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Good quality printing with reactive dyes using guar gum and biodegradable additives

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Abstract

In printing with reactive dyes sodium alginates or synthetic thickeners are typically used as thickening agents to prevent unacceptable fabric handle. A new reactive printing process for reactive dyes on cellulosic textiles has been developed using natural thickening agents and environmental-friendly additives. Printing trials with guar gums have shown that the use of different additives can prevent fabric stiffness. These additives have no significant influence on rheology and colour strength but contributed to soft fabric handle even when guar gums were used as thickening agent. The use of additives and guar gum provide good quality prints with reduced wastewater pollution.

Keywords: Textile printing; Guar gum; Additive; Fabric handle; Printing quality; Ecology

1. Introduction

In textile printing with reactive dyes sodium alginates or mixtures with carboxymethylated polysaccharides are usually used as thickening agent, but in some cases (using viscose and bifunctional reactive dyes) reaction occurs between the dyes and thickening agents resulting in unacceptable fabric handle. To prevent this, it is necessary to use synthetic thickeners (polyacrylic acids, polymaleic acids), which do not react with reactive dyes. However the uses of these polymers present two problems: the outline sharpness is poor and the synthetic thickener is not biodegradable, leading to persistence in the effluent. The use of biodegradable thickeners would lead to an environmental-friendly printing process with reduced wastewater pollution. Printing trials with natural thickeners have shown that different additives can prevent fabric stiffness [1,2], but it is unknown as to the type of chemical structure that will be successful. The aim of this research is the development of environmental-friendly additives for use in the printing with reactive dyes with non-persistent thickeners in order to enable good quality printing and to minimize water pollution.

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2. Experimental [1,2]

2.1. Materials

The thickeners used were sodium alginate and non-substituted as well as carboxymethylized guar gum (Table 1). Sodium alginate was obtained from Lamberti SPA, Lutexal (polyacrylic acids) from BASF and the guar gums used were produced by Cognis Deutschland GmbH.

The dye used was the vinylsulphone dye C.I. Reactive Black 5 (Fig. 1).

A palet of more than 30 surfactants with different ethyleneoxide units, side chains, estergroups and chemical structure were provided by Cognis Deutschland as well as by Lamberti. All experiments were performed on woven viscose fabric textiles (warp: 59% viscose filament 133 f30, weft: 41% viscose yarn 20 tex, 111.5 g m^{-2}).

2.2. Preparation of the printing paste and the printing process

The thickener and demineralised water were well stirred in a mixer and left in a refrigerator overnight to attain full swelling. Blends were prepared by adequate mixing of the stock pastes. To prepare the printing paste, 50 g kg^{-1} dyestuff and 25 g kg^{-1} of $NaCHO_3$ as well as 150 g kg^{-1} urea and 50 g kg^{-1} additive were added to each thickener solution and stirred for another 15 min. At a shear rate of $\gamma = 8.2$ s^{-1} all printing pastes were adjusted to a viscosity in the range of $\eta = 5$–10 Pas. Flat screen printing using a Zimmer laboratory printing machine was used to apply the paste to the viscose fabric. A squeegee diameter of 15 mm and a printing speed of 5 m min^{-1} at a pressure of 6 were used. The printed samples were fixed with steam at 102 °C for 10 min and then washed five times for 15 min in boiling water to remove unfixed dyes and thickener.

Table 1
Substitution levels (DS) and the amounts of used thickeners

Thickener	DS	(g thickener/ kg printing paste)
Sodium alginate	0	32.55
Lutexal	–	76.5
Guar gum	0	56.7
Guar gum	0.4	44.0
Guar gum	1.1	52

2.3. Methods

The rheometer Rheolab MC 100 (Physica) with a MK 25 cone and plate system was used to perform rheological measurements. Dynamic viscosity was determined by rotary measurements and viscoelasticity using oscillatory shear test method in the linear viscoelastic range. Dye penetration and the colour strength were determined by reflectance measurements using a spectrophotometer Spectraflash SF 600+ (Datacolor). Dye penetration was calculated as the ratio of colour strength from right and left side of the printed sample. The stiffness of the washed and conditioned printed samples was measured using a bending rigidity apparatus (Frank) according to DIN 53212. Size-Exclusion-Chromatochraphy (SEC) was performed with HEMA-Bio gel. Biodegradability tests were carried out according to OECD Guidelines for the Testing of Chemicals using method 301D (closed bottle test) [3].

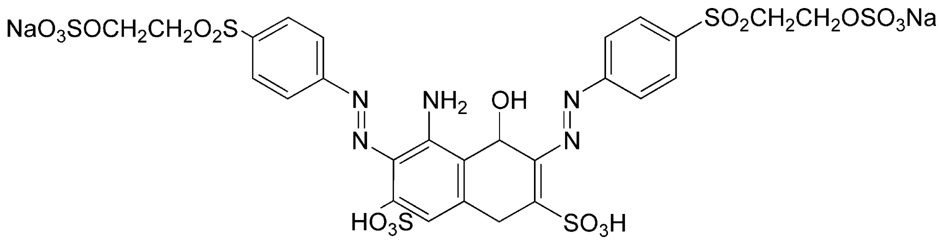

Fig. 1. Structure of dyestuff C.I. Reactive Black 5.

3. Results and discussion

3.1. Evaluation and assessment of additives

The screening started with the investigation of more than 30 surfactants with different ethylene-oxide units, side chains, estergroups and chemical structure. These additives were printed together with non-substituted guar gum and bifunctional reactive dyes in order to investigate their beneficial influence on soft fabric handle. Additives and dyestuffs were used in a concentration of 5% in a typical printing paste (recipe see Table 2) and efficiency of the additives were tested by using fabric stiffness measurements. The results obtained are summarized in Table 3 on the basis of fabric stiffness values.

On the basis of the screening data, reasonable additives have found to be ethoxylated stearyl- and oleylalcohols as well as some alkylpolyglycosides and some surfactants with amino-groups. The best products were polyoxyethylene stearylethers with 8-12EO, polyoxyethylene oleylether with 6EO as well as cocosamine with 2EO and alkylether-Na-carboxylate. The best concentration value for each additive was determined in extensive research [2] by variation of additive concentration. The optimum for most additives was at a concentration of around 5%. All of products improved fabric handle, but the results with unsubstituted guar gum were not as good as with pure alginate or polyacrylic acid. It was also obvious that many surfactants formed gels with guar gum, when the number of EO-units exceeded a value of 20. This can be attributed to strong interactions between the guar gum and the surfactant, which may arise by virtue of hydrophilic–hydrophilic interactions operating between the hydroxylgroups of guar gum and hydrophilic groups of the EO-units. These interactions and the presence of hydrophobic chains will change the hydrophilic–lipophilic-balance of the thickener, which may result in a more hydrophobic thickener or coagulation. Further tests have shown that the use of smaller quantities of such additives prevents gel formation and coagulation, but the additives do not prevent harsh fabric handle.

Printing trials without any additive and subsequent impregnation of the printed materials with a 5% aqueous solution of the additives revealed that these products act in the printing paste and, with the exception of cocosamine, do not function solely as softener.

Table 2
Printing paste recipe

Thickener (powder)	*X* g
Na_2CO_3	25 g
Urea	150 g
Dyestuff	50 g
Additive	50 g
H_2O	*Y* g
	1000 g

Table 3
Results of screening using Guar DS = 0

Name	Use of additive in printing paste: *K*/*S* (580 nm)	Use of additive in printing paste: Fabric handle
Without additive	27.4	–
Polyexyethylene-(4)-stearylether	19.96	0
Polyexyethylene-(8)-stearylether	20.5	+ +
Polyexyethylene-(10)-stearylether	19.23	+ +
Polyexyethylene-(12)-stearylether	19.5	+ +
Polyexyethylene-(20)-stearylether	5.4 (gel)	–
Polyexyethylene-(6)-oleylether	19.43	+ +
Polyexyethylene-(22)-oleylether	5.96	–
Polyoxyethylene-(2)-oleylamine	22.6	+
Polyoxyethylene-(20)-oleylamine	5.19 (gel)	–
Polyoxyethylene-(10)-oleylester	20.35	+
Polyoxyethylene-(13)-oleylester	21.37	+
Polyoxyethylene-(8)-stearylester	23.31	0
Polyoxyethylene-(100)-stearylester	22.7 (gel)	–
Polyoxyethylene-(14)-talloilfattyester	24.08	–
Polyoxyethylene-(6)-talloilfattyether	20.93	+
Alkylether-Na-carboxylate	20.4	+ +
Polyoxyethylene-(18)-cethylether	6.54	–
Polyoxyethylene-(11)-C16(branched)ether	22.92	–
Polyoxyethylene-(2)-cocosamine	22.24	+ +
Polyoxyethylene-(12)-cocosamine	19.4	–
Na-diisotridecylsulfosuccinate	19.83	+
Na-alkylpolyglycoside-sulfosuccinate	24.34	+
Na-alkylpolyglycosidecitrate	24.37	+
Na-alkylpolyglycosidetartrate	24.37	+

Abbreviations: –: gel or stiff fabrics, 0: no improvement, +: improvement, + +: significant improvement, soft fabric handle.

Interactions between dyes, guar gum and surfactant were characterized using Size-Exclusion-Chromatochraphy (SEC), as this method can also be used for determination of guar–dye reaction products (fabric stiffness is a result of such interactions). In analytical SEC-Chromatography, chemical crosslinking between thickener and dyestuff can be studied using RI- and UV-detectors. Colourless thickener can be identified by RI-detection. Dye-thickener intermediates can be identified as coloured species and detected using UV. The principle and some representative chromatograms are shown in Figs. 2 and 3.

The SEC investigations show that dyes-guar-intermediates (considering the peak area) were suppressed with increasing substitution level and in the presence of the most favourable additives. This can be attributed to a strong interaction between guar gum and surfactant, which may occur by hydrophilic–hydrophilic interactions operating between the hydroxylgroups of guar gum and the hydrophilic properties of the EO-units. These interactions and the presence of hydrophobic chains will change the hydrophilic–lipophilic-balance of the thickener resulting in a more hydrophobic thickener, which cannot be attacked by the reactive dye, because the reaction sites are blocked by the association with additive (Table 4).

Screening tests suggest that the kind of hydrophobic unit seems to be of little significance; the hydrophilic properties are of importance. Most reasonable additives are ethoxylated alkylalcohols as well as some alkylpolyglycosides and some surfactants with amino-groups. These additives could be applied with guar gums and result in improved fabric handle. A comprehensive study of the interactions that can occur between surfactants, guar gum and reactive dyes has been published [4].

3.2. Rheology of printing pastes

The influence of additives on paste rheology is shown in the case of non substituted guar gum and

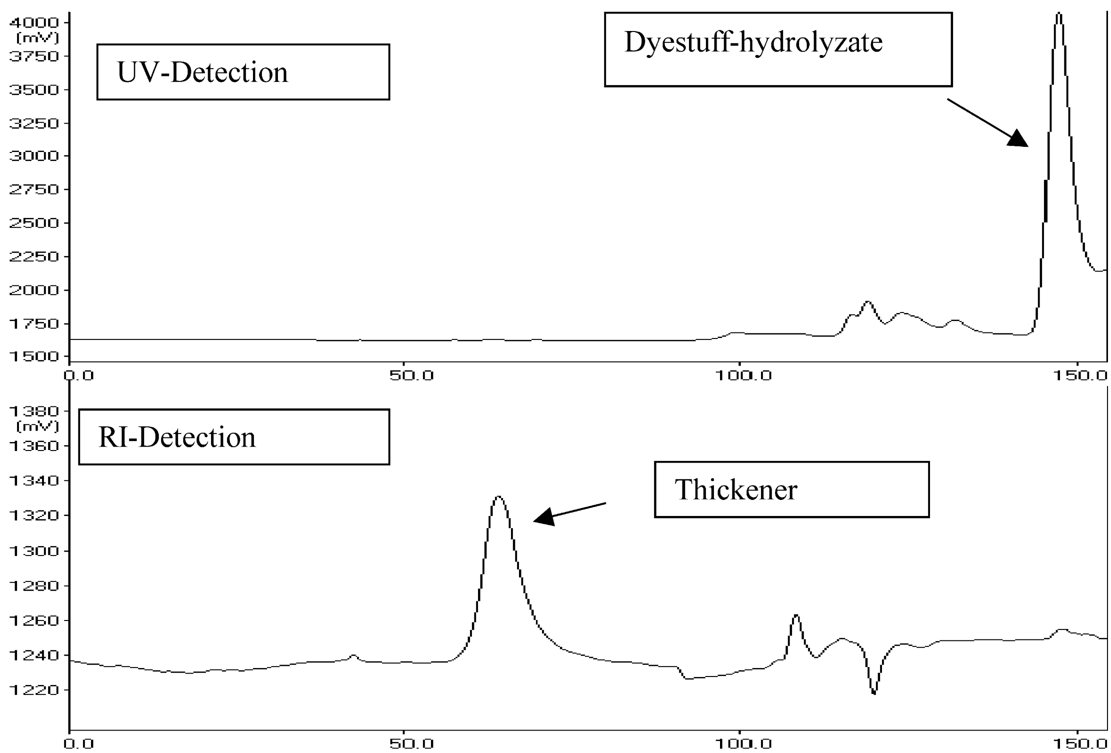

Fig. 2. SEC of guar gum/dyestuff hydrolyzate mixture.

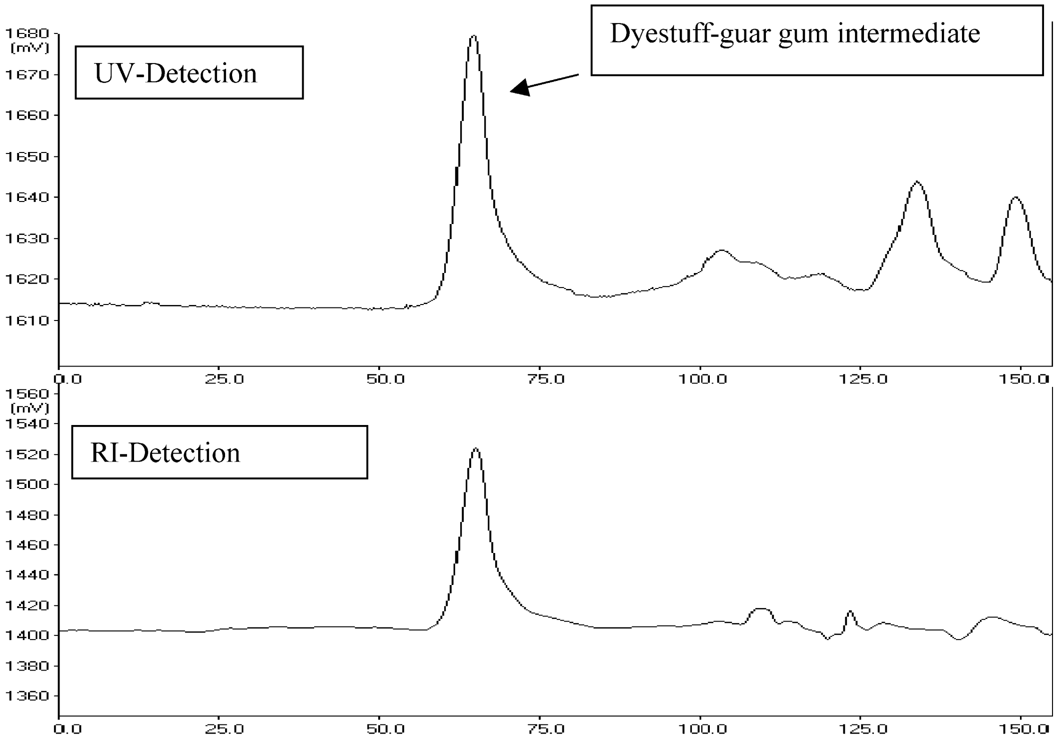

Fig. 3. SEC of guar gum–dyestuff intermediates.

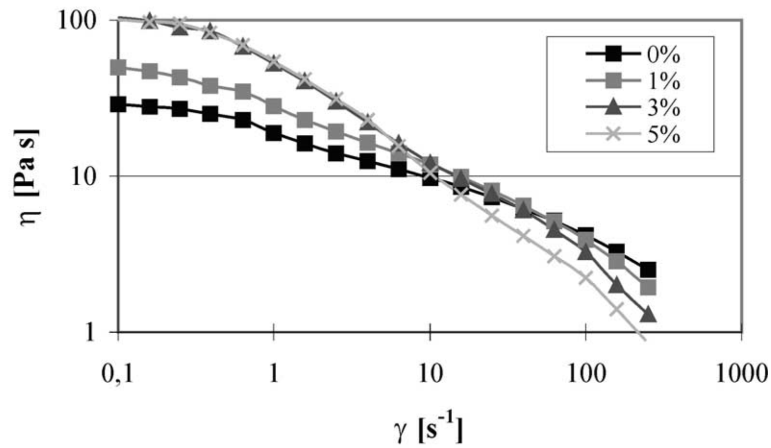

Fig. 4. Influence of additive Brij 76 on the rheology of printing paste.

Brij 76 [polyexyethylene-(10)-stearylether] as an example (Fig. 4).

The viscosity at lower shear rates increases markedly with increasing surfactant concentration. This is connected to increasing density of the primary polysaccharide cross-linking structure due to incorporation of associated surfactant molecules into the intermolecular structures, which are stable at low shear rates.

The pseudoplastic behaviour obtained for solutions at higher shear rates indicates that polysaccharide/surfactant complexes are more shear

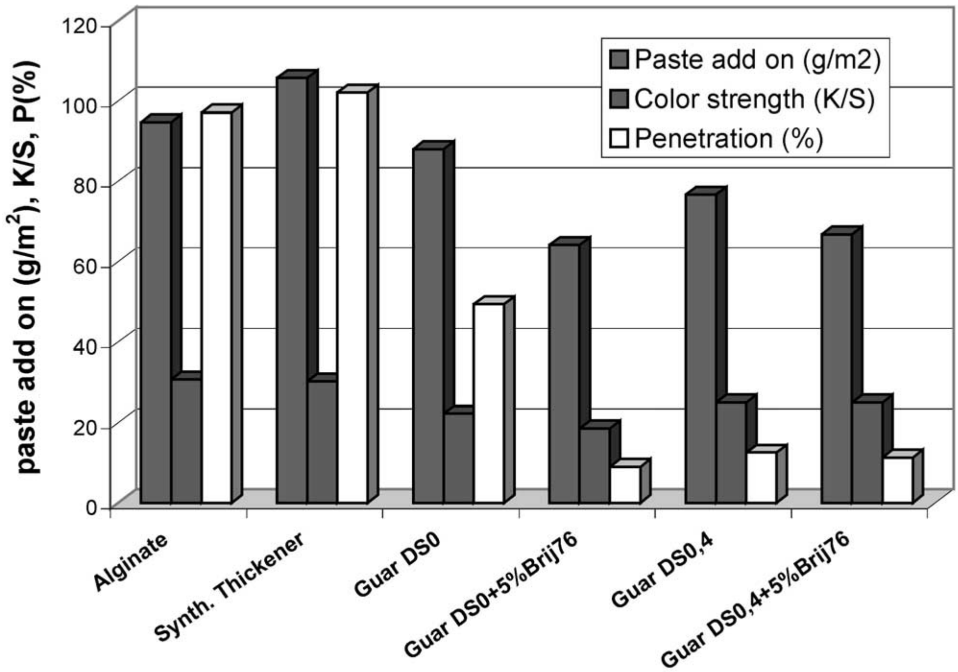

Fig. 5. Printing results with different thickeners and additive Brij76.

sensitive than are the guar gum clusters in pure solution. The marked reduction in the viscosity curves can be explained in terms of the exchange of hydrophilic polymer/polymer interactions by weaker polymer/surfactant interactions [5].

Application and testing of the additives have shown that the most promising additives can be used up to a concentration of 3% without any correction of paste recipe; however, the use of 5% additive can lower the apparent paste viscosity at shear rates $> 10\ s^{-1}$ significantly.

3.3. Printing results

A palet of different additives was used for printing trials with differently substituted guar gums. The printing properties of the printing pastes were characterized in terms of paste add on, colour strength and penetration.

The colour strength of the prints is related to the transfer rate of the paste on the material and the type of thickener. It is evident from Fig. 5 that the paste add-on and colour strength of the guar pastes was slightly lower compared to alginate and synthetic thickener. The use of additives caused a lower paste add-on and therefore effected a small reduction in colour strength but contributed to a soft fabric handle and satisfied printing quality. Furthermore, it was found that the degree of carboxymethylation could also have a significant influence on fabric handle. The higher the degree of carboxymethylation, the better was fabric handle.

Table 4
SEC-Analysis and fabric stiffness using different thickeners and additives

Thickener	Peak area of guar gum–dyestuff intermediate	Fabric stiffness (mN cm^2)
Alginate	100 000	2.0
Guar gum, DS = 0	6 400 000	17.0
Guar gum DS = 0 + 5% of the best additive	1 650 000	2.9
Guar gum, DS = 0.4	5 300 000	10.7
Guar gum, DS = 1.1	3 100 000	3.9

The fabric handle achieved using guar gum DS = 0.4 or DS = 1.1 and 5% of the best additive [i.e. polyexyethylene-(10)-stearylether] was comparable to that of prints obtained with pure alginate or synthetic thickener.

The very best printing results and a very soft fabric handle were obtained when alginate, together with the most reasonable additive at a concentration of up to 1% was used. Guar gum can also be used, but the use of non-substituted guar gum together with up to 5% additive will not give the required softness. Mixtures [2] of alginates with guar gum (up to 70% guar gum) and substituted guar gums were more favourable and gave very soft fabric handle at an additive concentration of 3%. All applications proved to be suitable and with outstanding good performance as far as fabric handle is concerned when printing trials are performed with the two-phase method in combination with the described additives. Results obtained were confirmed using printing trials in pilot plants and bulk production [2].

3.4. Biodegradation

An environmental-friendly printing process demands biodegradable printing pastes since textile auxiliaries will be washed out after printing and fixation. A comprehensive study on biodegradation was performed for both the newly developed printing pastes and the standard printing pastes. Table 5 shows the biodegradation values of these pastes (paste recipe of Table 2 at a concentration of 1 g l^{-1}).

The biodegradation tests of the printing pastes and wastewater investigations have shown that the printing pastes made of guar gums and additives are more favourable than pastes made of alginate or synthetic thickeners, even at an additive concentration of 5%. This means that the use of guar pastes and additives can lead to a significant wastewater depollution.

Table 5
Biodegradation analysis of printing pastes (1 g l^{-1})

Sample	DS	COD (mg O_2 l^{-1})	BOD_5 (mg O_2 l^{-1})	BOD_5/COD (× 100%)
Alginate	0	83	5	6.0
Lutexal	–	140	4	2.8
Guar gum	0	270	60	22.2
Guar gum	0.4	251	63	25.1
Guar gum	1.1	230	62	27.0

4. Conclusions

A new reactive printing process for reactive dyes on cellulosic textiles has been developed using natural thickening agents and environmental-friendly additives. The additives increased slightly the pseudoplastic behaviour of the pastes but imported no significant decrease in colour strength. The use of these additives contributed to soft fabric handle even when guar gums were used as thickening agent. Moreover, the use of biodegradable thickeners and additives will lead to reduced wastewater pollution compared to the use of synthetic thickeners.

These results show the possibility of marketing a new class of thickener for textile printing intended for use with reactive dyes. The mixture of polysaccharides with ethoxylated surfactants can present the customer with advantages in terms of environmental compatibility, provided that soft "hand" of the final article is achieved. A patent has been sought for the printing process [6].

Acknowledgements

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