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A study of fabric stiffness with guar gum in reactive printing

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Abstract

Alginate thickeners are the most frequently used thickeners in reactive printing. They hardly react with reactive dyes and consequently do not cause increased fabric stiffness. All other polysaccharides contain reactive hydroxyl groups of higher reactivity which must be substituted for their use in reactive printing. In view of the price, partly substituted guar gum represents an acceptable alternative. In the presented research the applicability of substituted guar gum was studied. It was shown by TLC and the measurement of fabric stiffness, that these thickeners are suitable for printing with monofunctional reactive dyes. If bifunctional reactive dyes are used, a chemical reaction that increases fabric stiffness takes place. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive printing; Guar gum; Sodium alginate; Reactive dyes; Fabric stiffness; Solid content; TLC

1. Introduction

At present, sodium alginates are the most widely used thickeners for reactive printing because their structure causes no chemical reaction with reactive dyes. They also wash out easily and cause no fabric stiffness. Most other polysaccharide-based natural thickeners react with reactive dyes, which results in less saturated colours and increased fabric stiffness. The fluctuation in price and quality, as well as the limited assortment of printing techniques they offer, affects the development and use of alternative thickeners [1]. Alternative thickeners are either synthetic or etherified natural thickeners that satisfy the printing quality requirements. In view of the price, the most interesting alternative thickener is substituted guar gum, also known for yielding very good print sharpness [2].

Guar gum is a locust bean gum. It is prepared from the seeds of annual leguminous plants growing in India, Pakistan and in the South of the USA. Unmodified guar gum has a large number of hydroxyl groups forming a very complex crosslinking with the dye, which prevents the printing paste to be washed off the fabric quantitatively [3]. For this reason only substituted guar gum, which is also relatively insensitive to additions of electrolytes, is suitable for use [4].

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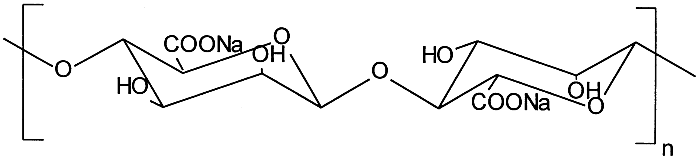
In our research, TLC was used to study the influence of dye concentration, substitution level and solid content on fabric stiffness.

2. Experimental

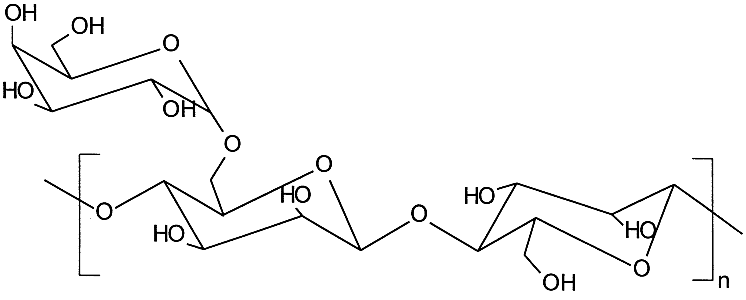
2.1. Substrate

All experiments were performed on viscose textiles for lighter garments (fabric weight 111.5 g/m^2). The thickeners used were sodium alginate, non-substituted guar gum and carboxymethylised guar gum (Fig. 1).

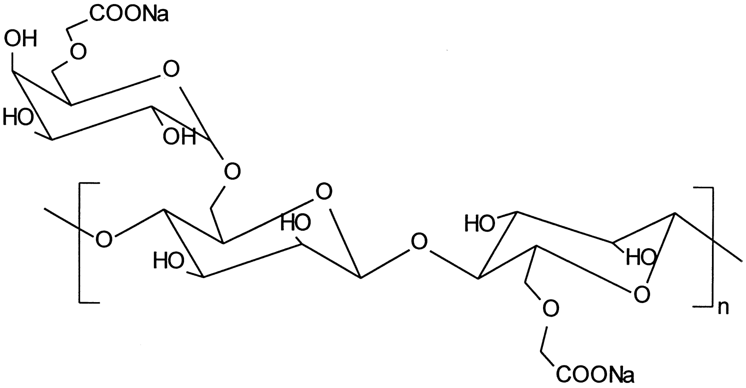
Sodium alginates are polymers with (1,4) linked β-d mannuronic acid and α-l-guluronic acid units. The chemical structure of guar gum consists of a linear main chain of mannose units linked via (1-4)-β-glycoside bonds. Every second mannose molecule carries a glycose molecule by a (1-6)-α-glycoside bonds [4,5]. The etherification of free hydroxyl groups with monochloroacetic acid



Sodium alginate



Non-substituted guar gum



Carboxymethylised guar gum

Fig. 1. The structure of thickeners.

prevents the chemical reaction between guar gum and the reactive dye.

In Table 1 the substitution levels and the amounts of used thickeners are given.

The sodium alginate is a product of Sigma Chemical Co., USA, and the substituted guar gum with DS = 1.1 is produced by Chemische Fabrik Grünau GmbH Illertissen in Germany. The non-substituted and the substituted guar gum DS = 0.18 are products of CHT R. Beitlich GmbH in Tübingen, Germany. Printing pastes were prepared with 1.5% concentrations of different mono- and bifunctional reactive dyes.

2.2. Preparation of the printing paste and the printing process

The thickener and added demineralised water were well stirred in a mixer and left in a refrigerator overnight to attain full swelling. To prepare the printing paste, 1.5% dye and 4.8% $NaCHO_3$ were added to each thickener and stirred for another 15 min. At the shear rate of $\dot{\lambda} = 10/s$, all printing pastes were calibrated to the constant viscosity of $\eta = 7140 \pm 400$ mPa s.

The flat screen printing technique was applied under the conditions presented in Table 2. All prints were carried out with one squeegee wipe with high reproducibility (max. 10 g paste/m^2 deviation).

2.3. Methods

In order to determine fabric handle, the stiffness of washed and climatised printed samples was measured according to DIN 53212. Even if the standard deviation of this method is more than ± 10%, any influence of the thickening agent on the fabric handle can be determined. The measurements were performed using a fabric stiffness measuring apparatus of Frank GmbH, Germany. Thin-layer chromatography was carried out on aluminium foils TCL-Alufolien/Kieselgel $60F_{254}$ of Merck. A mixture of *n*-butanol-acetone-water-ammonia (10:10:4:1) was chosen as the mobile system.

The synthesis of the pure dye C.I. Reactive Red 120 without textile auxiliaries was carried out according to the procedure of Vončina [6].

Table 2
Printing conditions

Stages of work	Conditions for work
Printing	Laboratory printing machine, (J. Zimmer) TypVP-RSF Flat printing screen parameters: 77 threads/cm, 80 μm threat distance Squeegee diameter: 15 mm Speed: 5 m/min Pressure grade: 3
Drying	5 min in drying machine at T = 40°C (W. Mathis)
Steaming	Steamer (W. Mathis) Typ DHE 15973 Saturated steam: 15 min at T = 102°C
Washing	Washing 5 times 15 min at T = 95°C with demineralised water

3. Discussion and measurement results

The basic problem in reactive printing is in the fact that during the fixing process some additional reactions take place between the reactive dye and

Table 1
The thickeners used

Thickener	Substitution level	Abbreviation	Amount of thickener (g/kg printing paste)
Sodium alginate Medium viscosity	0	AlMV	24
Substituted guar gum High viscosity	1.1	CMG	51
Substituted guar gum Low viscosity	0.18	CMGN	75
Substituted guar gum High viscosity	0.18	CMGH	39
Non-substituted guar gum Low viscosity	0	DPGN	82.5
Non-substituted guar gum High viscosity	0	DPGH	34.5

the hydroxyl groups of water (the hydrolysis of the reactive dye) and the thickener (crosslinking). The reaction of the reactive dye with cellulose, guar gum and water depends on the structure of the dye, the pH value and the temperature. Seen from the chemical aspect, the hydroxyl groups of polysaccharide are comparable with the primary and secondary hydroxyl groups of aliphatic alcohols, where the primary ones are the more reactive [7]. In the case of polysaccharides with side chains, the accessibility of the substrate is very important. With guar gum, this accessibility changes depending on the sugar unit. Cai et. al. [4] concluded from steric relations that the C(6) atom would most probably be attacked on the freely moving side galactose (Fig. 2). These primary OH groups are more reactive than those on mannose. With regard to better steric accessibility, the OH groups on atom C(2) of the straight mannose chain are slightly more reactive than the OH groups on atom C(2) of the branched mannose and galactose sugar. The reactivity of the hydroxyl groups on atoms C(2) and C(3) of galactose and mannose is about as low as the reactivity of alginate hydroxyl groups [8]. They react only 0.3%, and have no practical value in comparison with the C(6) hydroxyl group with an approximately 8% reactivity [4]. Due to the high reactivity of the atom C(6), guar gum cannot be used in reactive printing without prior modification. For this purpose, etherification with monochloracetic acid (carboxymethylised) has proved to be the best approach.

3.1. The influence of the substitution level (DS) and the solid content of the thickener on fabric stiffness

The reaction of the dye with the hydroxyl groups of guar gum depends on the reactivity of the dye and the substitution level of the thickener. Cai et al. [4] have confirmed that the use of unmodified guar gum in reactive printing with bifunctional dyes leads to massive fabric stiffness, which is due to the fact that the bifunctional dye forms a bridge between the cellulose material and the thickener. In theory, fabric stiffness should improve with an increasing substitution level and decreasing solid content. In Fig. 3 the influence of the substitution level on fabric stiffness in reactive printing with bifunctional reactive dyes is shown.

It is apparent from the results that all the thickeners used have slightly higher fabric stiffness values than pure viscose. This means that at least a small part of the thickener is bound to the fabric and also that reaction with alginate took place [8]. A stronger fabric stiffness was obtained when guar gum was used. Surprisingly, the fabric stiffness did not decrease with the increasing substitution level (CMG), even when the problematic bifunctional dyes were used. This result does not correlate with the theoretical model and contradicts the expected results. Knowing that the bond between the thickener, the reactive dye and viscose is defined by, and depends on, the concentration of the dye and the number of free hydroxyl groups, we can

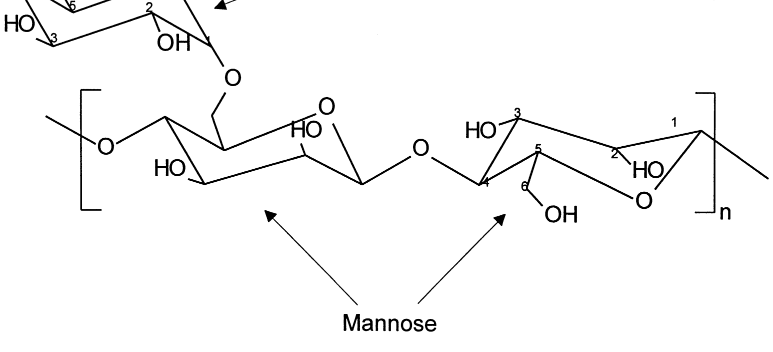


Fig. 2. Chemical structure of guar gum.

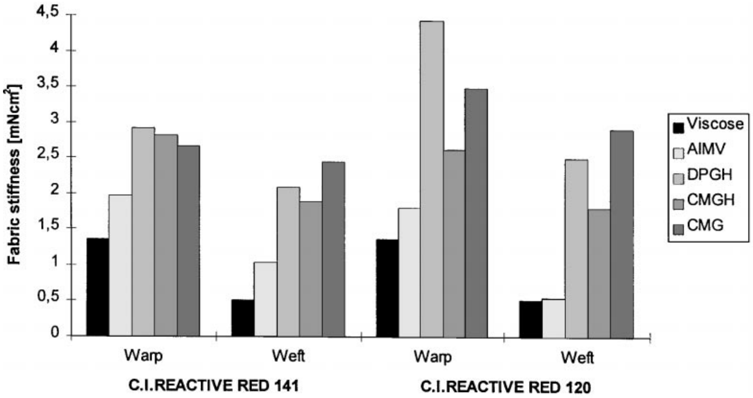


Fig. 3. The influence of the substitution level of the thickener on fabric stiffness of viscose at a low solid content.

assume that the influence of the solid content on crosslinking must be just as important. While non-substituted DPGH and low level substitution CMGH show comparable low solid content values, larger amounts of solid content must be added to the lower viscosity and high level substitution guar gum (CMG), which on the other hand increases the number of free hydroxyl groups in the printing paste. Consequently, improved fabric stiffness cannot be expected of CMG. Also, crosslinking reactions on secondary OH groups, which additionally affect fabric stiffness, are possible.

It can be concluded from the above that low molecular thickeners (DPGN, CMGN) yield higher stiffness values, which is confirmed in Fig. 4 The obtained results show that in low and non-substituted guar gum with low solid content (highly viscous) might also be used for reactive printing with bifunctional reactive dyes. The influence of the substitution level is apparent only with thickeners with a high solid content; this is negligible compared to the influence of the molecular mass.

3.2. *The influence of the reaction system of the reactive dye on fabric stiffness*

Mono- and bifunctional reactive dyes with different bonding systems (MCT, DCT, VS, DCCX) were included in our research. Since fabric stiffness is particularly strong with low viscosity thickeners (high solid content), we decided to use a low level substitution guar gum CMGN (DS = 0.18) in the experimental printing.

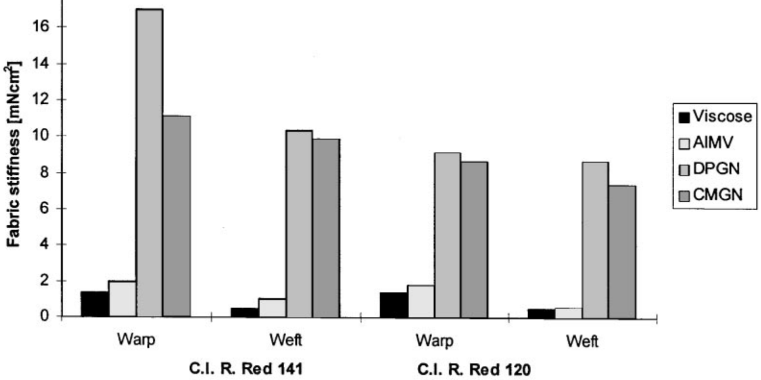


Fig. 4. The influence of the substitution level of the thickener on fabric stiffness of viscose at high solid content.

It is evident from the results presented in Fig. 5 that only a few representatives of MCT and DCT can be identified as creators of stiffness. Fabric stiffness could not be observed with the studied vinylsulphone dyes. The high fabric stiffness obtained when MCT is used is due to the fact that many of these dyes have a bifunctional character: the dyes C.I. Reactive Red 120, C.I. Reactive Red 141, C.I. Reactive Red 2 and C.I. Reactive Yellow 135 have two equivalent centres. On this basis they can form a chemical bond with the hydroxyl groups of viscose and the thickener, which explains fabric stiffness. Reactive dyes containing only one reactive centre (C.I. Reactive Red 3, C.I. Reactive Red 174, C.I. Reactive Blue 220, C.I. Reactive Blue 19, C.I. Reactive Yellow 15, C.I.

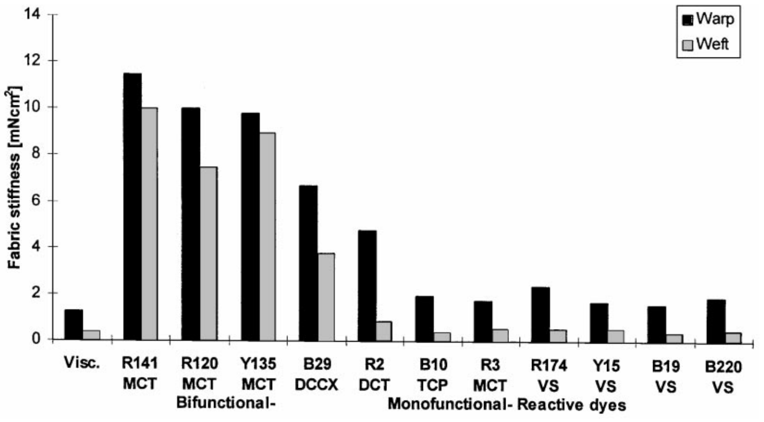


Fig. 5. The influence of the reaction system of the reactive dye on fabric stiffness with CMGN (DS = 0.18).

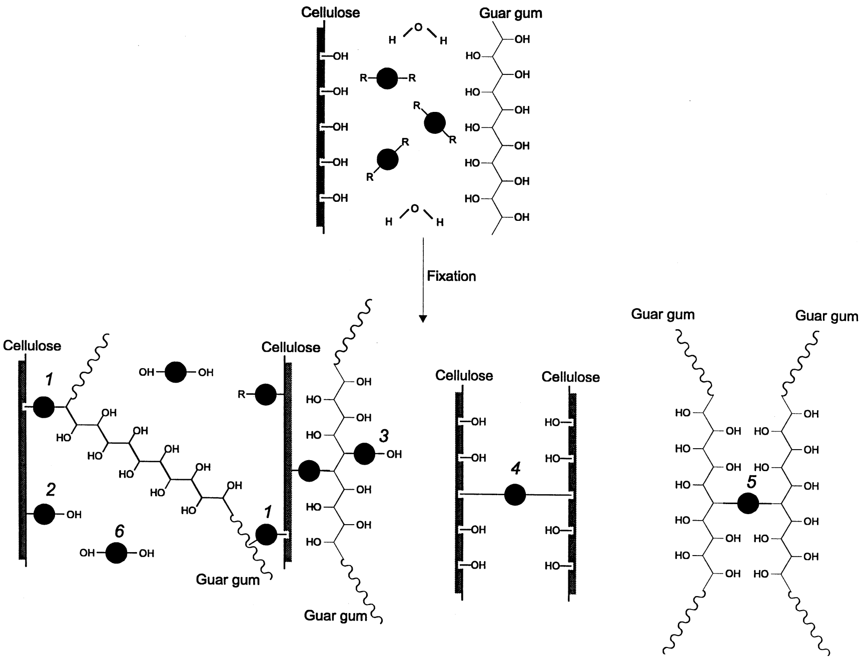


Fig. 6. Reaction products of the bifunctional reactive dye fixation on cellulose material with guar gum as the thickener.

Reactive Blue 10) cannot form a bridge between the thickener and the viscose, neither can they cause fabric stiffness.

The fact that a thickener containing a reactive dye can be fixed on the substrate is based on the fulfilment of certain assumptions. For better understanding, the products of reactions between the substrate, the thickener and water are given in Fig. 6 [9].

The bifunctional reactive dye can react with the following hydroxyl groups:

1. OH groups of cellulose and guar gum →crosslinking
2. OH groups of cellulose and water→etherification and hydrolysis
3. OH groups of guar gum and water→etherification and hydrolysis
4. OH groups of cellulose→crosslinking
5. OH groups of guar gum→crosslinking
6. OH groups of water→hydrolysis

As shown in Table 3, the findings about the influence of the solid content and the binding of bifunctional dyes also hold for a large number of other reactive dyes.

The stiffness values of high viscosity carboxymethylised guar gum are much lower than those of low viscosity thickeners, which makes this kind of guar gum much more appropriate for reactive printing. Reactive dyes with two centres may increase fabric stiffness in reactive printing. In general, no drastic crosslinking reactions were established with reactive dyes of the vinylsulphone type because they have only one reactive centre. Triazine and dichloro-quinoxaline reactive dyes form crosslinking with the reaction of nucleophilic substitution, whereas vinylsulphone dyes bind by means of addition reaction without any accompanying side-reactions [10]. This explains why vinylsulphone dyes are usable for reactive printing with guar gum.

Table 3
Fabric stiffness (in the warp direction) with reactive dyes and CMGN and CMGH

Dye—C.I.	Reactive	Fabric stiffness (mN cm^2)	
		CMGN	CMGH
C.I. Reactive Blue 5	MCT	0.89	0.92
C.I. Reactive Brown 2	MCT	0.85	0.84
C.I. Reactive Black 1	MCT	0.99	3.9
C.I. Reactive Green 15	MCT	6.16	1.26
C.I. Reactive Orange 4	DCT	2.53	0.7
C.I. Reactive Red 6	DCT	0.88	0.88
C.I. Reactive Yellow 81	DCT	15.85	3.9
C.I. Reactive Red 123	DCT	2.9	2.15
C.I. Reactive Red 11	DCT	1.5	1.06
C.I. Reactive Blue 68	DCCX	14.75	5.15
C.I. Reactive Blue 170	DCCX	16.2	5.3
C.I. Reactive Blue 116	DCCX	13.1	4.1
C.I. Reactive Blue 23	DCCX	10.46	4.6
C.I. Reactive Violet 29	DCCX	3.05	2.8
C.I. Reactive Red 41	DCCX	5.98	3.3
C.I. Reactive Red 22	VS	0.88	0.88
C.I. Reactive Red 198[a]	VS	1.53	0.89
C.I. Reactive Blue 21[a]	VS	10.78	3.45
C.I. Reactive Black 5[a]	VS	3.02	0.97
C.I. Reactive Black 31	VS	1.91	1.01
Viscose		0.88	0.88

[a] Reactive dyes with two reactive centres.

3.3. *The influence of dye concentration on fabric stiffness*

It is evident from the obtained results that the chemical bond between the dye, the fibre and the thickener is affected not only by the number of free hydroxyl groups, but also by the concentration of the dye, which is reflected in fabric stiffness. In Table 4 the impact of dye concentration on the fabric stiffness of viscose printed with C.I. Reactive Red 120 and C.I. Reactive Blue 19 is given. The influence of the thickener was additionally determined by fabric stiffness measurements of washed viscose printed with the thickener only.

As expected, the values of fabric stiffness decrease with dye concentration. This tendency is much stronger with C.I. Reactive Red 120 than with the vinylsulphone dye C.I. Reactive Blue 19. The explanation is in the bifunctional character of the first dye which allows chemical reaction with the free hydroxyl groups of viscose and of guar gum. It is evident from the results that dyes with several reaction centres create substantial fabric stiffness with low substitution guar gum, thus

Table 4
Influence of dye concentration on fabric stiffness with CMGN (heavy weight fabric)

Dye	Amount of dye (%)	Fabric stiffness ($mN\ cm^2$)	
		Warp	Weft
C.I. Reactive Red 120	1.5	15.43	12.85
	0.75	12.96	11.87
	0.25	8.12	5.41
C.I. Reactive Blue 19	1.5	2.90	1.99
	0.75	2.56	1.72
	0.25	2.21	1.63
Viscose		1.24	0.36

confirming the formation of a bridge between the thickener and the cellulose material.

3.4. *The influence of textile auxiliaries*

Commercial and synthesised dyes (without auxiliaries) were used to determine the influence of auxiliaries on fabric stiffness. Further investigations of printed and dyed fabric have shown that textile auxiliaries have a minor influence on fabric stiffness and that fabric stiffness depends on the crosslinking of the bifunctional dye with guar on the textile.

It is evident from Fig. 7 that the pure thickener washes off very well, and that no resulting fabric stiffness is observed. The same holds for the dyeing with C.I. Reactive Red 120. Thus, it is apparent that pure components alone (the thickener and the dye) do not cause fabric stiffness, but a mixture of these components does, which is attributed to the crosslinking of the thickener and the reactive dye in the mixture. If we compare the use of the commercial and the synthesised dye, the minor role of auxiliaries becomes evident.

3.5. *Proving guar gum crosslinking with thin-layer chromatography*

Thin-layer chromatography was used to confirm the reaction products of the crosslinking of the reactive dye C.I. Reactive Red 120 with the thickener CMGN. The printing paste with and without the addition of $NaHCO_3$ was printed on the carrying material (aluminium foil), to be subsequently dried and steamed with saturated steam for 15 min. The fixed material was removed from the foil by scraping and applied on the TLC alufoil in the form of a water solution. TLC was then carried out in the mobile system. For comparison, a commercial dye and the non-fixed printing paste with $NaHCO_3$ were additionally applied on TLC foils to be analysed. The results of this experiment are given in Table 5, where the retention factor (Rf) represents the ratio adsorbate/solvent and characterises the individual substances in the used mobile system.

It is clear from Table 5 that the Rf values of the dye differ depending on the addition of $NaHCO_3$

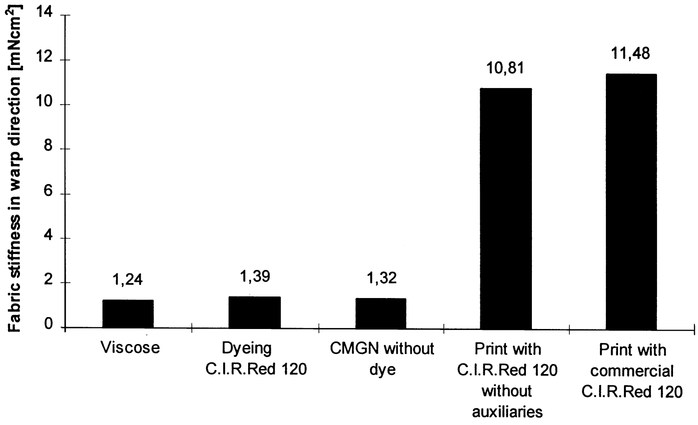


Fig. 7. The influence of textile auxiliaries and the printing paste on fabric stiffness (prints on viscose-mousseline quality).

Table 5
Crosslinking products obtained with thin-layer chromatography (C.I.Reactive Red 120/CMGN)

No.	Media and conditions	Rf values
1	Dye in water	0.35
2	Non-fixed printing paste	0.33
3	Fixed printing paste with $NaHCO_3$	0.28
4	Fixed printing paste without $NaHCO_3$	0.34

and heat treatment. The highest mobility is observed with the pure dye, with an Rf value of 0.35. If the printing pastes with and without $NaHCO_3$ are compared, it can be seen that the Rf value of the printing paste without $NaHCO_3$ is higher. It may be concluded that the molecular change of the dye takes place only in alkaline medium and will be amplified at higher temperature. Mobility may decrease due to hydrolysis or increased molecular size of the reactive dye. We may conclude from the lowest Rf value of the fixed printing paste (0.28) that a chemical reaction takes place between guar gum and bifunctional dye, which increases the size of the molecule and causes poorer mobility of the dye-guar gum product. The results of TLC clearly show that bifunctional dyes enable guar gum fixation on viscose, which will result in fabric stiffness. Further analysis using SEC (size-exclusion chromatography) will possibly identify the molecular reactions in more detail.

4. Conclusion

Due to its printing and technological properties, guar gum is very attractive for reactive printing. It has been proved, on the basis of high and low viscosity guar gum of different substitution levels, that fabric stiffness strongly depends on the solid content. While high viscosity guar gum is suitable for nearly all reactive dyes, it is imperative to increase the substitution level of guar gum with increasing solid content. The behaviour of mono-functional reactive dyes is more favourable than the behaviour of dyes with more reaction centres. High molecular guar gum can be used for printing with most reactive dyes, whereas low molecular thickeners are suitable only for mono-functional reactive dyes. It may be concluded that guar gum has very promising prospects in reactive printing.

Acknowledgements

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