New Thickening Agents for Reactive Printing of Cellulosic Fabrics

N. A. Ibrahim,[1] M. H. Abo-Shosha,[1] E. Allam M. R. El-Zairy,[2] E. M. El-Zairy[2]

[1]*Textile Research Division, National Research Center, Dokki, Cairo, Egypt*
[2]*Faculty of Applied Arts, Helwan University, Cairo, Egypt*

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ABSTRACT: Four adducts were prepared by polymerizing acrylic acid (AA) in presence of either a pyrodextrin (D) or gum Arabic (GA), and termed as PAA/D_1, PAA/D_2, PAA/GA_1, and PAA/GA_2. These adducts were utilized as thickeners in reactive printing of cotton fabric in comparison with Na-Alginate. Printing was carried out at different conditions including: $NaHCO_3$ concentration (0–40 g/K), urea concentration (0–200 g/k), steaming temperature (100–130°C) and time (5–35 min). At optimal $NaHCO_3$ concentration (30 g/K) the depth of shade of the prints, expressed as K/S values, depended on the nature of the thickener used, and followed the descending order PAA/D_2 > PAA/GA_1 > Na-Alginate ≫PAA/D_1 ≥ PAA/GA_2. Accordingly, PAA/D_1 and PAA/GA_2 were omitted in subsequent trials. Optimal printing conditions were found to be $NaHCO_3$ concentration (30 g/K), urea concentration (100 g/k), steaming temperature (110°C), and time (15 min). The apparent viscosity of a printing paste, as well as both of K/S value and fastness properties of a print were governed by the nature of the reactive dye and type of thickener. Storing of a printing paste up to 7 days resulted in a decrease in its apparent viscosity along with a slight reduction in K/S value and a little variation in some fastness properties of prints. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4430–4439, 2006

Key words: additives; cellulose; dyes; fibers; printing

INTRODUCTION

Thickeners are polymeric materials used in the preparation of the print paste to restrict the spreading of the dye as well as to maintain the design outlines even under high pressure. Factors affecting the selection of a thickening agent for textile printing include chemical and physical nature of both the dyestuff and the textile substrate, printing style and machine, fixation conditions along with washing off process.[1–4]

Many attempts have been carried out to search for and to develop new thickening agents to overcome the inherent drawbacks of natural thickeners such as availability, cost, purity, consistency, hazardous preservatives, based on phenols or formaldehyde, as well as storage stability.[5–10]

In a previous study,[11] the authors prepared four adducts based on either dextrin (D) or gum Arabic (GA) through free radical polymerization of acrylic acid (AA) in presence of either of them. The present work is undertaken to investigate the feasibility of utilizing these adducts as thickening agents for reactive printing of cotton fabric in comparison with the conventional alginate thickener.

EXPERIMENTAL

Materials

Mill-scoured and bleached cotton fabric (110 g/m^2), supplied by Misr spinning and weaving co., Mehalla El-Kobra, Egypt, was used.

The following materials were used in the preparation of four poly acrylic acid (PAA) adducts, viz. PAA/D_1 ,PAA/D_2, PAA/GA_1, and PAA/GA_2 as described in a previous study.[11] These materials were Dexy 85, a powder pyrodextrin, kindly supplied by Starch and Glucose co., Mostorod, Cairo (it was based on Egyptian maize starch that was heat treated for 5 h in the presence of an acid), Gum Arabic, GA, locally purchased from Al Haraz co., Cairo, and ground before use, acrylic acid, AA, pure grade and containing 200 ppm hydroquinon monomethylether, supplied by Fluka Chemika, Switzerland, as well as sodium persulfate ($Na_2S_2O_8$), sodium hydroxide, sodium thiosulfate ($Na_2S_2O_3$) supplied by Merck. Conditions of preparation and some properties of these adducts are listed in Table I.

Na-alginate of medium viscosity (Na-Alg), (cecalginate HV/KL –600, Ceca Kolloid –Chemie, Paris) was used.

Correspondence to: N. A. Ibrahim (nabibrahim49@yahoo.co.uk).

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TABLE I
Conditions of Preparation, % Total Conversion (% TC), Visual Appearance and Water Solubility of Adducts

Substrate	LR	%TC	Visual appearance	Water solubility	Designation
GA	1.25/1	99.01	Brownish white solid	The two adducts are mixed with water in all proportions	PAA/GA1
	6.3/1	99.96	Brownish white solid		PAA/GA 2
Dexy 85 (D)	1.25/1	99.16	Yellowish white solid	The two adducts are mixed with water in all proportions	PAA/D 1
	6.3/1	99.98	Yellowish white solid		PAA/D 2

(AA), 6.75 mol/L; ($Na_2 S_2 O_8$), 34.9 × 10^{-3} mol/L; ($Na_2 S_2 O_3$), 26.87 × 10^{-3} mol/L; degree of neutralization of AA, 20% (Na salt); temp., 90°C; time, 30 min. All concentrations are based on the liquid phase before the addition of substrates. After preparation all adducts were neutralized with NaOH to a pH of 7.
LR, liquid-to-substrate ratio.

Mild oxidizing agent (Ludigol® –BASF) of a technical grade, Na-bicarbonate as well as urea were laboratory grade chemicals (Merck).

Reactive dyes used were Remazol® Brill. Blue BB (Dystar), Procion® Red H-HE(Zeneca), Drimarene® Red CL (Clariant –India)Drimarene® Red HF as well as Drimarine® Blue PXN.

Methods

Printing paste

The printing pastes were prepared according to the following recipes:
Reactive dye 30 g/kg
Stock thickening 700 g/Kg
Urea 100 g/Kg
Na-bicarbonate 30 g/Kg
Ludigol® 10 g/kg
Water 130 g/Kg
Total weight 1000 g

Printing procedure

Printing was performed using flat screen technique. Printed fabric samples were then dried at 100°C for 5 min and fixed by steaming at 110°C for 15 min using Ariolt® CSL Steamer –Italia.

Washing was carried out for 15 min in cold water, 15 min in boiling water, 15 min in hot water containing Hostapal® CV-ET (2g/L), NaOH (2g/L), and Na_2CO_3 (2 g/L), 15 min in hot water, 5 min in cold water, then rinsed well and dried at ambient conditions.

Testing

Depth of the reactive prints, expressed as K/S, was measured at the wavelength of maximum absorbance using an automatic filter spectrophotometer and calculated by the KubelKa–MunK equation:[12]

$$K/S = (1 - R)^2/2R$$

Where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the printed samples at the wavelength of maximum absorbance. The higher the K/S value, the greater the dye receptivity of the cellulosic fabric.

Color fastness to washing, rubbing, and perspiration were assessed according to AATCC test methods (61–1972), (8–1972), and (15–1973), respectively.

RESULTS AND DISCUSSION

In this study, attempts have been made to investigate the technical feasibility of using new types of thickening agents, based on polymerization reactions of gum arabic or dextrnie with acrylic acid in presence of $Na_2S_2O_8/Na_2S_2O_3$ redox system, in the printing of cellulosic fabrics with reactive dyes, as well as to find out the proper conditions for attaining printed fabrics with high performance properties. Results obtained along with their appropriate discussion follows.

Na HCO_3 concentration

As for the changes in the printability of cotton fabric, expressed as K/S values, with Drimarene® Red HF reactive dye as a function of type of thickening agent, i.e., Na-alginate, PAA/GA_1, PAA/GA_2, PAA/D_1, or PAA/D_2 as well as the concentration of $NaHCO_3$, as an alkaline catalyst, Figure 1 shows that increasing $NaHCO_3$ concentration in the printing paste up to 30 g/K results in a significant improvement in the K/S value of the printed fabric, regardless of the thickening agent used, as a direct - consequence of: (i) enhancing both the swellability of the used thickeners as well as the extent of neutralization of their free carboxyl groups ,i.e., higher viscosity,[13] and (ii) improving the accessibility and reactivity of the cellulose structure, thereby promoting the dye (Dye-X)/fiber (Cell. OH) interaction and fixation:[14]

$$\text{Cell.OH} + OH^- \rightarrow \text{Cell.O}^- + H_2O \qquad (1)$$

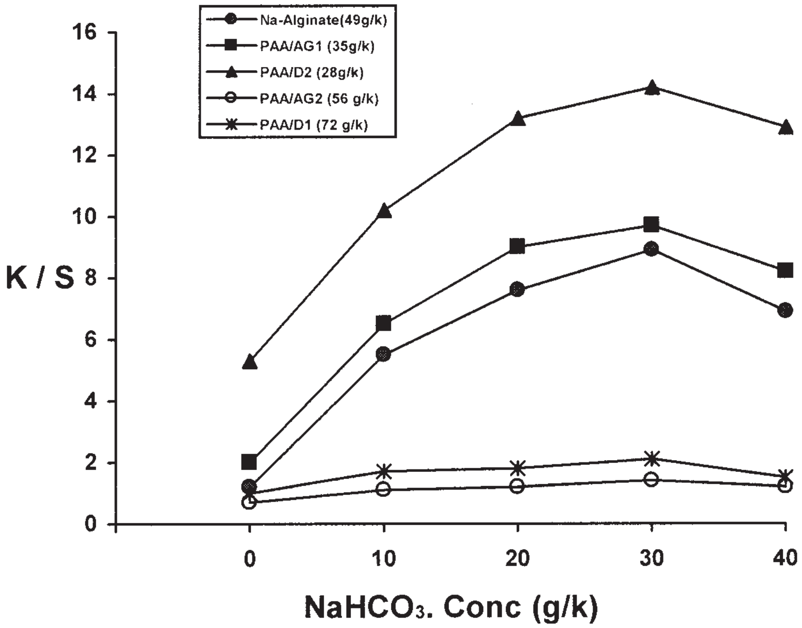

Figure 1 Effect of $NaHCO_3$ concentration on the depth of cotton prints using different thickening agents: Drimarene® Red HF (30 g/k); urea (100 g/k); $NaHCO_3$ (0–40 g/k); Ludigol® (10 g/k); steaming at 110°C/15 min.

$$\text{Cell.O}^- + \text{Dye–X} \xrightarrow{\text{OH}} \text{Cell.O.Dye+HX} \qquad (2)$$

The *K/S* values of the printed fabric samples are governed by the type of thickening agent and follow the descending order.

$PAA/D_2 > PAA/GA_1 > \text{Na-algiante} \gg PAA/D_1 \gg PAA/GA_2$ reflecting the differences among these thickening agents in their chemical nature, chemical composition, functionality, molecular weight, extent of swelling, compatibility with other ingredients, rheological properties, extent of releasing, or entrapping the dye molecules during the steam-fixation step.[4]

Further increase in $NaHCO_3$ concentration, i.e., beyond 30 g/k, brings about a decrease in the *K/S* values of the cellulosic prints, most probably due to (i) enhancing the extent of dye hydrolysis[15]

$$\text{Dye–X} + H_2O \xrightarrow[\Delta]{OH^-} \text{Dye–OH} + HX \qquad (3)$$

thereby minimizing its extent of fixation during steaming step, (ii) reducing the viscosity of the printing paste, thereby facilitating undue penetration of the used dye within the cellulose structure, (iii) partial hydrolysis of Cell.O.Dye chemical bonds under the steaming conditions, and (iv) facilitating side interactions with other competitors, i.e., paste ingredients.[9]

It can be also seen, at a concentration of 30 g/k, that the *K/S* value obtained upon using PAA/D_1 or PAA/GA_2 as thickeners is very small compared to the other three thickeners. Accordingly, in the following study, these two thickeners are omitted.

Urea concentration

As far as the variation in the printability of cotton fabric, expressed as *K/S* values, with Drimarene® Red HF (30 g/k) as a function of urea concentration (0–200 g/k) using Na-alginate, PAA/GA_1, or PAA/D_2 as a thickening agent, Figure 2 shows that increasing urea concentration up to 100 g/k brings about a significant improvement in the *K/S* values of the obtained prints, irrespective of the used thickening agent as well as the cellulosic substrate. This improvement in *K/S* values is a direct consequence of: (i) improving the swellability of the cellulose structure, (ii) enhancing disaggregating and solubility, of dye molecules, (iii) facilitating diffusion of the dye molecules from the paste into the cellulosic fibers, (iv) attracting moisture and retarding the evaporation of water during dyeing, and (v) increasing the extent of water condensation on the print during the steaming step.[4,6,9]

Figure 2 shows also that further increase in urea concentration, i.e., beyond 100 g/k, has a negative impact on the depth of the obtained prints, irrespective of the used thickener, most probably due to a side interaction with the used reactive dye, thereby minimizing the extent of dye fixation and a side interaction with the used thickeners,

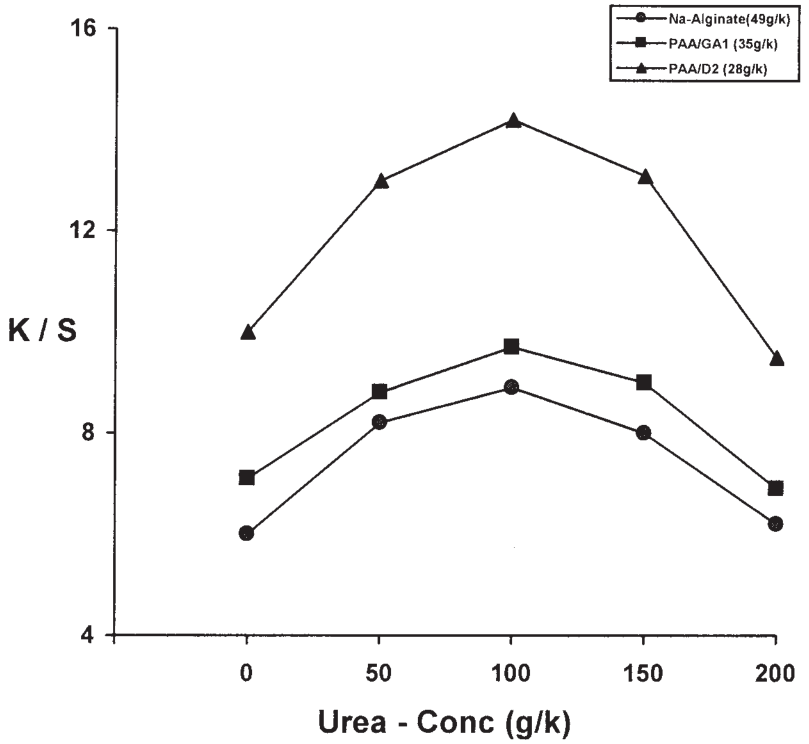

Figure 2 Effect of urea concentration on the depth of cotton prints using different thickening agents. Drimarene® Red HF (30 g/k); urea (0–200 g/k); $NaHCO_3$ (30 g/k); Ludigol® (10 g/k); steaming at 110°C/15 min.

thereby altering their rheological properties and facilitating undue penetration of the dye molecules within the highly swelled cellulose structure.[9,16] The net effect of the aforementioned factors is a reduction in the extent of dye fixation, i.e., lower depth of shades.

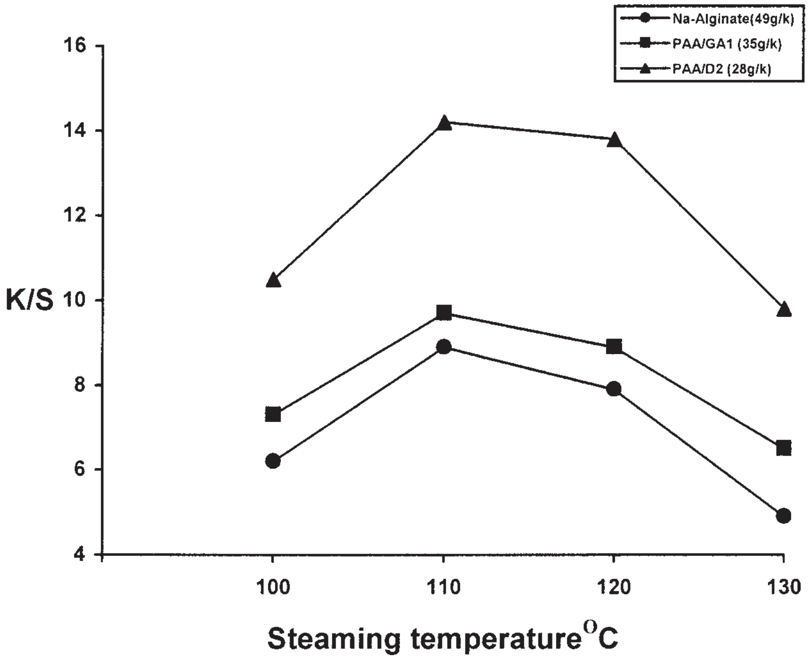

Figure 3 Effect of steaming temperature on the depth of cotton prints using different thickening agents. Drimarene® Red HF (30 g/k); thickening agent (700 g/k); urea (100 g/k); $NaHCO_3$ (30 g/k); Ludigol® (10 g/k); steaming for 15 min.

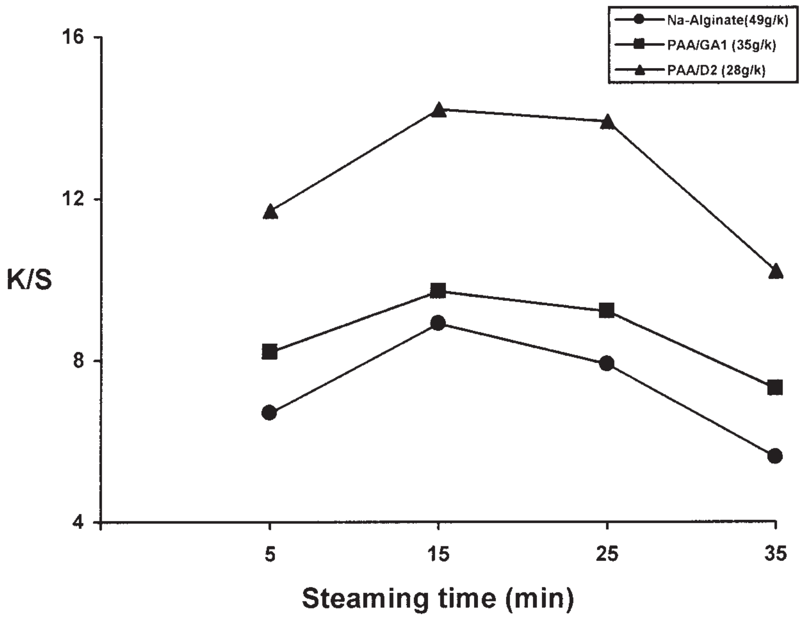

Figure 4 Effect of steaming time on the depth of cotton prints using different thickening agents. Drimarene® Red HF (30 g/k); thickening agent (700 g/k); urea (100 g/k); $NaHCO_3$ (30 g/k); Ludigol® (10 g/k); steaming at 110°C.

Needless to say, the extent of variation in *K/S* values is determined by the type of thickener, which can be arranged discerningly as follows $PAA/D_2 > PAA/GA_1 >$ Na-alginate

Steaming temperature

Figure 3 shows the effect of steaming temperature on the extent of printing, *K/S*, of the used cotton fabric of Na-alginate, PAA/GA_1, and PAA/D_2 independently as thickening agents. For a given printing conditions, it is clear that the *K/S* value increases initially very fast by raising the steaming temperature up to 110°C for 15 min, then slows down with further increases in steaming temperature, i.e., beyond 110°C, regardless of the used thickener.

The improvement in *K/S* values by raising the steaming temperature is a direct consequence of (i)

TABLE II
Effect of Storing Time on the Depth of the Cotton Prints Using Different Thickening Agents Along With Different Reactive Dye

		Thickening agent used					
		Na-Alginate		PAA/GA_1		PAA/D_2	
Reactive dye	Storing Time	K/S	% Dec	K/S	% Dec	K/S	% Dec
Remazol® Brill. Blue (VS)	I	12.09	0.0	17.17	0.0	18.64	0.0
	II	11.57	4.30	16.78	2.27	18.29	1.87
	III	11.18	7.52	16.73	2.56	17.89	4.02
Drimarene® Blue. P (MC)	I	7.82	0.0	9.77	0.0	10.97	0.0
	II	7.51	3.96	9.61	1.63	10.52	4.10
	III	7.06	9.71	9.12	6.65	9.94	9.38
Drimarene® Red HF, (TFP/VS)	I	8.90	0.0	9.30	0.0	14.26	0.0
	II	8.50	4.49	9.20	1.07	13.73	3.70
	III	8.01	10.01	8.93	3.97	13.09	8.20
Procion® Red H-HE (MC)	I	9.17	0.0	14.11	0.0	16.59	0.0
	II	9.08	0.98	14.08	0.2	16.07	3.1
	III	8.91	2.83	13.73	2.69	15.65	5.66
Drimarene® Red CL (MCT/VS)	I	12.99	0.0	16.74	0.0	19.20	0.0
	II	12.73	2.01	16.11	3.76	19.18	0.10
	III	11.28	13.16	15.37	8.18	18.26	4.89

I, Freshly prepared, % Dec = % Decrease; II, Stored For 3 days; III, Stored for 7 days. MC, Monochlorotriazine; VS, Vinyl sulphone; TFP/VS, Triflorolopyrmedene. Reactive dye (30 g/k); $NaHCO_3$ (30 g/k); Urea (100 g/k) Ludigol® (10 g/k) Steaming at 110°C for 15 min.

TABLE III
Effect of Storing Time on the Washing Fastness Properties of the Cotton Prints Using Different Thickening Agents as Well as Different Reactive Dye

		Thickening agent used					
		Na-Alginate		PAA/GA$_1$		PAA/D$_2$	
Reactive dye	Storing Time	60°C	90°C	60°C	90°C	60°C	90°C
Remazol® Brill. Blue (VS)	I	5	4	5	5	5	5
	II	5	4	5	5	5	5
	III	5	4	5	4.5	5	5
Drimarene® Blue. P (MC)	I	5	5	5	5	5	5
	II	5	4.5	5	5	5	5
	III	5	4	5	4.5	5	4.5
Drimarene® Red HF, (TFP/VS)	I	5	5	5	5	5	5
	II	5	5	5	5	5	5
	III	5	4.5	5	5	5	5
Procion® Red H-HE (MC)	I	5	5	5	5	5	5
	II	5	5	5	5	5	5
	III	5	4	5	4.5	5	5
Drimarene® Red CL (MCT/VS)	I	5	4.5	5	5	5	5
	II	5	5	5	5	5	5
	III	5	4.5	4.5	4.5	4.5	4.5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days. MC, Monochlorotriazine, VS, Vinyl sulphone; TFP/VS, Trifloroloprymedene. Reactive dye (30 g/k); NaHCO$_3$ (30 g/k); Urea (100 g/k) Ludigol® (10 g/k) Steaming at 110°C for 15 min.

increasing the solubility of the reactive dye in the print paste, (ii) improving the swellability of the cellulose structure, (iii) facilitating the dye release from the thickener film to the cellulosic fiber, and (iv) enhancing the extent of dye fixation, thereby giving rise to deeper depth of shades.[9,17]

On the other hand, the decrease in *K/S* values beyond 120°C could be discussed in terms of higher extent of dye hydrolysis, undue penetration of the released dye, side interactions with the used thickeners, and shortage in accessible active sites, i.e., —OH groups.[9,17]

The *K/S* values of the obtained prints is governed by type of thickening agent, i.e., PAA/D$_2$ > PAA/GA$_1$ > Na-alginate (Fig. 3).

Steaming time

Figure 4 shows the effect of steaming time, at 110°C for 5–35 min, on the depth of the reactive prints. It is

TABLE IV
Effect of Storing Time on the Rubbing Fastness Properties of the Cotton Prints Using Different Thickening Agents as well as Different Reactive Dye

		Thickening agent used					
		Na-Alginate		PAA/GA$_1$		PAA/D$_2$	
Reactive dye	Storing time	Dry	Wet	Dry	Wet	Dry	Wet
Remazol® Brill. Blue (VS)	I	4	3–4	5	5	5	5
	II	4	3–4	4–4	4	4	4–5
	III	4	3–4	4–5	4	3–4	4
Drimarene® Blue. P (MC)	I	5	4	5	4	5	5
	II	4	3–4	4–5	4	5	4
	III	4	3–4	4	3–4	4–5	3–4
Drimarene® Red HF, (TFP/VS)	I	4	3–4	5	4–5	5	4–5
	II	4	3–4	5	4–5	5	4–5
	III	3–4	2–3	4–5	3–4	4–5	3–4
Procion® Red H–HE (MC)	I	4	3–4	5	4–5	5	4–5
	II	4	3–4	5	4–5	5	4
	III	3–4	2–3	4–5	4	4	3–4
Drimarene® Red CL (MCT/VS)	I	4	3–4	5	4–5	5	5
	II	4	3–4	5	4–5	5	5
	III	4	3–4	5	4–5	5	5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days. MC, Monochlorotriazine; VS, Vinyl sulphone; TFP/VS, Trifloroloprymedene. Reactive dye (30 g/k); NaHCO$_3$ (30 g/k); Urea (100 g/k) Ludigol® (10 g/k) Steaming at 110°C for 15 min.

TABLE V
Effect of Storing Time on the Perspiration Fastness Properties of the Cotton Prints Using Different Thickening Agents as Well as Different Reactive Dye

		Thickening agent used					
		Na-Alginate		PAA/AG		PAA/D	
Reactive dye	Storing time	Acidic	Alkaline	Acidic	Alkaline	Acidic	Alkaline
Remazol® Brill. Blue (VS)	I	4–5	5	4–5	5	5	5
	II	4–5	5	4–5	5	5	5
	III	4	5	4–5	5	4–5	5
Drimarene® Blue. P (MC)	I	5	5	5	5	5	5
	II	4	5	5	5	5	5
	III	4	5	4–5	5	4–5	5
Drimarene® Red HF, (TFP/VS)	I	4–5	5	5	5	5	5
	II	4	5	5	5	5	5
	III	4	5	4–5	5	4	5
Procion® Red H–HE (MC)	I	4–5	5	5	5	5	5
	II	5	5	5	5	4–5	5
	III	5	5	4–5	5	4	5
Drimarene® Red CL (MCT/VS)	I	4–5	5	5	5	5	5
	II	4–5	5	4–5	5	5	5
	III	4	5	4	5	4–5	5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days. MC, Monochlorotriazine; VS, Vinyl sulphone; TFP/VS, Trifloroloprymedene. Reactive dye (30 g/k); $NaHCO_3$ (30 g/k); Urea (100 g/k) Ludigol® (10 g/k) Steaming at 110°C for 15 min.

evident that, within the range examined and for a given printing conditions, the *K*/*S* values of the obtained prints improve by prolonging the steaming time up to 15 min, whereas further steaming time, i.e., beyond 15 min, has a negative impact on the *K*/*S* values, irrespective of the used thickening agent and the cellulosic substrate.

It is understandable that proper steaming time is needed for (i) swelling of the thickener film, (ii) facilitating the release of the dye molecules from the thickener film onto the cellulose structure, (iii) opening up the cellulose structure, thereby enhancing sufficient dye diffusion and penetration, (iv) assisting decomposition of $NaHCO_3$ to give a proper alkaline pH, and finally (v) enabling the dye–fiber interaction and fixation via the formation of covalent bonds.[17,18]

Figure 4 also shows that, further extending in steaming time, i.e., beyond 15 min at 110°C, brings

TABLE VI
Effect of Storing Time on the Handle of the Cotton Prints Using Different Thickening Agents as well as Different Reactive Dye as Well as Different Reactive Dye

		Thickening agent used		
Reactive dye	Storing Time	Na–Alginate	PAA/GA_1	PAA/D_2
Remazol® Brill. Blue (VS)	I	S	S	S
	II	S	S	S
	III	S	S	S
Drimarene® Blue. P (MC)	I	S	S	S
	II	S	S	S
	III	S	H	S
Drimarene® Red HF, (TFP/VS)	I	S	S	S
	II	S	S	S
	III	S	S	S
Procion® Red H–HE (MC)	I	S	S	S
	II	S	S	S
	III	S	S	S
Drimarene® Red CL (MCT/VS)	I	S	S	S
	II	S	S	S
	III	S	S	S

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days. MC, Monochlorotriazine; VS, Vinyl sulphone; TFP/VS, Trifloroloprymedene; S, Soft; H, Harsh. Reactive dye (30 g/k); $NaHCO_3$ (30 g/k); Urea (100 g/k) Ludigol® (10 g/k) Steaming at 110°C for 15 min.

TABLE VII
Effect of Storing Time on the Apparent Viscosity of Printing Paste Containing Remazol® Brilt. Blue

Thickening agent used	Storing time (day)	Shear rate (S^{-1})									
		2	6.222	10.44	14.67	18.89	32.11	27.35	31.56	35.78	40
		Viscosity (Po.s)									
Na–Alginate	I	3.5	3.1	2.9	2.78	2.70	1.87	1.7	1.56	1.6	1.58
	II	3.1	3	2.5	2.3	2.2	1.8	1.65	1.6	1.4	1.35
	III	2.9	2.7	2.3	2.1	2.03	1.75	1.60	1.53	1.3	1.21
PAA/D_2	I	7.9	7.4	7.19	6.9	6.85	6.8	6.7	6.88	6.65	6.6
	II	7.6	7.2	6.9	6.8	6.7	6.69	6.67	6.65	6.62	6.6
	III	7.2	6.1	6.6	6.5	6.42	6.4	6.39	6.38	6.35	6.3
PAA/GA_1	I	6.5	6.4	6.38	6.35	6.3	6.28	6.26	6.25	6.23	6.2
	II	6.4	6.35	6.3	6.29	6.25	6.2	6.14	6.13	6.1	6.1
	III	6.2	6.12	6.18	6.12	6.1	5.9	5.8	5.7	5.5	5.3

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days.

about a decrease in *K/S* values, regardless of the used thickener, which could be discussed in terms of : (i) accelerating the tendency toward hydrolysis of the used reactive dye, thus minimizing the ability of dye to form covalent bonds with the hydroxyl groups, (ii) adversely affecting the thickener film properties, thus hindering the release of the entrapped reactive dye molecules, and (iii) enabling alkaline attack on the dye–fiber bonds, thereby lowering the *K/S* value of the obtained reactive prints.[9,17,18] Nevertheless, the extent of printing is determined by the chemical nature of the thickening agent, i.e., PAA/D_2 > PAA/GA_1 > Na-alginate.

Effect of storing time

Performance properties of the prints

As for the changes in the *K/S* values, fastness properties, i.e., washing, rubbing, and perspiration, as well as softness of the printed cotton fabric samples using the thickening agents under investigation along with different reactive dyes, as a function of storing time, the results are shown in Tables II–VI. Data in Table II signify that: (i) storing the printing pastes thickened with any of PAA/D_2, PAA/GA_1, or Na-Alginate results in a decrease in the *K/S* values, (ii) the extent of decrease is governed by both the type of thickening agent as well as the functionality and stability of the reactive dye, (iii) the decrease in *K/S* values by storing can be discussed in terms of partial hydrolysis of the reactive dye under the used alkaline conditions and as variation in the thickener structure as well as in its rheological properties.[9] Table III shows that the washing fastness properties of cotton prints, were found to be marginally decreased, especially at longer storing period, i.e., 7 days, and at higher washing temperature, i.e., at 90°C, regardless of the used reactive dye. Table IV reveals that (i) prolonging storing time up to 7 days brings about a decrease in dry and wet rubbing fastness properties of the prints, and the extent of decrease in rubbing fastness rate is governed by the extent of dye fixation, and (ii) for a given storing time as well as printing conditions the wet rubbing fastness is lower than the dry rubbing fastness most probably due to the presence of unfixed dye entrapped in the print. Table V indicates that the alkaline perspiration

TABLE VIII
Effect of Storing Time on the Apparent Viscosity of Printing Paste Containing Drimarene® Blue, P/NX

Thickening agent used	Storing time (day)	Shear rate (S^{-1})									
		2	6.222	10.44	14.67	18.89	32.11	27.35	31.56	35.78	40
		Viscosity (Po.s)									
Na-Alginate	I	5.19	4.86	4.8	4.7	4.6	4.55	4.5	4.3	4.21	4.1
	II	5	4.78	4.71	4.7	4.69	4.5	4.3	4.23	4.1	3.91
	III	4.9	4.78	4.69	4.5	4.43	4.29	4.2	4.18	3.91	3
PAA/D_2	I	8.6	8.1	7.8	7.7	7.6	7.5	7.4	7.2	7.19	7.1
	II	7.9	7.7	7.5	7.3	7.1	6.9	6.8	6.7	6.65	6.6
	III	7.6	7.3	7.2	7.1	7	6.8	6.69	6.5	6.4	5.7
PAA/GA_1	I	6.9	6.6	6.56	6.5	6.48	6.4	6.36	6.3	6.28	6.2
	II	6.5	6.49	6.48	6.4	6.3	6.29	6.26	6.2	6.1	6
	III	6.19	6.1	6	5.98	5.95	5.9	5.8	5.7	5.6	5.5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days.

TABLE IX
Effect of Storing Time on the Apparent Viscosity of Printing Paste Containing Drimarene® Red HF

		Shear rate (S^{-1})									
		2	6.222	10.44	14.67	18.89	32.11	27.35	31.56	35.78	40
Thickening agent used	Storing time (day)	Viscosity (Po.s)									
Na-Alginate	I	6.5	6.1	5.9	5.85	5.81	5.78	5.7	5.56	5.51	5.5
	II	6.3	5.8	5.78	5.7	5.65	5.6	5.55	5.52	5.51	5.5
	III	6.2	5.7	5.75	5.65	5.6	5.5	5.53	5.51	5.45	5.4
PAA/D_2	I	9.4	8.8	8.3	8	7.9	7.8	7.7	7.68	7.6	7.5
	II	9	8.4	8	7.9	7.8	7.75	7.7	7.65	7.6	7.5
	III	8.6	8.1	7.8	7.79	7.71	7.68	7.6	7.55	7.5	7.4
PAA/GA_1	I	7.6	7.5	7.4	7.2	7	6.95	6.8	6.78	6.7	6.6
	II	6.7	6.65	6.6	6.5	6.4	6.39	6.34	6.33	6.31	6.3
	III	6.3	6.2	6.18	6.1	6	5.9	5.8	5.78	5.7	5.5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days.

fastness rates are better than the acidic ones, regardless of the used thickening agent and reactive dye; and the storing time has a slight negative effect especially under acidic conditions> Finally, Table VI manifests that storing time has practically marginal or no effect on the handle of the obtained prints.

Apparent viscosities

Tables VII–XI show the effect of storing time on the apparent viscosities (upper curve), at different shear rates, of printing pastes containing Remazol® Brill Blue BB (Dystar), Procion® Red H-HE (Zeneca), Drimarene® Red CL (Clariant –India) Drimarene® Red HF, as well as Drimarene® Blue PXN.

It can be seen, at zero storing time, that the apparent viscosity of a printing paste depends on the specific dye used, though the concentration of the latter is kept constant in all pastes. It can be generally seen that the apparent viscosity of a paste containing Procion® Red H-HE is the highest, and that of a paste containing Remazol® Brill. Blue is the lowest, whereas other pastes have viscosity values in between.

This suggests that the internal structure of the printing pastes under study is not the same for all the dyes used. That is, the extent of molecular or particle entanglement of printing paste depends not only on the specific dye used, but on the impurities associated with the dye itself as well. The higher the extent of entanglement is, the higher the viscosity will be.[19] This suggests that Procion® Red H-HE brings about higher entanglement, while Remazol® Brill. Blue brings about the lowest entanglement, and other dyes results in extent of entanglement in between.

Storing the printing pastes in question up to 7 days results in decreasing their apparent viscosities, at a given set of conditions. The viscosity decrease is higher at 7 days than that at 3 days. It is probable that storing allows better swelling, compatibility, and uniformity of the macromolecules of pastes, which results, more or less, in releasing the entanglement, thereby decreasing the viscosity. However, the effect of microorganism attack, especially on alginate, cannot be ruled out.

TABLE X
Effect of Storing Time on the Apparent Viscosity of Printing Paste Containing Procion® Red H-HE

		Shear rate (S^{-1})									
		2	6.222	10.44	14.67	18.89	32.11	27.35	31.56	35.78	40
Thickening agent used	Storing time (day)	Viscosity (Po.s)									
Na-Alginate	I	7.4	6.5	6.1	6	5.9	5.85	5.8	5.79	5.75	5.7
	II	6.4	6.1	6	5.9	5.86	5.8	5.7	5.67	5.65	5.6
	III	6.2	5.9	5.78	5.69	5.65	5.5	5.3	5.2	5.15	5.1
PAA/D_2	I	10.3	9.5	8.8	8.6	8.5	8.4	8.3	8.2	8.1	8
	II	9.9	8.9	8.6	8.4	8.39	8.3	8.1	8	7.9	7.8
	III	9.2	8.6	8.3	8.1	8	7.9	7.8	7.2	7.6	7.5
PAA/GA_1	I	9.9	8.9	8.6	8.4	8.39	8.3	8.1	8	7.9	7.8
	II	9.2	8.6	8.3	8.1	8	7.9	7.8	7.7	7.6	7.5
	III	7.6	7.1	6.9	6.8	6.7	6.68	6.65	6.6	6.59	6.5

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days.

TABLE XI
Effect of Storing Time on the Apparent Viscosity of Printing Paste Containing Drimarene® Red CL

		Shear rate (S^{-1})									
Thickening agent used	Storing time (day)	2	6.222	10.44	14.67	18.89	32.11	27.35	31.56	35.78	40
		Viscosity (Po.s)									
Na-Alginate	I	6.2	6.15	6.12	6.1	5.95	5.9	5.88	5.81	5.8	5.7
	II	6.18	5.13	6.1	5.92	5.9	5.84	5.81	5.8	5.78	5.62
	III	6.15	6.11	6	5.95	5.89	5.8	5.72	5.7	5.65	5.59
PAA/D_2	I	9.2	9.15	9.13	9.12	9.1	8.9	8.82	8.8	8.75	8.7
	II	9.16	9.12	9.1	9	8.9	8.85	8.8	8.75	8.7	8.6
	III	9.12	9.1	9	8.9	8.85	8.8	8.78	8.72	8.7	8.65
PAA/GA_1	I	7.5	7.4	7.3	7.25	7.2	7.18	7.1	6.89	6.85	6.8
	II	7.4	7.35	7.29	7.23	7.19	7.15	6.95	6.85	6.8	6.7
	III	7.25	7.2	7.17	7.15	7.1	6.95	6.9	6.8	6.78	6.6

I, Freshly prepared; II, stored for 3 days; III, stored for 7 days.

CONCLUSIONS

At optimal $NaHCO_3$ concentration (30 g/K) the depth of shade of the prints, expressed as *K/S* values, depended on the nature of the thickener used, and followed the descending order PAA/D_2 > PAA/GA_1 > Na-Alginate $\gg$PAA/D_1 $\geq$ PAA/GA_2. Optimal printing conditions were found to be $NaHCO_3$ concentration (30 g/K), urea concentration (100 g/k), steaming temperature (110°C), and time (15 min). The apparent viscosity of a printing paste, as well as both of *K/S* value and fastness properties of a print were governed by the nature of the reactive dye and type of thickener. Storing of a printing paste up to 7 days resulted in a decrease in its apparent viscosity along with a slight reduction in *K/S* value and a little variation in some fastness properties of prints.

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