Mixture Printing Pastes from High Substitued Guar Gum and Alginates on Reactive Printing of Viscose

E. Perrin Akçakoca Kumbasar

Department of Textile Engineering, Ege University, Izmir, Turkey

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ABSTRACT: The rheology of binary mixtures of two alginates and one carboxymethyl guar has been measured. Two reactive dyes were printed from pastes based on mixtures. The printing and the final print (color yield, levelness, and fabric stiffness) were assessed. Most of the mixtures reacted in accordance with the dye, and interacted especially with one of the dyes for which CMG was used. However, it is seen that mixture of CMG with alginates can be used in reactive printing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 745–751, 2007

Key words: biopolymers; viscosity; dyes; printing; rheology

INTRODUCTION

Textile printing is an important method for coloration of textile fabrics. The coloration is achieved either with dyes or pigments in a printing paste. Print paste rheology is a key word for printing quality. It affects color, sharpness of mark, levelness, hand, and color yield.

Cellulose fibers form the most commonly printed substrate, and reactive dyes are the most commonly used dyes in textile printing. The consumption of reactive dyes continues to increase, since they produce brilliant shades with very good fastness. Sodium alginate, a derivative of seaweed, is widely used for reactive dye printing. Although sodium alginate contains hydroxyl groups, the reaction between alginate and dye is limited by mutual anion repulsion of the alginate's carboxyl groups and the dye's sulfonic acid groups. The repulsion additionally promotes migration of dye from the thickener into the fabric during steaming.[1] Alginates are also washed out easily and cause no fabric stiffness.

The relatively high cost, limited supply of alginates, has spurred efforts to find alternatives. Synthetic thickeners can be used as an alternative,[2] but in spite of the potential advantages, the use of synthetic thickeners in reactive dye printing has been limited. It is suggested that the synthetic thickeners are very sensitive to electrolytes in the dye and to other chemicals in the paste, so it is difficult to control the viscosities of print pastes.

The less expensive substituted guar can be used as an alternative in reactive printing. The gum obtained from the guar plant is a natural hydrocolloid and is described chemically as a galactomannan. The macromolecular backbone forms a long chain, consisting of galactan and mannan units combined throughout glycoside linkages. Unmodified guar gum has a large number of hydroxyl groups, so it can react with reactive dyes. It was reported that the combination of low substituted guar gums with bifunctional reactive dyes causes fabric stiffness, though printing of most monofunctional vinylsulphone reactive dyes with guar gums results in good printing quality and fabric handle. Fabric stiffness increases with guar gum thickener composed of high solid content, which decreases with an increase in the degree of carboxymethylation of the thickener.[3,4]

The use of mixed thickeners is not new. Indeed, the mixture of starch and gum tragacanth was widely used when natural thickeners were the norm. In the era before the development of reactive dyes, Zonnenberg[5] described the properties and viscosities of mixtures of starch, its derivatives and natural gums. Many of these mixtures showed viscosities either significantly higher or drastically lower than the individual components. Notwithstanding the wide use of starch and gum tragacanth mixtures, he concluded that mixed thickeners were probably best avoided. In the time since, printers have ignored this advice, most notably with the use of ''half emulsions'' for pigment printing containing both an oil-in-water emulsion and alginate.

Recently, usage of binary mixtures of CMS (carboxymethyl starch), alginate, and synthetic thickener for printing reactive dyes has been examined.[6] Sostar et al.[7] studied printing properties of a high substituted

Correspondence to: E. P. Akçakoca Kumbasar (perrin.akcakoca@ege.edu.tr).

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guar gum and its mixture with alginate. However, results obtained from the previous studies[6,7] have shown that usage of mixture pastes in reactive printing is advantageous.

Today most of the researches are on ink-jet printing but still direct print coloration is widely used on the world. So the pressure to print reactive dyes economically with high quality has led to the commercial development of mixed thickeners in this application. However, the critical evaluation of researches suggests that such mixtures have not been examined in detail until yet. The aim of this study is to examine the rheology and printing properties of a series of reactive dye pastes based on binary mixtures of the two alginates and the guar gum and to determine whether such mixing is able to overcome disadvantages, while especially not losing the advantages for which alginates are known.

EXPERIMENTAL

Materials

All experiments were performed with woven viscose fabric (warp: 29 threats/cm, weft: 26 threats/cm, fabric weight 114 g m^{-2}).

The thickeners used were low viscosity and high viscosity sodium alginates, and the substituted guar gum. The sodium alginates used in this study were obtained from CHT-Tubingen Germany and the substituted guar gum with DS = 1.5 was produced by Meyhall AG.

The dyes used were MCT dye Levafix Rot PN-FB (C.I. Reactive Red 187, with small molecule, 736.16 g/mol) and Levafix Turquoise PN-G (C.I. Reactive Blue 21, with big molecule, 1214.23 g/mol).

Preparation of the stock paste and printing pastes

Following initial trials, stock paste concentrations of 140 g/kg for the carboxymethyl guar gum, 40 g/kg for the high viscosity alginate and 85 g/kg for the low viscosity alginate were determined to be suitable. Stock pastes of each thickener were prepared as shown in Table I. Each was mixed with demineralized water for 15 min on a lab-type electronic mixer (Fimat) with 2500 rpm and allowed to stand 24 h at 25°C to attain full swelling.

TABLE I
Stock Paste Recipes

	A	B	C
Calgon T (g)	5	5	5
High viscosity alginate (g)	40	–	–
Low viscosity alginate (g)	–	85	–
Carboxymethyl guar gum (g)	–	–	140
Water (g)	955	910	855
Total	*1000*	*1000*	*1000*

TABLE II
Print Paste Recipes

Ingredient	Amount (g)
Water	50
Sodium bicarbonate	20
Ludigol F	10
Urea	150
Thickener blend (from stock paste)	750
Dye	20
Total	*1000*

Printing pastes were prepared from those stock pastes according to the formulas given in Table II. Mixtures of pairs of the main stock pastes formed the thickener in the print paste recipes. There were, therefore, three series of mixtures (high viscosity alginate/low viscosity alginate, high viscosity alginate/carboxymethyl guar gum, low viscosity alginate/carboxymethyl guar gum). Each series was printed with both of the dyes in the study. The ratio of thickeners and abbreviations of each series are given in Table III.

Measurement of the rheology

Rheological properties of the thickeners and printing pastes were measured (coaxial cylinder geometry) by using Brookfield DV-III Rheometer (USA); with a sc4-29 spindle at increasing and decreasing shear rates. Rheological measurements were evaluated according to the empirical model of Ostwald (power law) with the aid of equations of Brookfield Rheocalc IPC Paste Analysis [eqs. (1) and (2)]. This method is intended to calculate the shear sensitivity factor value of pastes.[8]

$$\tau = kD^n \quad (1)$$

TABLE III
The Ratio of Thickeners

Thickener	Ratio (%)	Abbreviation
High viscosity alginate	100	HVALG
Low viscosity alginate	100	LVALG
Carboxymethyl guar gum	100	CMG
HVA:LVA	20 : 80	HLAL2:8
HVA:LVA	40 : 60	HLAL4:6
HVA:LVA	60 : 40	HLAL6:4
HVA:LVA	80 : 20	HLAL8:2
HVA:CMG	20 : 80	HALG2:8
HVA:CMG	40 : 60	HALG4:6
HVA:CMG	60 : 40	HALG6:4
HVA:CMG	80 : 20	HALG8:2
LVA:CMG	20 : 80	LALG2:8
LVA:CMG	40 : 60	LALG4:6
LVA:CMG	60 : 40	LALG6:4
LVA:CMG	80 : 20	LALG8:2

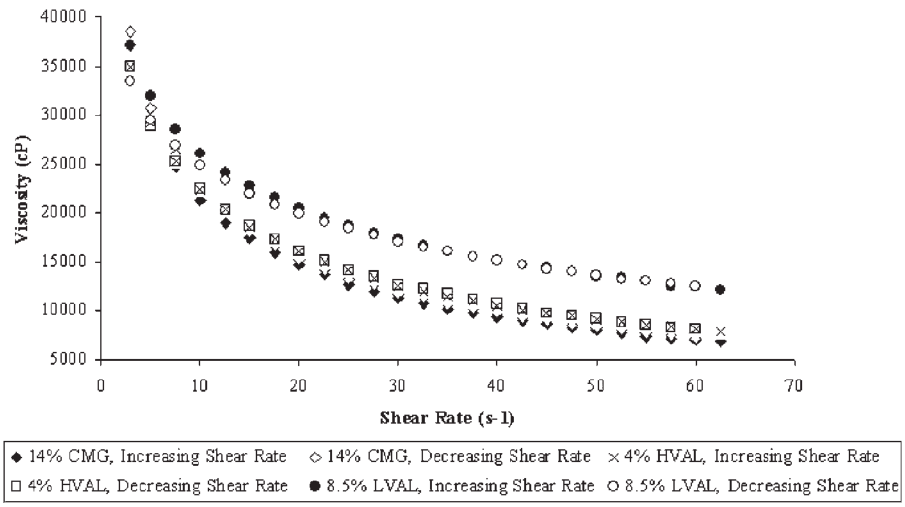

Figure 1 Rheological profiles of high viscosity alginate, low viscosity alginate, and CMG.

where τ is the shear stress (dynes/cm^2), k the consistency index (cP), D the shear rate (s^{-1}), and n is the flow index (no units).

$$\eta = k'R^{n'} \quad (2)$$

where η is the viscosity (cP), k' the consistency multiplier, R the rotational speed (rpm), and n' is the shear sensitivity factor.

Value n and n' are used to define fluidity[7] in eq. (1), and shear sensitivity factor in eq. (2), respectively.

Methods

The pastes were printed through a 55-mesh 100% PA screen on a Zimmer MDK lab print machine using a magnetic squeegee (no. 8) with 4% speed. The magnet force was 2. Printed fabrics were weighed immediately, and paste add on was calculated in g/m^2, and the printed samples were dried for 5 min at 70°C and fixed for 10 min in saturated steam. The prints were washed once in cold, twice in hot water, soaped for 15 min at the 90°C, washed once in hot water, and then rinsed, dried, and ironed. The extent of dye penetration and the color strength (K/S) of the printed fabric were determined by reflectance measurements using X-Rite SP78 Spectrophotometer. The values of the K/S at the wavelength of maximum absorption were calculated and were used as a measure of color value. K/S values of the nonprint side of the textile were measured and, using eq. (1), a value for the percent penetration of the paste into the fabric was obtained.

$$\text{Penetration} = (K/S)_b/(K/S)_f \times 100(\%) \quad (3)$$

where $(K/S)_b$ and $(K/S)_f$ are the color strength on the back and the front side of the printed substrate respectively.

For stiffness, a Shirley stiffness tester was used. The bending length in the warp direction was used directly as a measure of fabric stiffness.

Levelness was assessed visually. Unlevelness in prints is referred to either as piney, where insufficient flow causes a speckled appearance or thready where the paste wicks deeply into the fabric and leaves light/dark areas that correspond with the fabric weave.

RESULTS AND DISCUSSION

Rheological properties of the thickeners

Figure 1 clearly shows that all of the thickeners are pseudoplastic and they show decreasing viscosity with increasing shear rate. The data in Figure 1 suggests that they are similarly shear-thinning: the curves follow a similar path. The rheological profiles in Figure 1 also indicate that the high viscose alginate and CMG stock pastes follow the same profile with increasing and decreasing shear rates. Additionally, flow index of the thickeners are listed as CMG < HVAL < LVAL, as it can be seen from Table IV. On the other hand, for shear sensitivity the order is LVAL < HVAL < CMG. In the light of this data, out of these thickeners, low viscosity alginate is more close to Newtonian character.

TABLE IV
Flow Index and Shear Sensitivity Values of the Thickeners

Thickener (%)	Flow index	Shear sensitivity
High viscosity alginate (4)	0.52	0.48
Low viscosity alginate (8.5)	0.66	0.35
CMG (14)	0.46	0.54

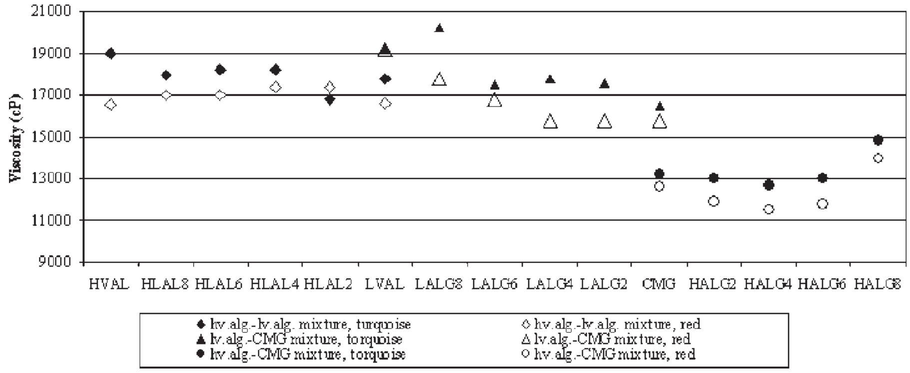

Figure 2 Viscosity versus mixture ratio at 5 s^{-1} shear rate.

Figure 2 shows viscosity versus mixture ratio at a shear rate of 5 s^{-1} for pastes containing dyes. First, change in viscosity of the mixture of high and low viscosity alginates is less. On the other hand, increasing amount of CMG in mixtures decreases viscosity, and viscosity increases with the addition of high viscosity or low viscosity alginate. The overall suggestion is that increasing amounts of alginate are effective as a viscosity modifier for CMG pastes. In addition, generally, all of the mixtures show little if any dye-related variation.

The shear sensitivity of printing pastes prepared with guar gum and alginates varies depending on the ratio of these components; higher amounts of low viscosity alginate in the mixture reduce the pseudoplastic behavior of the printing pastes (Fig. 3).

In general, increase in the low viscose alginate percentage of the mixture decreases the shear sensitivity of the system. Additionally, shear sensitivity of print pastes of high viscosity and low viscosity alginate mixtures containing turquoise dye is higher than the print paste of high viscosity alginate containing red dye. This may be due to the different in the molecule size, chemical configuration and the substituted groups in the two dyes used. When mixtures with guar are considered, increase in the guar amount also increases shear sensitivity, and no important difference is observed between two dyes.

Paste add-on, penetration, and color strength values of the mixtures

Shear sensitivity influences paste add-on, penetration, and color strength. As shown in Figures 4 and 5, broadly speaking both paste add-on and the extent of penetration strongly depend on the amount of alginate in the printing paste. Paste add-on as well as penetration of the guar paste was low, compared with that of alginates, which can be attributed to the high shear sensitivity value. Paste add-on, extent of penetration as well as color strength, (Fig. 6) each increase with increasing amount of alginate in the paste, as the system becomes more Newtonian with decreased shear sensitivity.

The results bear out the earlier findings[6] that kind of dye is not important in paste transfer. Kind of dye used affects paste flow properties such as shear sensitivity and fluidity. This contrast is interesting when it

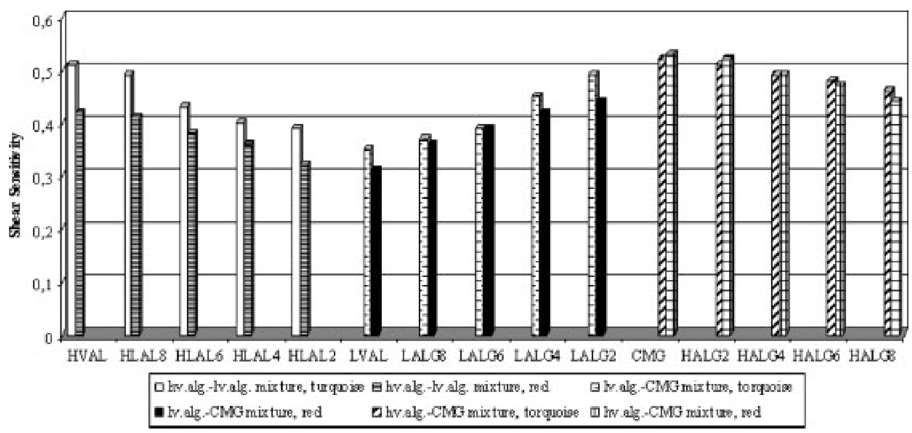

Figure 3 Shear sensitivity versus mixture ratio.

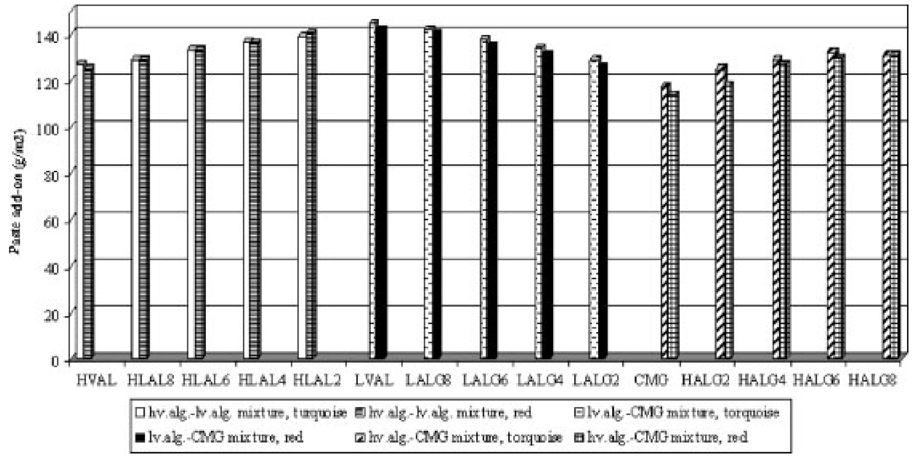

Figure 4 Paste add-on versus mixture ratio.

is considered that penetration and paste add-on values are affected by the paste flow properties.

As it can be seen from Figure 5, for high and low viscosity alginate mixtures, as the amount of low viscosity alginate increases penetration of red dye that has low molecular weight increases, whereas penetration of turquoise dye stays almost the same. For alginate–alginate mixtures, penetration will also increase besides the amount of paste add-on, because increase in the amount of low viscosity alginate decreases shear sensitivity of the system. However, this fact did not affect penetration of dye with large molecular size such as phythalocyanine turquoise in great extent. On the other hand, red dye having small molecular weight penetrates more in line with the decreasing shear sensitivity as the amount of low viscosity alginate increases.

For alginate/CMG mixtures, penetration increases as the amount of alginate increases, and it is minimum when CMG amount is higher. Additionally, when low viscosity alginate is used in guar mixtures generally penetration increases. Printing with CMG/high viscosity alginate mixtures is mainly on the surface, and value of transfer to the back is low, since these mixtures have higher shear sensitivity than CMG/low viscosity alginate mixtures. Penetration values of dyes with small and big molecules do not differ much in line with this data. However, as the amount of high viscosity alginate increases, the effect of molecular size of the dye on penetration is more apparent, because shear sensitivity of high viscosity alginate is lower than CMG.

Figure 6 shows the K/S values of the printed fabrics as the thickener mixture ratios change. As it is known, an increase of K/S can be caused by a lack of penetration (typically associated with higher shear sensitivity), a higher paste add-on (associated with lower shear sensitivity), or a greater fixation. In general, red dye has given almost the same color efficiency in all mixtures. On the other hand, color efficiency of tur-

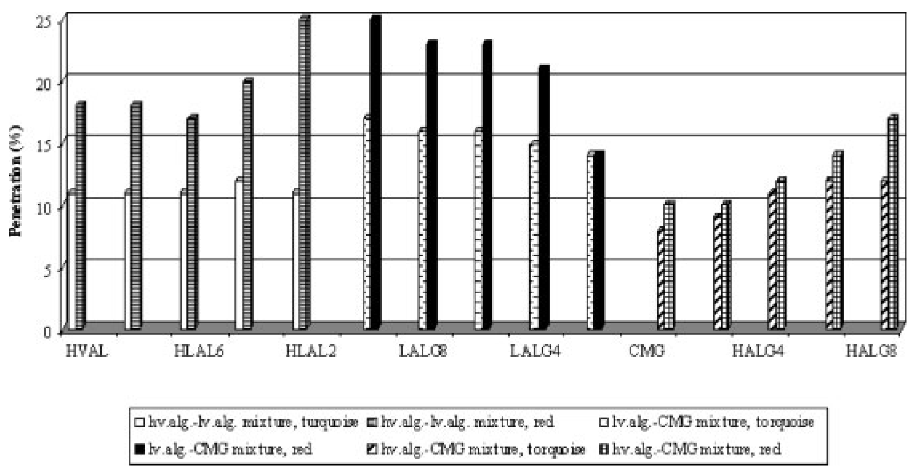

Figure 5 Penetration versus mixture ratio.

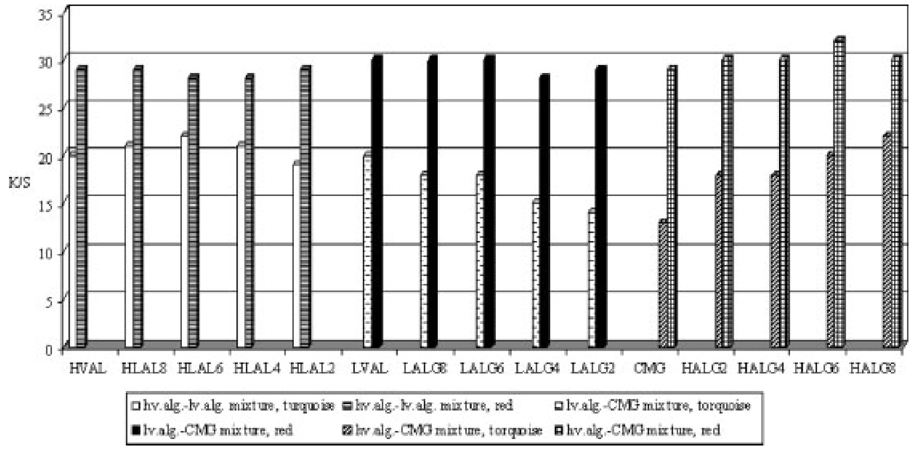

Figure 6 K/S versus mixture ratio.

quoise dye decreases as amount of CMG increases. Reactive dyes may undergo a reaction with CMG depending on the degree of substitution of CMG. Other dye-fiber type interactions may also occur, particularly with dyes of a large molecular size such as this phythalocyanine turquoise. The suggestion of an interaction between CMG and turquoise dye is borne out by the increased stiffness of these fabrics.

Fabric stiffness, levelness, and color fastness

Fabric stiffness, measured as bending length, is $\sim$ 2.0 cm for red dye in all mixtures and for turquoise dye in low and high viscosity alginate mixtures, whereas fabric stiffness reaches to 2.8 cm in CMG turquoise paste mixtures. As the proportion of CMG increases in the mixtures containing turquoise dye, the fabric stiffness of the printed fabrics increases, lending support to the supposition of a difficulty in removing dye/thickener interaction products.

Prints were examined for levelness visually. Level prints were achieved with red dye in all mixtures. However, in case of turquoise dye, prints results were good in high viscosity and low viscosity alginate mixtures. On the other hand, in mixtures of CMG with low and high viscosity alginates, prints with piney appearance were obtained with turquoise dye as the CMG percentage increased in the mixture.

Color fastness is one of the parameters determining the quality of printing. It can be concluded that CMG provides the same fastness as alginate thickeners from the fastness properties given in Table V.

CONCLUSIONS

In this study, usage of mixtures of high and low viscosity alginate thickeners with CMG, having high

TABLE V
Fastness Properties

Sample	Color fastness to washing at 60°C			Color fastness to wet and dry rubbing			
	Change in color of the sample	Change in color of the adjacent material		Dry		Wet	
		Co	Wo	Sample	Cotton	Sample	Cotton
HVAL	4–5	4–5	5	5	5	4	3
LVAL	4–5	5	5	5	5	4–5	3
CMG	4–5	4–5	5	5	5	4–5	3
HLAL2:8	4–5	4–5	5	5	5	4–5	3
HLAL4:6	4–5	5	5	5	5	4–5	3
HLAL6:4	4–5	5	5	5	5	4–5	2–3
HLALS:2	4–5	5	5	5	5	4–5	2–3
HALG2:8	4–5	5	5	5	5	4–5	3
HALG4:6	4–5	5	5	5	5	4–5	3
HALG6:4	4–5	5	5	5	5	4–5	3
HALGS:2	4–5	5	5	5	5	4–5	3
LALG2:8	4–5	5	5	5	5	4–5	3
LALC4:6	4–5	5	5	5	5	4–5	3
LALG6:4	4–5	5	5	5	5	4–5	3
LALGS:2	4–5	5	5	5	5	4–5	3

substitution degree, in reactive printing is investigated. Printing pastes made of highly substituted guar gums possess pseudoplastic rheological behavior and display lower paste add-on and penetration than alginate pastes. With the addition of alginate to CMG pastes, pseudoplastic property and shear sensitivity of the system decreases; thus, this means that paste add-on and penetration increases. When penetration values of the mixtures are considered, it can be seen that especially low viscosity alginate/CMG mixtures give much better results. On the other hand, penetration and stiffness values show that there is an interaction between CMG and turquoise reactive dye used. One must pay attention to dye selection when CMG will be used, because this kind of interaction will cause piney, unlevel, stiff handled printing. However, when it is considered that red dye gives almost the same K/S values in all mixtures and provides the same stiffness of printing, usage of CMG with alginate thickeners as a mixture; even in some cases alone by itself is recommended for reactive printing.

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