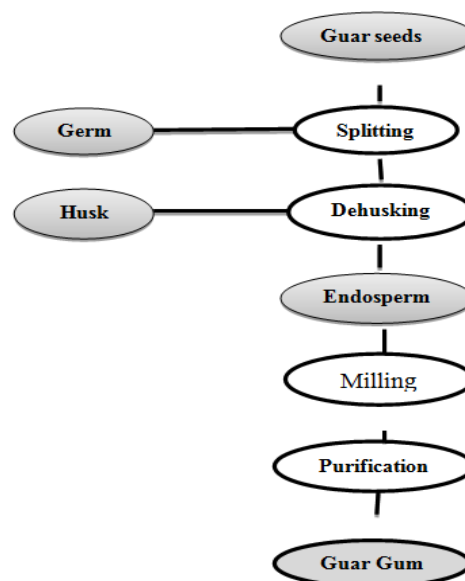
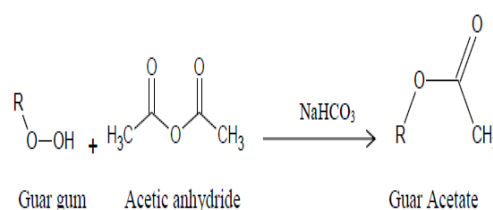


Figure 2: Schematic representation of steps of Guar gum separation.

Acetylation of Guar

Acetate derivative of Guar galactomannan gum was obtained using dry acetylation reaction conditions at 50°C in presence of sodium bicarbonate as a catalyst. The conditions used avoided the use of strong alkali and excess water which made the process cost effective.

Guar galactomannan gum reacts with acetic anhydride to yield the acetate derivative of the gum as per the following equation:



Presence of acetate groups in the molecular structure of guar galactomannan gums was identified by IR spectral analysis. Absorption at 1738cm^{-1} , is attributed to stretching $\text{C}=\text{O}$. The increase in the intensity of the absorption at 1360 and 810 cm^{-1} is attributed to deformation of CH_3 and CH_2 groups, as also the split signal in the region of 2900 cm^{-1} , due to the $\text{C}-\text{H}$ stretching of these two groups.

Rheological Properties

Since guar galactomannan gum and its acetylated derivatives lend generally themselves for use in the form of viscous solutions, it is therefore, of interest to investigate the viscometric and rheological properties of the pastes prepared thereof. Hence, pastes prepared from the aforementioned isolated guar gum and its acetylated derivative were prepared at a concentration of 2% and assessed for their rheological properties.

Figures 3 and 4 depict the rheograms of native guar gum and its acetylated derivative before and after storing for three and seven days respectively. All the rheograms reveal that the pastes are characterized by a non-Newtonian behaviour since the relation between shearing stress and rate of shear is not linear. It also shows that the up and down flow curves - as depicted by the rheograms - are coincident and the rheogram obtained are concaved toward the rate of shear axis indicating that all the pastes are characterized by a non-Newtonian pseudoplastic behaviour.

The implication of current data is that, if the viscosity (resistance to flow) of these pastes is measured using a large applied force (shearing stress) which causes a high velocity of flow (shear rate), the apparent viscosity is less than that of the same paste determined with a smaller force and a slower rate of flow.

Figures 3 and 4 signify further that, although acetylation has no effect on the type of the rheological properties, yet the location of the rheograms depends on both, the presence of acetyl groups as well as the time of storing. A more clarified picture may be realized from Table 1 which shows the effect of acetylation as well as the time of storing on the apparent viscosity of Guar gum, and its acetylated derivative. The apparent viscosity was monitored using 2% solution before and after storing for 24, and 72 hours. Results of Table 1 show that the acetylated guar galactomannan gum acquires low DS values (0.463). However the presence of the hydrophobic acetate groups attached chemically to the polysaccharide chain would be expected to disrupt the macro-molecular structure of the gum thereby changing the physiochemical properties of the solution as well as its viscosity.

It is clear (Table 1) that the apparent viscosity decreases by: increasing the rate of shear, and the storing time. The apparent viscosity of guar galactomannan gum decreases also by introducing the acetate groups in its macromolecular structure.

In the present work, acetylation method of Guar galactomannan gums was carried out with NaHCO_3 as a mild base catalyst in anhydrous reaction conditions. Acetylation reaction generally takes place by the formation of carbanion with the elimination of a molecule of water and release of CO_2 . The carbanion subsequently reacts with acetic anhydride to form the gum acetate.

The decrease in the viscosity by acetylation suggests that the macromolecular structure of the galactomannan gum undergoes molecular scission during degradation of the gum under the influence of the esterifying agent and the medium of modification.^{23,31}

A comparison among the viscosity values before and after storing for 24 and 72 hours would reveal the following (cf table 1). A remarkable decrease in the apparent viscosity of the untreated Guar gum from 718.41 poise for freshly prepared solution to 113.03 poise after storing for 24 hours at rate of shear of 2.18 sec^{-1} and 2.7196 poise at rate of shear of 3.11 sec^{-1} after storing for 72 hours which reflects its instability to fermentation and microorganism degradation. On the other hand, acetylation of Guar gum enhances its solution storing stability since the viscosity values of the modified gum pastes remain nearly the same before and after storing for 24 and 27 hours.

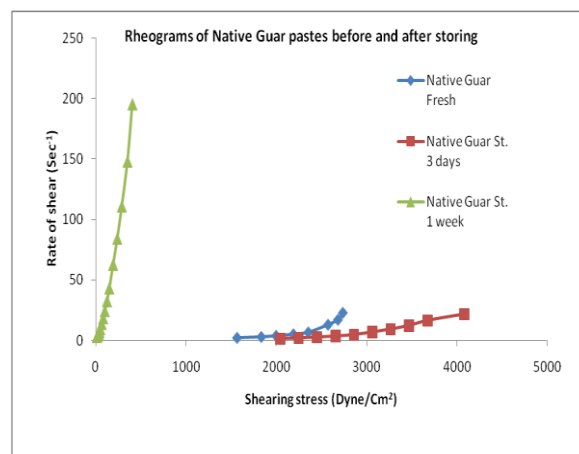


Figure 3: Rheological properties of native guar pastes before and after storing for three and seven days

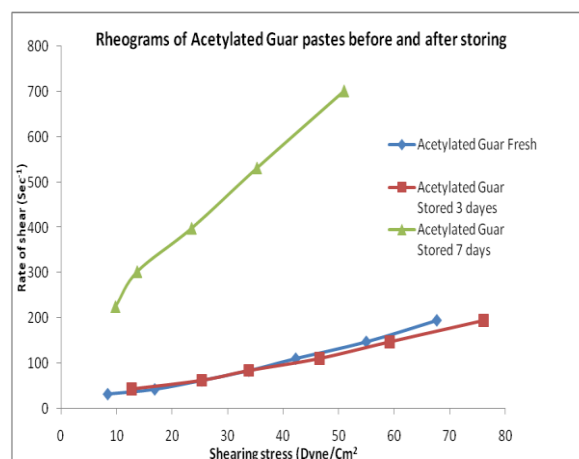


Figure 4: Rheological properties of acetylated guar pastes before and after storing for three and seven days

Eco-friendly “Green” Textile Printing

Work in this section aims at investigation of the suitability of the isolated Guar galactomannan gum and its acetate derivative along with a natural dye in printing biopolymeric textile materials, namely, wool, silk and cotton fabrics.

The alkanine dye used was extracted from alkanet roots. Thus two printing pastes were prepared containing the castor oil extract of alkanine dye and thickened with either Guar gum or its newly prepared acetate derivative. The so prepared pastes were employed in printing of the aforementioned textile fabrics with or without simultaneous mordanting.

After printing and drying, the printed goods were submitted to thermofixation for print fixation.

At this end, the printed goods were washed, and assessed for fastness properties as described in the experimental section. Results obtained are set out in Tables 2 and 3.

As is evident (Table 2 and 3) pastes thickened with either the Guar galactomannan gum or its acetate derivatives together with the alkanine natural dye succeed to bring about beautiful prints with a wide variety of colours.

The shade of colour relies depends on: (i) Structure and chemical reactivity of fabric, (ii) Chemical and rheological

properties of the thickening agent and (iii) the type of mordant.

The attachment of Alkanine dye to the fabric occurs through bonding of Alkanine phenolic groups, with the (NH₂ or COOH) groups of the protein fabrics (wool and silk) and with the hydroxyl group of cellulosic fabric (cotton).

The darker shade obtained in case of wool than silk fabrics, could be associated with the larger amount, number and kind of functional groups present in wool structure (COOH, NH₂, and SH) than silk (COOH and NH₂) depending on the constituting amino acids.²⁷

Differences in shades and tones of prints obtained using Guar galactomannan gum thickener and those obtained with its acetate derivative (Table 2 and 3) are rather interesting.

They could be interpreted in terms of differences among the two thickeners in: a) substituent on the thickener backbone, b) compatibility of the thickener with the alkanine dye and other paste ingredients and c) rheological properties of the thickener. Such differences would certainly reflect on the behavior of the paste and in turn, the shade and tone of the prints.

Table 1: Dependence of the apparent viscosity of Guar galactomannan gum and its acetylated derivative on rate of shear and time of storing

Guar galactomannan gum					Acetylated galactomannan gum (DS 0.463)			
Rate of shear (sec ⁻¹)	Fresh	After 3 days	After 1 week		Rate of shear (sec ⁻¹)	Fresh	After 3 days	After 1 week
	Viscosity in poise	Viscosity in poise	Rate of shear (sec ⁻¹)	Viscosity in poise		Viscosity in poise	Viscosity in poise	Viscosity in poise
2.18	718.41	113.03	3.11	2.72	2.18	351.67	376.78	376.78
2.927	626.74	93.54	4.177	5.06	2.927	280.34	336.41	308.37
3.851	519.02	84.10	5.495	5.39	3.851	234.69	277.35	256.02
5.139	426.23	69.26	7.333	5.19	5.139	191.77	234.38	207.71
6.779	347.35	60.58	9.673	4.81	6.779	161.53	197.87	165.57
9.771	196.17	37.56	13.94	4.55	9.771	123.31	154.13	126.11
13.12	155.46	33.31	18.72	4.29	13.12	104.34	125.21	104.34
17.26	118.89	29.72	24.63	3.98	17.26	88.83	104.69	82.48
23.03	-	24.33	32.86	-	23.03	71.33	89.16	64.19
30.38	-	20.48	43.35	-	30.38	59.48	76.61	50.47
44.10	-	16.18	62.93	-	44.10	45.32	60.22	37.25
59.22	-	14.05	84.50	-	59.22	36.99		28.2
77.92	-	11.85	111.2	-	77.92	30.92		22.14
103.9	-	9.985	148.3	-	103.9			17.13
137.1			195.7	-	137.1			

Table 2: Colouration properties of fabrics printed using Alkanine dye, and thickened with unmodified Guar gum.
















Mordant used	$\lambda_{\text{max.}}$ of dilute paste solution (nm)	Wool		Silk		Cotton	
		Sample	K/S	Sample	K/S	Sample	K/S
Without mordant	525		2.70		2.96		3.2
Chitosan	526		3.8		3.11		2.65
Tannic acid	520		3.12		2.58		2.41
Copper sulphate	532		3.19		2.70		2.78
Potassium Dichromate	523		3.14		2.89		2.57

Table 3: Colouration properties of fabrics printed using Alkanine natural dye, and thickened with Guar acetate.


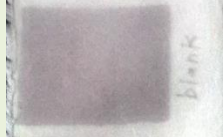

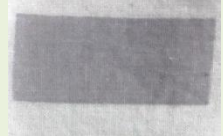






Mordant used	$\lambda_{\text{max.}}$ of dilute paste solution (nm)	Wool		Silk		Cotton	
		Sample	K/S	Sample	K/S	Sample	K/S
Without mordant	525						
Chitosan	526						
Tannic acid	520						
Copper sulphate	532	No samples could be obtained due to screen clocking					
Potassium Dichromate	523						

Table 4: Comparison between fastness properties of fabrics printed using alkanine dye printing pastes thickened with either native Guar gum or the prepared Guar acetate derivative.

Thickener Used	Fabric	Mordant used	Washing Fastness		Light fastness
			Alt.	St	
Guar gum	Wool	Without mordant	3	3-4	4-5
		Chitosan	4	4	5-6
		Tannic acid	4-5	4	5
		Copper sulphate	4	4	5
		Potassium Dichromate	4-5	4-5	5-6
	Silk	Without mordant	3	4	4
		Chitosan	4	4-5	5
		Tannic acid	4-5	4	5-6
		Copper sulphate	3-4	4	5
		Potassium Dichromate	4	4	4-5
	Cotton	Without mordant	2-3	3	3-4
		Chitosan	4	4	4-5
		Tannic acid	4-5	4	5-6
		Copper sulphate	4	4-5	5-6
		Potassium Dichromate	4	4	5
Guar acetate	Wool	Without mordant	2-3	3	3-4
		Chitosan	4	4-5	5-6
		Tannic acid	4-5	4	5
		Copper sulphate	4	4	5
		Potassium Dichromate	4	4	5-6
	Silk	Without mordant	3	2-3	3-4
		Chitosan	4-5	4-5	5
		Tannic acid	4	4-5	5-6
		Copper sulphate	4	4	5
		Potassium Dichromate	4	4	5
	Cotton	Without mordant	3	3	3-4
		Chitosan	4	4-5	5-6
		Tannic acid	4	4	5
		Copper sulphate	4	4	5
		Potassium Dichromate	4-5	4-5	5-6

Alt: Alteration, St: staining

Effect of Mordants

Most natural dyes are not substantive and should be used in conjunction with mordants which can be attached to the fiber and also combines with the dye.^{18,28,29} The challenges in the application of natural dyes is the need to use metallic mordants that are themselves harmful and polluting. Scientists are still looking for natural mordants that can enhance the affinity of natural dyes to fabrics. Tannins (such as tannic acid), are the most widely known natural mordants.

In this work, chitosan which is an antibacterial natural polysaccharide extracted from shrimp shells³⁰ is utilized as an eco-friendly natural mordant. Its performance is shown in comparison with copper sulphate and

potassium dichromate as metallic mordants and tannic acid as an organic non-metallic natural mordant. (Tables 2 & 3)

Results of Tables 2 & 3 show that the purple solution of alkanine dye was found to have maximum absorption value at wavelength (λ_{max}) of 525nm. Dilute solutions of the mordant printing paste were found to have nearly the same absorption peak value. This implies that the variation of colours obtained for printed fabrics with these mordanted pastes after fixation could be attributed to the chelation of the mordant to the dye which occurs during the fixation step.

Figure 5 illustrates the chemical structure of alkanine dye and the possible structure of the complex obtained with

metallic mordants (Copper Sulphate and Potassium Dichromate), where M^+ represents metal ion, and \bullet represents the functional group in the fabric (OH, COOH, NH_2 , or SH).

Tables 2 & 3 show that, a variety of colour shades and tones could be obtained for the printed fabrics upon using different types of mordants.

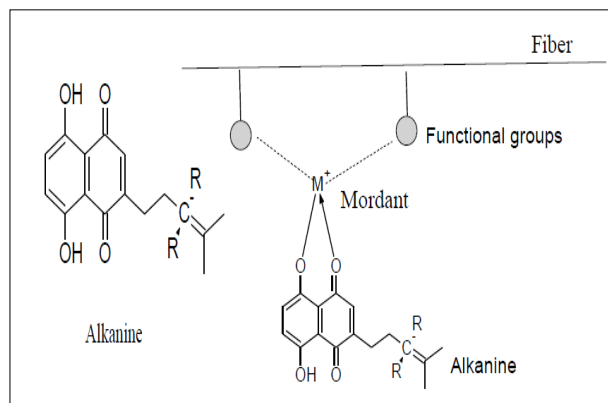


Figure 5: Chemical structure of Alkanine and possible complex formed due to presence of mordant.

The prints obtained using alkanine in presence of chitosan have darker shades compared to the purple colour obtained for samples printed with unmordanted paste. Chitosan have amino groups which can be protonated forming sites of attraction of the alkanine dye.

Tannic acid changes the purple colour of the unmordanted prints to pink because of its ability to form the same types of bonding with the fabric as those formed in with the dye (Hydrogen and covalent bonds). Metallic Mordants also changed the prints colour to redish brown in case of potassium permanganate, and greenish grey in case of copper sulphate.

It should be noted, however, that current work discloses that metallic mordants cause coagulation in case of printing pastes thickened with Guar acetate and mordanted with copper sulphate (Table 3). This could be attributed to cross linking formed via interaction of the acetate groups of the thickener with the divalent copper ions. Needless to say that coagulation of the printing paste causes blocking of the pores of the screen thereby preventing printing.

Fastness Properties

Results of Table 4 depicts that the colour fastness properties for washing and light for fabrics printed using Guar gum or its acetylated derivative in thickening the printing paste are comparable.

Samples printed without mordant showed colour fastness properties inferior to those obtained using mordants, which reflect the positive role of the mordant in linking the alkanine dye to fabric. For example the colour fastness to washing for sample of unmodified guar gum exhibits a value of 3 for the unmordanted printing whereas with chitosan mordanted printing, the sample

acquires a value of 4-5. In both cases cotton fabric was used as the substrate for printing.

By and large the fastness to washing obtained varies assumes values in the range of good to very good (Table 4). The latter reveals also that light fastness displays certain improvement which is quite obvious due to the well-known poor light fastness of natural dyes.

Summing up, Guar galactomannan gum and its acetate derivative proved that they are practically suitable for use as thickening agents for printing wool, silk and cotton fabrics using alkanine natural dye.

Colour fastness of the fabrics printed using Guar gum or its acetate derivative to washing and light are comparable and satisfactory for industrial application.

CONCLUSION

A strategy was formulated aiming at the development of environment-friendly nonpolluting thickeners for making printing pastes together with a natural dye. The thickeners were Guar galactomannan gum and its acetylated derivative whereas the dye was alkanine natural dye. Isolation and purification of the gum and its acetylation derivative as well as extraction of the dye from alkanet roots are described. Galactomannan acetate acquires DS value of 0.463 and IR spectral analysis signifies the presence of the acetyl groups.

These groups enhance stabilization of the viscous solution of the gum during storing: Apparent viscosity of the viscous solutions of the thickeners under investigation decreases by increasing the rate of shear and storing time.

It also decreases by acetylation.

Printing of wool, silk and cotton fabrics was performed using printing pastes containing the gum or its acetylated derivative and the natural dye along with mordant including chitosan or tannic acid as natural mordents.

Metallic mordents, e.g., copper sulphate and potassium dichromate were independently used also for comparison.

Variety of colours is obtained on the said fabric which is made of natural fibers.

Shade of colour depends on type of fabric and nature of the thickening agent as well as type and kind of mordant used.

Colour fastness to washing and light of fabrics printed using Guar gum or its acetylated derivative are comparable and satisfactory for industrial application.

Obviously, then, the Guar galactomannan gum and the acetylated galactomannan gum can be used successfully in thickening printing pastes containing natural dye along with chitosan as natural mordant.

REFERENCES

1. Schmidt-Prezewozona K. The Textile Institute 82 Conference, Egypt, 2002, March.
2. Gulrajani ML. Natural Dyes-Part I: Present Status of Natural Dyes, *Colourage*, 46(7), 1999, 19-28.
3. Jordao CP, Pereira MG, Bellato CR, Pereira JL, and Matos AT. Assessment of Water Systems for Contaminants from Domestic and Industrial Sewages, *Environmental Monitoring and Assessment*, 79, 2002, 75-100.
4. Harrison RM, *Understanding our Environment*, 2nd. Ed, The Royal Society of Chemistry, London, 1995.
5. Anastas PT, and Kichhoff MM. Origins Current Status and Future Challenges of Green Chemistry, *Acc. Chem. Res.* 35, 2002, 686-694.
6. Perlatti B, Forim MR, and Zuin VG. Green Chemistry Sustainable Agriculture and Processing Systems: A Brazilian Overview, *Chemical and Biological Technologies in Agriculture*, 1:5, 2014.
7. Tang S, Bourne R, Smith R, and Poliakoff M. The 24 Principles of Green Engineering and Green Chemistry: "IMPROVEMENTS PRODUCTIVELY" *Green Chem.*, 10, 2008, 268-269.
8. Miles LWC, "Textile Printing", Society of Dyers and Colourists, England, 2nd Ed, 1994.
9. Kamat S.Y. and Alat D.V. Natural Dyes-A dying Craft?, *Indian Textile J.*, 100, 1990, 66-70.
10. Walsh WK and Gupta BS. Solventless Fabric Coating By Radiation Curing Part I. Background and Potential, *Journal of Industrial Textiles*, 7(4), 1978, 253-262.
11. Iqbal D, and Hussain EA. Green Biopolymer Guar Gum and Its Derivatives, *Int. Pharm Biol. Sci.*, 4(3), 2013, 423-435.
12. Gupta AP and Verma DK. Guar Gum and Their Derivatives: A Research Profile, *International Journal of Advanced Research*, 2(1), 2014, 680-690.
13. Zahid MS, Majid A, Rischkowsky B, Khan S, Hussain A, Shaffeq S, Gurmani ZA, Mounir M, Rahman S, and Imran M. Improved Goats Milk and Meat Production Feeding Guar Hay in Marginal Rainfed Areas of Pothwar Region of Pakistan, *Sarhad J. Agric.*, 28(3), 2012, 477-483.
14. Sharma R. Guar Gum Grafting and Its Application in Textile, *Asian J. Exp. Sci*, 19(2), 2005, 77-81.
15. Nassar SH. Preparation and Characterization of Guaran Carbamate as A Thickener in Disperse Dye Printing Pastes, *Indian Journal of Fiber & Textile Research*, 27(3), 2002, 274-279.
16. Coviello T, Matricardi P, Alhaique F, Farra R, Tesei G, Fiorentino S, Asaro F, Milcovich G, Grassi M. Guar Gum/Borax Hydrogel: Rheological, Low Field NMR and Release Characterizations, *EXPRESS Polymer Letters*, 7(9), 2013, 733.
17. Gogoi N, and Kalita B. Dyeing of Silk With Natural Dyes (Part-I), *Colourage*, 46(1), 1999, 23.
18. Chavan RB. Revival of Natural Dyes – A Word of Caution to Environmentalists, *Colourage*, 42(4), 1995, 27.
19. Arnold K, and Connie K. "The Complete Illustrated Book of Dyes from Natural Sources", Doubleday & Company Inc., Garden City, 1974, NY.
20. Kreuzner C, Alkanna Tinctoria (L.) Tausch as Purple Dye in the Recipes of Papyrus Holmiensis and Papyrus Leidensis X, *e Preservation Science*, 10, 2013, 123-130.
21. Vandana T, and Vankar PS. Unconventional Natural Dyeing Using Microwave and Sonicator with Alkanet Rook Bark, *Asian textile journal*, 10, 2001, 54-57.
22. Ali HB, Agarwala BK, and Kaddou IK. New Records of Aphids of the Subfamily Aphidinae (Homoptera: Aphididae) Infested Herbaceous Plants and Shrubs for Iraqi Aphid Fauna; *Advances in Bioresearch*, 3(4), 2012, 66-75.
23. Hebeish A. in a book entitled "Achievements in Chemistry of Fibrous and Nonfibrous Textile Material- Science – Based Technological Innovation For Textile Development; Published by Scholars' Press, Omni Scriptum GmbHs & Co KG, Deutschland Germany, 2015.
24. Savitha Prashanth MR, Parvathy KS, Susheelamma NS, Prashanth KVH, Tharanathan RN, Cha A, and Anilkumar G. Galactomannan Esters—A Simple, Cost-Effective Method of Preparation And Characterization; *Food Hydrocolloids*, 20, 2006, 1198-1205.
25. Bello-Perez LA, Agama-Acevedo E, Zamudio-Flores PB, Montealvo G M, and Rodriguez-Ambriz SL. Effect Of Low And High Acetylation Degree In The Morphological, Physicochemical And Structural Characteristics Of Barley Starch; *LWT-Food Science and Technology*, 43, 2010, 1434-1440.
26. Society of Dyers and Colorists, report of fastness tests Coordination Committee, Yorkshire, England, 3rd, 1995.
27. Silvaa AB, Silvaa MG, Arreoyob PA, and Barros MASD. Dyeing Mechanism of Wool and Silk with Extract of Allium Cepa, *Chemical Engineering Transactions*, 32, 2013, 715-720.
28. Dweck AC. Natural Ingredients for Colouring and Styling; *International journal of Cosmetic Science*, 24(5), 2002, 287-302.
29. Ansari A & Thakur BD. Extraction, Characterization and Application of A Natural Dye: The Eco-Friendly Textile Colorant, *Colourage*, 47(7), 2000, 15-20.
30. Teli MD, Sheikh J, and Shastrakar P. Eco-friendly Antibacterial Printing of Wool Using Natural Dyes, *Journal of Textile Science & Engineering*, 4(2), 2014, 1-5.
31. Opinion of the Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials, Authority Question N EFSA-Q-2006-122, *The European Food Safety Journal*, 514, 2007, 1-17.

Source of Support: Nil, Conflict of Interest: None.

