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New Synthetic Thickeners for Printing Cotton with Reactive Dyes

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ABSTRACT

Four water soluble resins, viz. polyacrylic acid (PAA), polyacrylic acid/polyethylene glycol-1000 (PAA/PEG-1000), polyacrylic acid/polyethylene glycol-6000 (PAA/PEG-6000), and polyacrylic acid/polymethacrylic acid (PAA/PMA), were utilized as pastes for printing cotton fabric with reactive dyes. The prints were evaluated for their depth of shade as well as other properties. The properties of the prints were found to depend not only on the nature of the thickener and of the reactive dye, but also on the concentration of the basic catalyst and urea in the printing paste, storing time and the conditions of fixation. In comparison with sodium alginate, and for a given set of printing conditions, the results indicate that the depth of the print, as well as other properties, follow the order:

$$(PAA/PMA) > (PAA/PEG - 1000) > \text{sodium alginate} > PAA/PEG\text{-}6000 > PAA$$

1 INTRODUCTION

Several studies have been recently carried out with respect to the evaluation of alternative thickeners as a substitute for the widely utilized thickener in reactive dye printing, i.e. sodium alginate, due to the high cost, limited availability and non-uniformity of the latter.[1–5]

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In respect of this, we have described[6] the preparation and rheology of some water soluble synthetic resins based on a bulk polymerization of acrylic acid (AA) in the absence of, and in the presence of, polyethylene glycol-1000 (PEG-1000), polyethylene glycol-6000 (PEG-6000) or methacrylic acid (MAA).

This paper describes the results obtained using these resins as thickeners as substitutes for sodium alginate in the reactive dye printing of mercerized cotton fabric.

2 EXPERIMENTAL

2.1 Materials

Mill-scoured, bleached, and mercerized plain weave cotton fabric (145 g/m^2) was used.

PAA, PAA/PEG-1000, PAA/PEG-6000, and PAA/PMA soluble resins were prepared according to a previous report.[6]

A high viscosity sodium alginate (Cecalginate HV/KL 600) was supplied by Ceca Kolloid (Chemie of Paris, France).

The reactive dyes used were Remazol Brilliant Blue BB and Remazol Brilliant Red F3B (sulphatoethylsulphone type, FH), Procion Red P-8B and Procion Yellow MXGR (chloro-1 : 3 : 5 triazine, ICI) and Levafix Yellow P-GNA (alkylsulphonyl-pyrimidine, (By)). Non-ionic detergent (Hostapal CV-ET, FH), and a mild oxidizing agent (Ludigol, BASF) were technical grade reagents.

2.2 Methods

The printing pastes were prepared using the following recipes:

reactive dye	30 g
stock thickening	800 g (5%)
urea	0–75 g
sodium carbonate	20–50 g
Ludigol®	10 g
water	*x* g
Total weight of the paste	1000 g

2.3 Printing procedure

Printing was carried out using the flat screen technique. Printed samples were then dried at 100°C for 5 min and fixed either by steaming at 120°C for 15 min or by thermal treatment at 150°C for 5 min. Samples were rinsed with cold water for 15 min and then with water at 60°C for 15 min, followed by soaping with a non-ionic detergent (2 g/litre), soda ash (2 g/litre), and sodium hydroxide (2 g/litre) for 15 min at the boil. Subsequently, the soaped samples were rinsed thoroughly with hot, and then cold, water and finally dried at ambient conditions.

2.4 Testing

The printed samples were evaluated for depth of the prints (expressed as *K/S*, where *K* is the absorption coefficient and *S* is the scattering coefficient),[7] as well as the fastness properties, e.g. washing, rubbing, perspiration, using standard methods.[8] The apparent viscosity (η) of the printing pastes was assessed as in a previous study,[6] and calculated using the following formula:

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

where τ is the shearing stress (dyne/cm^2) and D is the rate of shear (s^{-1}).

3 RESULTS AND DISCUSSION

3.1 Sodium carbonate concentration

Figure 1 shows the effect of the concentration of sodium carbonate on the depth of the prints (expressed as *K/S*), using the new synthetic

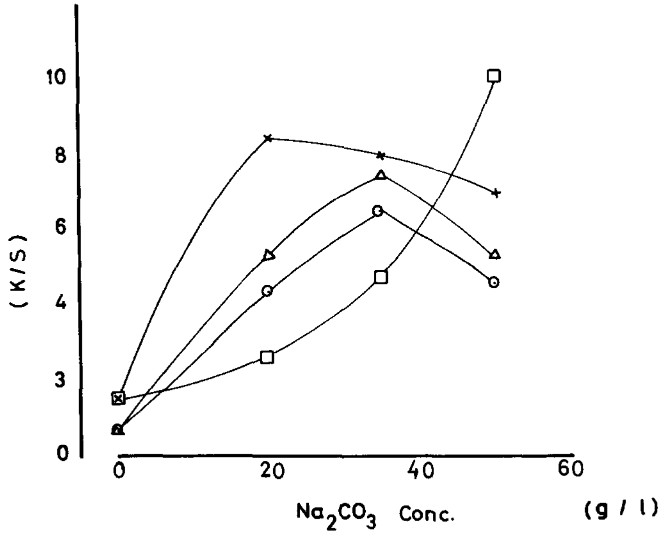

Fig. 1. Effect of sodium carbonate concentration on the depth of the prints (*K/S*). PAA (O); PAA/PEG-1000 (X); PAA/PEG-6000 (Δ); PAA/PMA (□). Remazol Brilliant Blue BB (30 g/kg); thickener (40 g/kg); urea (50 g/kg); steaming at 120°C for 15 min.

thickeners. It is apparent that, within the range examined, increasing the sodium carbonate concentration up to 20 g/kg (in the case of using PAA), 35 g/kg (in the case of using 'PAA/PEG-1000 or PAA/PEG-6000', or up to 50g/kg (in the case of using PAA/PMA), results in a noticeable increase in the depth of prints. However, further increase in the concentration of sodium carbonate when using the first three pastes resulted in a reversal of this trend, as far as depth of the print was concerned.

This suggests that the presence of sodium carbonate in these printing pastes seems, up to a certain concentration, to (i) neutralize the free carboxyl groups of the thickener:[9]

$$\sim\!\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow \sim\!\text{COONa} + \text{H}_2\text{O} + \text{CO}_2 \qquad (1)$$

(ii) enhance the 'swellability' and the viscosity of the thickener, (iii) catalyse the dye fixation via ether links with the hydroxy groups in the cellulose substrate:[10]

$$\text{Cell . OH} + \text{D-X} \xrightarrow{\text{OH}-} \text{Cell . O . D} + \text{H-X} \qquad (2)$$

and (iv) facilitate the removability of the thickener after printing, hence producing prints with a softer handle.[11] The net effect of all these factors leads to a higher depth of the prints, irrespective of the paste used. However, further increase in sodium carbonate beyond these levels, in the case of the first three pastes, appears to (i) reduce the dye stability in the printing paste or dye fixation during the steaming step via hydrolysis:[10]

$$\text{D-X H}_2\text{O} \xrightarrow{\text{OH}-} \text{D-OH} + \text{H-X} \qquad (3)$$

$$\text{Cell . O . D} + \text{H}_2\text{O} \xrightarrow[\Delta]{\text{OH}-} \text{Cell . OH} + \text{D . OH} \qquad (4)$$

(ii) minimize the paste viscosity, thereby enabling undue penetration of used dye into the fabric,[9] and (iii) enable the dye to react and/or interact with some of the resins used, especially with the polyethylene glycol component,[12] thereby minimizing the dye release and transfer from the thickener film to the fibre phase during steaming, hence producing prints with a lower depth of shade.

On the other hand, differences in the depth of colour values obtained using different thickening agents could be associated with differences between the thickeners with respect to their chemical nature, chemical composition, molecular weight, number and location of acidic groups as well as compatability and affinity with other components in the printing paste, and the rheological properties of the paste.

3.2 Steaming conditions

Based on the above results, reactive printing of cotton fabric was carried out and fixation of the prints was effected by subjecting the dried prints to steaming. The relationship between steaming conditions, i.e. temperature and time, and the *K/S* values of the printed samples are shown in Figs 2 and 3.

Figure 2 shows the variation of *K/S* with the steaming temperature. It is apparent that, within the range examined, raising the steaming temperature to 120°C for 15 min is accompanied by a significant improvement in the depth of the prints (expressed as *K/S*), irrespective of the thickener used. This enhancement may be attributed to the comparatively easier dye release from the thickener film to the cellulosic—fibre phase, as well as to the higher degree of reactive dye fixation when steaming is carried out at a higher temperature, thereby giving a progressive increase in the depth of shade.

Figure 3 shows the effect of steaming time on the depth of shade of the printed fabric. It is apparent that prolonging the steaming period up to 15 min at 120°C is accompanied by a sharp increase in *K/S* values, for

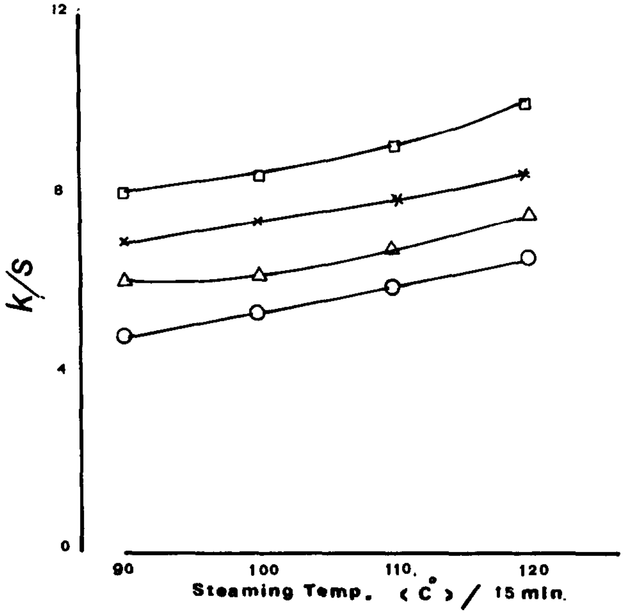

Fig. 2. Effect of steaming temperature on the depth of the prints (*K/S*). PAA (○); PAA/PEG-1000 (×); PAA/PEG-6000 (Δ); PAA/PMA (□). Remazol Brilliant Blue BB (30 g/kg); thickener (40 g/kg); sodium carbonate: 35 g/kg for PAA, 20 g/kg for PAA/PEG-1000, 35 g/kg for PAA/PEG-6000, 50 g/kg for PAA/PME, urea (50 g/kg); steaming for 15 min.

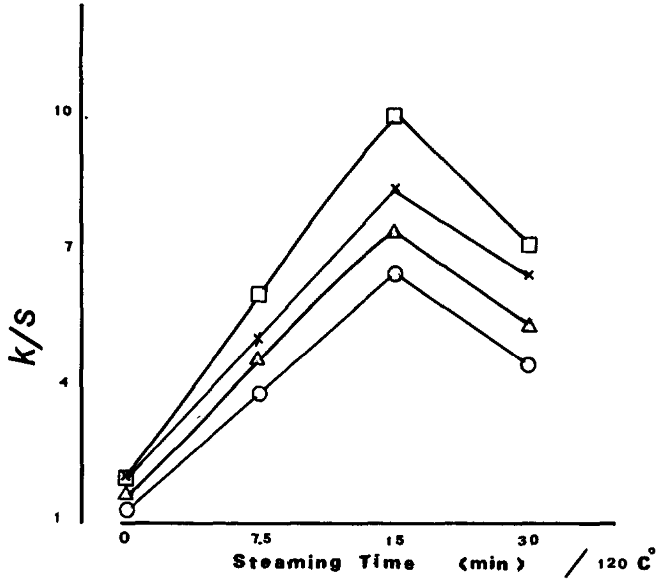

Fig. 3. Effect of steaming time on the depth of the prints (*K/S*). PAA (○); PAA/PEG-1000 (×); PAA/PEG-6000 (Δ); PAA/PMA (□). Remazol Brilliant Blue BB (30 g/kg); thickener (40 g/kg); sodium carbonate (as in Fig. 2); urea 50 g/kg; steaming at 120°C.

the given set of printing conditions. It is understandable that an adequate period of time is necessary to achieve not only a high degree of dye release from the thickener film and transfer to the fibre phase, but also an enhanced degree of dye fixation. Further increase in steaming time, i.e. beyond 15 min at 120°C, results in printed samples with less depth of colour, irrespective of the thickener used. This can be related to partial cleavage of the dye–fabric bonds during the fixation step in the presence of sodium carbonate, thereby minimizing the depth of the print, and/or changes in the fabric structure which adversely affect the depth of shade.

3.3 Urea concentration

Figure 4 shows the effect of the concentration of urea in the printing pastes on the depth of colour (*K/S*) of the printed fabric. It is apparent that increasing the urea concentration up to 25 g/kg results in a significant enhancement in the extent of dye fixation, regardless of the thickener used. This is probably relatable to the advantageous effect of urea on the disruption of hydrogen bonds, and/or the disaggregation of dye molecules in addition to its solvation effect; the depth of the print thus increases. It is also apparent that little or no enhancement

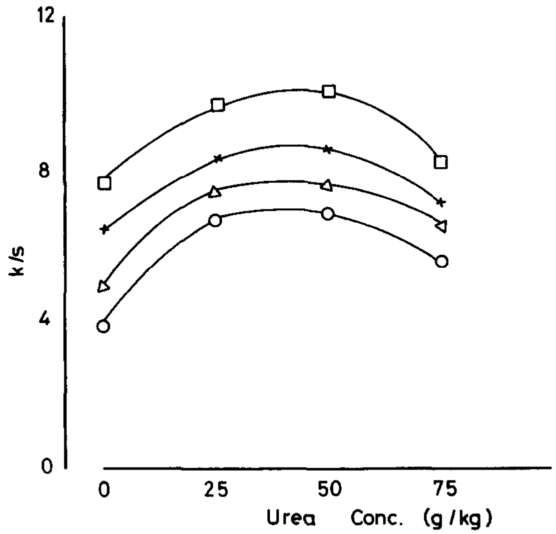

Fig. 4. Effect of urea concentration on the depth of the prints (*K/S*). PAA (○); PAA/PEG-1000 (×); PAA/PEG-6000 (Δ); PAA/PMA (□). Remazol Brilliant Blue BB (30 g/kg); thickener (40 g/kg); sodium carbonate (as in Fig. 2); steaming at 120°C for 15 min.

in the depth of the prints occurs on increasing the urea concentration from 25 to 50 g/kg. However, above 50 g urea/kg there is a noticable decrease in the depth of shade, which could result from side reactions and/or interactions of urea with the reactive dye to form a relatively inert product, thereby reducing the extent of dye–fibre covalent reaction,[13] and/or interaction with the thickeners, thereby altering their rheological properties and resulting in undue penetration both of the thickener film and of the dye within the swollen fabric structure, thereby adversely affecting the extent of dye fixation and the depth of the prints.

3.4 Fixation method

When the influence of the fixation method (i.e. steaming or thermosoling) on print performance is evaluated in terms of the *K/S* value and fastness properties, it is evident (Table 1) that, when the thickeners were used individually in the printing pastes, the *K/S* values were higher when the prints were fixed by the steaming method, irrespective of the thickener used. This can be attributed to the fact that dye dissolution, thickener swellability, and increased electrostatic repulsion between the anionic dye present in the thickener film and its —COO^- groups (giving rise to the dye transfer from the thickener film to the fabric) occur more readily in the steaming process than in thermosoling at high temperature, thereby

TABLE 1
Effect of Fixation Method on the Print Performance

Thickener used	*Fixation method*	*K/S*	*RF*		*WF*			*PF*						*Handle*	*Sharpness*
			Wet	*Dry*	*Alt.*	*St.*		*Acidic*			*Alkaline*				
						c	*w*	*Alt.*	*St.*		*Alt.*	*St.*			
									c	*w*		*c*	*w*		
PAA	Sm	6·5	2–3	3	2–3	2–3	3	2–3	2–3	2–3	2–3	2–3	2–3	S	Ex
I	Tm	4·5	2	2–3	2	2	2–3	2	2	2	2	2	2	H	Ex
PAA/PEG-1000	Sm	8·2	4–5	4–5	5	4–5	5	5	4–5	5	5	4–5	5	S	Ex
II	Tm	6·7	3–4	4	4	3–4	3–4	4	3–4	4	3–4	3–4	3–4	H	Ex
PAA/PEG-6000	Sm	7·4	3	3–4	3	3–4	4	3	3	3–4	3–4	3	3	S	Ex
III	Tm	5·2	2	2–3	2–3	2–3	2–3	2	2–3	2–3	2	2–3	2–3	H	Ex
PAA/PMA	Sm	9·8	4–5	5	5	5	5	5	5	5	4–5	5	5	S	Ex
IV	Tm	7·5	4	4	4	4	4	3–4	4	4	3–4	3–4	3–4	H	Ex

Na_2CO_3: for I (35 g/kg), for II (20 g/kg), for III (35 g/kg), for IV (50 g/kg); Urea (25 g/kg); Remazol Brilliant Blue BB (30 g/kg); thickener (40 g/kg).

Alt., Alteration; c, cotton; Ex, excellent; H, harsh handle; PF, perspiration fastness; RF, rubbing fastness; S, soft handle; Sm, steaming at 120°C for 15 min; St., staining on cotton or wool; Tm, thermosoling at 150°C for 5 min; VG, very good; w, wool; WF, washing fastness at 90°C.

improving the extent of dye fixation as well as increasing the *K/S* values of the prints.[4] The situation is different when the thermosoling method is used. Dehydration of the poly(acrylic) based thickeners, as well as the formation of some inter- and/or intramolecular condensation products,[9] seem to prevail under the conditions used (150°C for 5 min). This results in unwashed thickener products, which hinder not only the release and transfer of the dye from the thickener film to the fabric but also its fixation on the fabric, thus minimizing the depth of the print and also enhancing the 'roughness' of the prints, as was observed practically.

It is also interesting to note that the fastness properties of the thermo-fixed prints were lower than those of steam-fixed samples. This was observed regardless of the paste composition used. However, the initial difference in the rating of the evaluated fastness properties of the thickeners were more relatable to their specific nature for the reasons discussed above.

It can be concluded that, for a given set of printing conditions, steam-fixed prints have higher depth and improves fastness properties, as well as a softer handle, than those from thermo-fixed samples. Fastness property differences must, however, also be considered in terms of variation in the depths of the prints.

3.5 Dye type

Using the new thickening agents, printing with reactive dyes was carried out in which four dyes, viz. Remazol Brilliant Blue BB, Procion Red P-8B, Procion Yellow MXGR, and Levafix Yellow EGNA, were used. The fixation of the prints was effected by subjecting the dried prints to steaming at 120°C for 15 min.

As far as the change in *K/S* values, as well as other properties of the prints, is concerned, the results (Table 2) show that, based on the properties of the prints as a function of the thickening agent used, the following order of effectiveness may be drawn:

$$\text{PAA/PMA} \geq \text{PAA/PEG-1000} > \text{PAA/PEG-6000} > \text{PAA}$$

regardless of the dye used. This can be rationalized on the basis of the comparatively easier dye release and transfer from the thickener film, in addition to the higher extent of dye fixation on the cotton fabric. The differences in the properties of the prints can be related to differences in dye substantivity and reactivity, mode of interaction, molecular size and state of aggregation, location and extent of fixation, affinity towards the used thickeners as well as stability, irrespective of the thickener and conditions used. The wet rubbing fastness was found to be marginally

TABLE 2
Effect of Dye Type on the Print Performance

Reactive dye	*Thickener used*	*K/S*	*RF*		*WF*			*PF*						*Handle*	*Sharpness*
								Acidic			*Alkaline*				
			Wet	*Dry*	*Alt.*	*St.*		*Alt.*	*St.*		*Alt.*	*St.*			
						c	*w*		*c*	*w*		*c*	*w*		
Remazol Brilliant Blue BB	I	6·5	2–3	3	2–3	2–3	3	2–3	2–3	2–3	2–3	2–3	2–3	S	Ex
	II	8·24	4–5	4–5	5	4–5	5	5	4–5	5	5	4–5	5	S	Ex
	III	7·38	3	3–4	3	3–4	4	3	3	3–4	3–4	3	3	S	Ex
	IV	9·78	4–5	5	5	5	5	5	5	5	4–5	5	5	S	Ex
Procion Red P-88	I	8·16	3	3	3	3	3	2–3	3	2–3	3	3	3	S	VG
	II	13	4	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	S	Ex
	III	9·8	3	3	3	3	3	3–4	3	3	3	3	3	S	VG
	IV	13·7	4	4–5	5	4–5	4–5	5	5	5	5	5	5	S	Ex
Procion yellow MX GR	I	12·3	2	2–3	2–3	2–3	2–3	2–3	2–3	2–3	2–3	2–3	2–3	S	VG
	II	14·5	3–4	4	3–4	3	3	3–4	3	3	3	3	3	S	Ex
	III	12·8	2–3	2–3	3	2–3	2–3	2–3	2–3	2–3	2–3	2–3	2–3	S	VG
	IV	18·9	3–4	4	3–4	3–4	3–4	3–4	3–4	3–4	3–4	3–4	3–4	S	Ex
Levafix Yellow EGNA	I	8·23	3	3	3	3	3	3	2–3	2–3	3	3	3	S	VG
	II	8·9	4–5	5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	S	Ex
	III	8·5	3	3–4	3–4	3–4	3–4	4	3–4	3–4	4	3–4	3–4	S	VG
	IV	9·15	5	5	5	4–5	4–5	5	4–5	4–5	5	4–5	4–5	S	Ex

Na_2CO_3: for I (35 g/kg), for II (20 g/kg), for III (35 g/kg), for IV (50 g/kg); thickener (40 g/kg); urea (25 g/kg); reactive dye (30 g/kg); steaming at 120°C for 15 min.

For explanation of abbreviations, see footnote to Table 1.

TABLE 3
Effect of Thickening Agent Type on the Print Performance Before and After 8 Days of Storing

Thickener used	*Storing time (h)*	*η (poise)*	*K/S*	*RF*		*WF*			*PF*						*Handle*	*Sharpness*
				Wet	*Dry*	*Alt.*	*S*		*Acidic*			*Alkaline*				
							c	*w*	*Alt.*	*St.*		*Alt.*	*St.*			
										c	*w*		*c*	*w*		
Sodium	0	20·6	9·12	4	4–5	4	4	4	4	3–4	4	4–5	4	4	S	Ex
alginate	192	28·75	8·2	3–4	4	3	3	3	3–4	3–4	4	3–4	3	3–4	S	Ex
PAA	0	21·25	8·16	3	3	3	3	3	2–3	3	2–3	3	3	3	S	VG
I	192	28·25	6·7	2	2–3	2–3	2	2	2–3	2	2	2–3	2	2	S	G
PAA/PEG-1000	0	20	13	4	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	S	Ex
II	192	26·26	12·4	4	4	4	3–4	4	4	3–4	4	4	3–4	4	S	Ex
PAA/PEG-6000	0	15	9·8	3	3	3	3	3	3–4	3	3	3	3	3	S	VG
III	192	19·4	9·5	2–3	3	3	2–3	2–3	3	2–3	2–3	2–3	2–3	2–3	S	VG
PAA/PMA	0	12·5	13·7	4	4–5	5	4–5	4–5	5	5	5	5	5	5	S	Ex
IV	192	17·2	13·4	4	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5	4–5	S	Ex

Na_2CO_3: for sodium alginate (30 g/kg); for I (35 g/kg), for II (20 g/kg), for III (35 g/kg), for IV (50 g/kg); thickener (40 g/kg); urea (25 g/kg); Procion Red P-8B (35 g/kg); steaming at 120°C for 15 min.
For explanation of abbreviations, see footnote to Table 1.

lower than the dry rubbing fastness, which is attributed to unfixed dye–thickener complex entrapped in the print, irrespective of the thickener and dye used. All prints exhibited a soft handle.

3.6 Comparison of the new thickeners with sodium alginate

Table 3 shows the effect of using the new thickeners on the apparent viscosity (η) of 5% solutions before and after storing for 8 days at 80 s^{-1} rate of shear, as well as on the properties of the printed samples, using Procion Red, in comparison with sodium alginate. It is evident that storing of the printing pastes thickened with sodium alginate, or with the new thickeners, is accompanied by a substantial increase in the apparent viscosity values, regardless of the thickener used. This can be interpreted in terms of increased intramolecular forces in the thickener structure due to hydrogen bonding, with a resultant increased resistance to flow and an increased solution viscosity.

It is also apparent (Table 3) that the *K/S* values of the samples tend to decrease slightly on storing the printing pastes for eight days prior to printing. This could be attributed to partial hydrolysis of the dye in the presence of alkali and/or changes in the thickener structure brought about by its interaction with the other components of the printing paste, thereby reducing the extent of dye release and transfer from the paste phase to the fabric phase. As a result, the extent of dye fixation and fastness properties of the printed samples decreased marginally.

Table 3 also shows that the samples thickened with PAA/PMA and PAA/PEG-1000 acquire a higher depth of colour, as well as improved fastness to rubbing, washing and perspiration compared with those printed using sodium alginate. This indicates that these pastes have a higher ability to transfer the dye from the printing paste to the fabric, with a lower tendency to react with the dye.

The results (Table 3) also show that, for a given set of printing conditions, the properties of the printed samples using the thickening agents follow the order:

PAA/PMA > PAA/PEG-1000 > Na-alginate > PAA/PEG-6000 > PAA

The differences in the magnitude of the apparent viscosity of the printing pastes, the *K/S* values, and also other fastness properties within the range of thickeners used, are probably due to differences in the physical and chemical nature, molecular weight, rheological properties, number and location of functional groups (e.g. COOH, OH), as well as compatibility, stability and reactivity with the other components in the printing paste.

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