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Guar Gum as an Environment-friendly Alternative Thickener in Printing with Reactive Dyes

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ABSTRACT

The future development of new products and technologies will be marked with respect to a clean and unpolluted environment. The principal critical effects of reactive printing on the environment are the coloration of wastewater and pollution with thickeners and urea. The development of new dyes with a better fixing capability demands new, less hazardous and more environment friendly thickeners. In our research the rheological and the technological behaviour of different guar thickeners was studied during the printing process and compared with the behaviour of other available printing pastes. It has been established from the analysis of waste waters that the guar thickeners are less harmful to the environment and quite as good as alginates in terms of printing quality. © 1998 Elsevier Science Ltd. All rights reserved

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1 INTRODUCTION

Textile printing effects a very high wastewater pollution in the textile industry since all of the unfixed components of the printing paste are washed off the fabric into wastewater. At present, sodium alginates are the most widely

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used thickeners in reactive printing, simply because their chemical structure causes no chemical reaction with reactive dyes. They also wash out easily and cause no fabric stiffness. Pure alginates tend to decompose biologically very easily, so they need to be stabilised with 0.1—0.3% preservatives, which causes environmental and technological problems. In practice, the use of alginate thickeners with low solid contents is very limited, and so is the possibility to lower COD values in wastewaters. Also, complex forming agents must be added to high molecular alginate thickeners in order to prevent the reaction with multivalent cations (gelating), thus causing an additional source of harm to the environment [1].

These are the problems underlying the research of alternative thickeners in reactive dye printing. Modified natural thickeners or synthetic thickeners can be used as an alternative, but the less expensive substituted guar which yields sharp prints has been considered to be more suitable [2]. An important advantage of guar thickeners is that no additions of preservatives are needed to improve the stability of the thickener [3].

In our research, the rheological, technological, colorimetric and ecological parameters of thickeners have been studied and compared with alginate thickeners, using the most favourable reactive dyes for guar gum [3, 4].

2 EXPERIMENTAL

2.1 Substrate

The thickeners used were sodium alginate, non-substituted guar gum and carboxymethylized guar gum (Fig. 1). Sodium alginates are polymers with (1,4) linked β-D mannuronic acid and α-L-guluronic acid units [5]. 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 the (1–6)-α-glycoside bonds [6–8]. The etherification of free hydroxyl groups with the monochloroacetic acid prevents the chemical reaction between guar gum and the reactive dye.

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

Sodium alginate used in these studies was from Sigma Chemical Co., USA, and the substituted guar gum with DS = 1.1 was produced by Chemische Fabrik Grünau GmbH Illertissen (Germany). The non-substituted and the substituted guar gum DS = 0.18 are products of the company CHT R. Beitlich GmbH in Tübingen (Germany). Printing pastes were prepared using a 1.5% concentration of the monofunctional vinylsulfone reactive dye C.I. Reactive Blue 220.

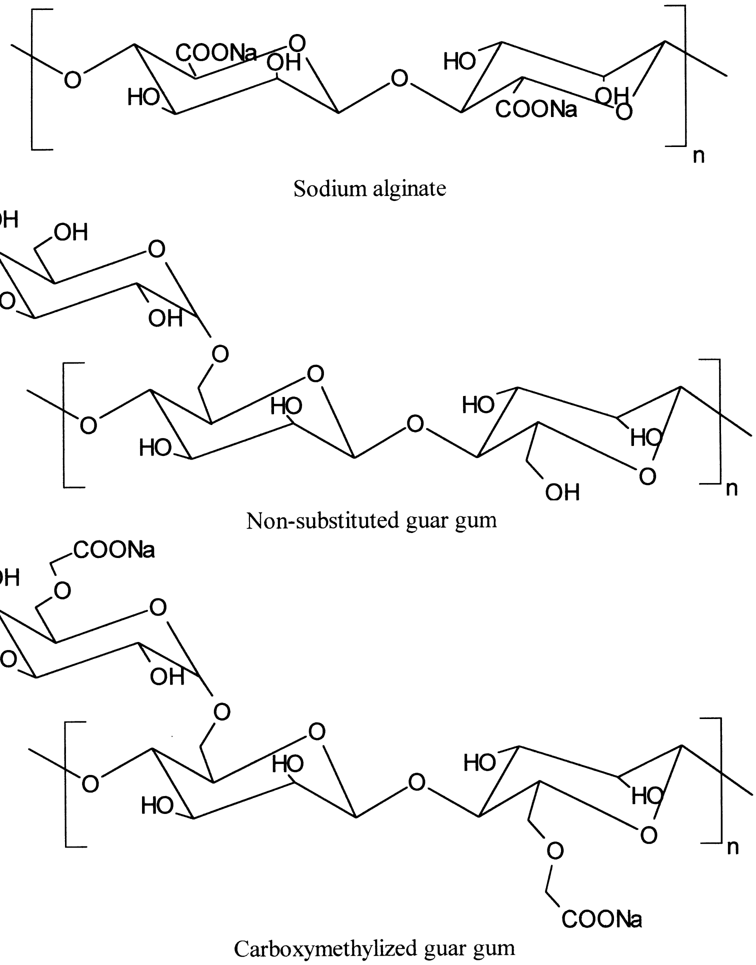

Fig. 1. The structure of thickeners.

TABLE 1
The Thickeners Used

Thickener	*Substitution level*	*Abbreviation*	*Amount of thickener ($g\ kg^{-1}$ 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

2.2 Preparation of the printing paste and the printing process

The thickener and the added demineralized 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% $NaHCO_3$ were added to each thickener and stirred for another 15 min. At the shear rate of $\dot{\gamma} = 10\,s^{-1}$ all printing pastes were calibrated to the constant viscosity of $\eta = 7140 \pm 400$ mPa s.

The flat screen printing technique was applied on viscose fabric for lighter garments (111.5 g m^{-2}) with a squeegee diameter of 15 mm and a printing speed of 5m min^{-1} at the pressure grade 3. The printed samples were dried for 5 min at 40°C and fixed for 15 min in saturated steam. Then the samples were washed five times for 15 min at 95°C in demineralized water, dried in the air and ironed.

2.3 Methods

The viscometer Rheometrics Fluids Spectrometer RFS II (Rheometrics) with a cone-plate measuring system was used to perform the rheological measurements. The dynamic viscosity was determined by rotary measurements, and viscoelasticity by the oscillatory shear test in the linear viscoelastic range.

Dye penetration and the depth of colour were determined by remission measurements using the colorimetric apparatus Texflach DC 3881 (Datacolor). Dye concentrations in washing baths were determined by extinction measurements with a UV/VIS spectrometer Lambda 2 (Perkin–Elmer). COD measurements were performed on the single-beam photometer Universal Photometer MPM 2010/300, (WTW) based on DIN 3809. BOD values were measured according to the standard dilute method (DIN Norm 38412) on the high performance oxygen measuring system OXI 200, (WTW). TOC values were determined in the liqui TOC Analysator (Heraeus) according to the combustion method DIN 38409 TI 3. Colour fastness to washing, as well as colour fastness to perspiration and pressing were determined according to DIN 54010. In addition, colour fastness to dry and wet rubbing was determined with respect to DIN 54021. Colour fastness was determined colorimetrically or according to the grey scale (DIN 54002).

3 RESULTS AND DISCUSSION

3.1 Rheological properties of thickeners

The shear sensitivity of printing pastes prepared from different thickeners varies depending on the solid content. In Fig. 2 the viscosity curves of the used thickeners are shown.

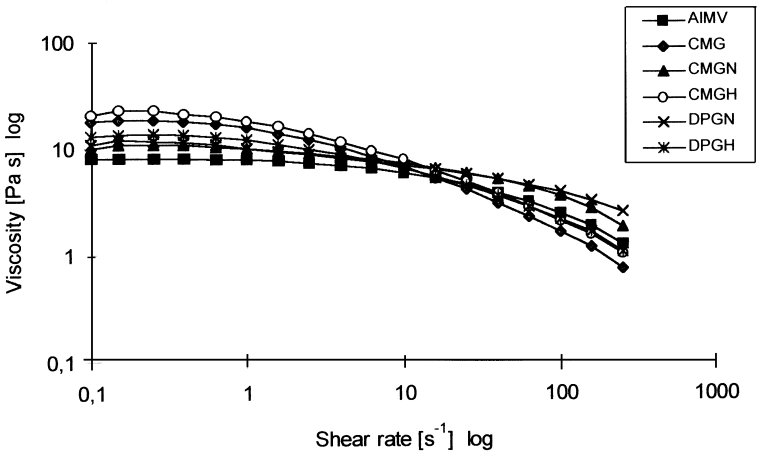

Fig. 2. The influence of the thickener on the viscosity curves of printing pastes with the reactive dye C.I. Reactive Blue 220.

In the first Newtonian range, the high viscosity guar thickeners CMG, CMGH and DPGH show a strong decrease of viscosity under the influence of the increasing shear rate in comparison with thickeners with a high solid content and with alginate thickeners. In contrast, the low viscosity guar thickeners (CMGN, DPGN) and the alginate thickener (AIMV) have a Newtonian character, which is evident from their constant viscosity. The transition from the first Newtonian range into the range of shear sensitivity depends on the thickener's solid content. In the case of low viscosity thickeners, the transition takes place at higher shear rates than it does in the case of high viscosity thickeners.

The solid content also affects the viscoelastic properties of the printing pastes (Fig. 3). The loss factor (tan δ) of high viscosity shear-sensitive thickeners (CMG, CMGH, DPGH) is lower in the entire frequency range than it is in case of all other discussed thickeners. This is the result of higher elasticity caused by the higher molecular mass of the polymers.

Irrespective of the thickener used, the loss factor (tan δ) decreases with increasing angular frequency, which means that elasticity is increasing. Consequently this thickener shows the lowest elasticity at high shear rates.

It is evident from the results of the rheological measurements that the low viscosity DPGN and CMGN guar gum are suitable alternatives to the alginate thickener.

3.2 Determining penetration and the depth of colour

Viscoelasticity and the solid content have a strong influence on penetration and on the depth of colour.

As seen in Fig. 4, the penetration of thickeners with a low solid content (CMG, CMGH and DPGH) into the fabric is much weaker than that of thickeners with a high solid content.

The reason for the weaker penetration of these systems is the result of the smaller paste transfer and the higher elasticity. In the case of thickeners with a low solid content, the penetration of the printing paste is less important than the separation from water and dye from the paste into the capillaries on the surface of the fabric. The reduction of paste transfer will have only little

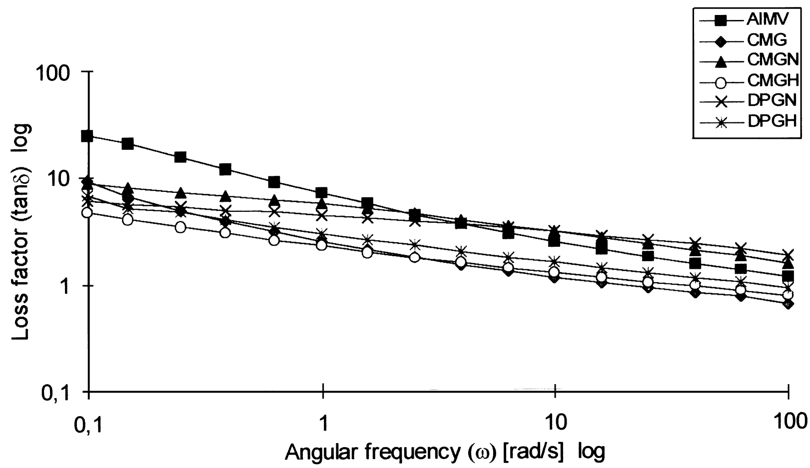

Fig. 3. The influence of the thickener on the loss factor (tan δ) in relation to the angular frequency of the used printing paste with the C.I. Reactive Blue 220.

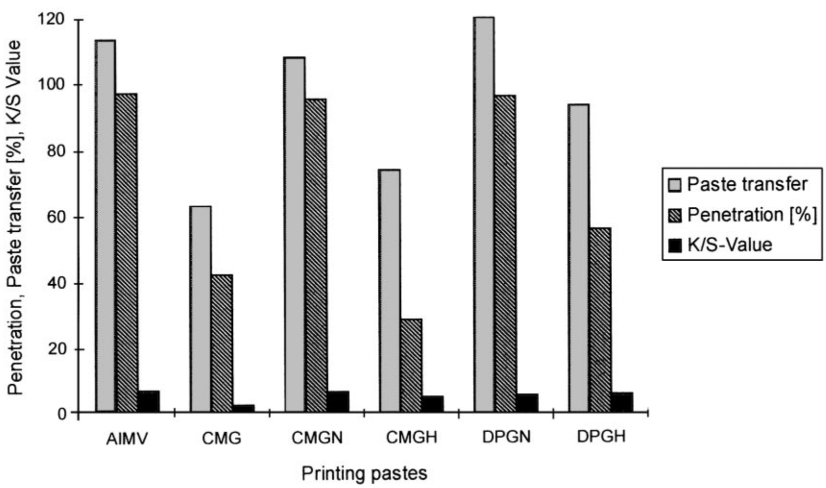

Fig. 4. The relations between penetration, paste transfer and K/S values.

effect on the depth of colour when the printing paste is mainly deposited on the surface of the fabric. Thickeners with a high solid content (AIMV, CMGN, DPGN) yield good penetration, which is caused by the non-elastic behaviour of the printing paste (high loss factor, tan δ). Due to the low elasticity and the high solid content of alginates and guar gum, a high paste transfer is obtained, resulting in high depth of hue and penetration.

3.3 Determining the dye concentration in washing baths

After washing, the thickeners, the textile auxiliaries and the unfixed dyes are rinsed directly into wastewater. In Fig. 5 the rinsed quantity of the dye is given depending on the type of thickener and the number of washing baths.

Irrespective of the thickener, the majority of the hydrolysed dye is washed out in the first washing bath. The absolute values depend on the deposit of the printing paste, the solid content and on the substitution level. A significant difference is noted between systems like CMGN, DPGN and the alginate, although they have equal deposits of the printing paste. The reactivity of unsubstituted guar gum DPGN with reactive dyes is greater. This accompanying reaction causes weaker dye fixation and, at the same time, a higher hydrolysis of the dye in the wastewater.

A much better dye fixation is obtained with the low substituted guar CMGN than with the alginate. Results comparable with the alginate thickener are obtained with low solid content thickeners, which is due to the lower deposit of the printing paste and the weaker influence of the diffusion and migration of the dye in combination with the low solid content. The smallest amount of hydrolysed dye in the wastewater is explained by the smallest dye deposit and the CMG thickener. In comparison with the alginate, the studied

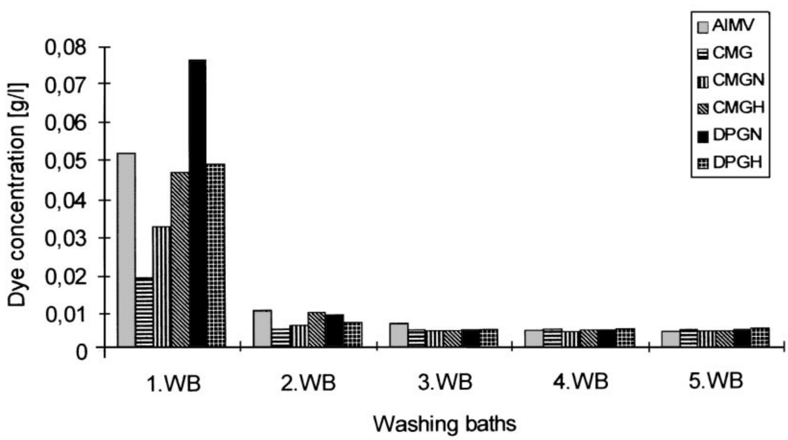

Fig. 5. Dye concentration of C.I. Reactive Blue 220 in washing baths.

guar gum has a low hydrolysis of the dye in waste water. An exception to this is unsubstituted guar gum with a high solid content.

3.4 Ecological analysis of washing baths

The ecological parameters BOD5, COD and TOC were used to characterise the organic substances in the washing baths [9]; these are shown in Table 2.

It is clear from Table 2 that the major part of the hydrolysed dye, auxiliary agents and thickeners are removed in the first washing bath. This, of course, is the reason for the high COD values of the wash baths. TOC and COD values of high viscosity thickeners are lower than those of low viscosity thickeners, which is due to the low solid content. Printing with low viscosity thickeners produces bigger deposits of polymers on the fabric, so higher numerical values are obtained as a result of washing. High COD values at a low COD/BOD_5 ratio present no problem, since the biological decomposition of COD in mechanical–biological waste water treatment plants gets easier with the ratio approaching 1 [10]. As we can see in Table 2, the results obtained with unsubstituted guar gum are comparable with those obtained with alginate, while the COD/BOD_5 ratio values are even more favourable. Thus the ratio value 2.45 of unsubstituted guar DPHG with a low solid content is very low. The quotient of the printing paste CMGH is 8.77, although the thickener is only low substituted. According to the expertises of the producer, this carboxylmethylized guar gum contains a considerable amount of preservatives, which explains the high value of the quotient and the harmful effect it represents for the environment. The same applies to the CMGN printing paste with a high solid content.

Although guar gum with a high solid content, closely approaching the alginate thickener, produces high COD and TOC values in wastewater, it is

TABLE 2
The Values of Ecological Parameters of Different Washing Baths

Ecological parameters	*Washing baths*	*AlMV*	*CMG*	*CMGN*	*CMGH*	*DPGN*	*DPGH*
COD (mg O_2 litre^{-1})	1	560.00	550.00	1283.3	600.00	1540.0	635.00
	2	65.00	106.00	93.00	67.00	210.00	146.50
	3	51.00	89.00	49.67	47.00	94.00	88.50
BOD_5 (mg O_2 litre^{-1})	1	124.72	135.22	160.24	68.43	372.16	259.60
	2	45.79	15.63	28.29	53.64	51.44	37.87
	3	44.83	13.20	14.34	49.53	21.84	10.69
TOC (mg C litre^{-1})	1	182.70	172.00	439.57	173.60	456.30	200.90
	2	10.45	14.22	16.98	12.08	51.96	22.13
	3	4.78	5.31	5.24	5.41	9.88	6.75
COD/BOD_5	1	4.49	4.07	8.01	8.77	4.14	2.45

nevertheless easily biologically decomposed, which is a very interesting property for reactive printing.

3.5 The determination of colour fastness

One of the most interesting criteria for quality printing in terms of serviceability is colour fastness, which is also a measure of the stability of the dye-fibre system. The results of relevant tests are presented in Tables 3–6

TABLE 3
Colour Fastness to Washing at 60°C

Sample	*Change in colour of sample*	*Change in colour of adjected material*	
		Viscose	*Wool*
AlMV	3–4	5	5
CMG	3-4	5	4-5
CMGN	3–4	5	5
CMGH	4	5	5
DPGN	3-4	5	4–5
DPGH	3	5	5

TABLE 4
Colour Fastness to Perspiration

Sample	*Change in colour of sample*	*Change in colour of adjected material*	
		Viscose	*Wool*
AlMV	3–4	5	5
CMG	3–4	5	5
CMGN	3–4	5	5
CMGH	4–5	5	5
DPGN	3–4	5	5
DPGH	3–4	5	5

TABLE 5
Colour Fastness to Pressing

Sample	*Dry pressing*	*Damp pressing*		*Wet pressing*	
		Change in colour of sample	*Change in colour of cotton*	*Change in colour of sample*	*Change in colour of cotton*
AIMV	5	5	5	4	5
CMG	5	4–5	5	4–5	5
CMGN	5	5	5	4–5	5
CMGH	4–5	4–5	5	4–5	5
DPGN	4–5	4	5	4–5	5
DPGH	4–5	4–5	5	4–5	5

TABLE 6
Colour Fastness to Rubbing

Sample	*Colour fastness to rubbing*	
	Dry	*Wet*
AlMV	5	3–4
CMG	5	4
CMGN	5	3–4
CMGH	5	4
DPGN	5	3–4
DPGH	5	3–4

It is evident from the results of the testing of colour fastness to washing (at 60°C), perspiration, pressing and rubbing that the colour fastness using guar gum compares to the colour fastness using alginates, and that no decrease of quality is observed.

4 CONCLUSION

The rheological measurements have shown that the viscosity and the elasticity of thickeners depend on the solid content. Viscosity properties prevail in alginates and guar gum with a high solid content, and elasticity prevails in guar gum with a low solid content. Due to the dominating viscous character, thickeners with a high solid content yield better penetration and depth of colour than thickeners with a low solid content. Non-substituted guar gum and high molecular systems cause less wastewater coloration than the applied alginate. The measurements of COD, BOD_5 and TOC indicate that guar gum is a well decomposable thickener with almost more favourable values than alginate. The ecological suitability improves with decreasing solid content, which correlates with the lowered organic pollution (TOC) of wastewaters. The colour fastness to washing, ironing, rubbing and perspiration is very good with all used thickeners and does not deviate from the values of alginate thickeners. Considering the presented favourable results, it may be concluded that the use of carboxymethylized guar thickeners in reactive printing is very promising.

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