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Reactive dye printing with mixed thickeners on viscose

E. Perrin Akcakoca Kumbasar [a], Martin Bide [b,*]

[a]*Department of Textile Engineering, Ege University, E.U Muh. Fak. Tekstil Bol., 35100 Bornova-Izmir, Turkey*
[b]*Department of Textiles, University of Rhode Island, Kingston, RI 02881, USA*

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Dedicated to Dr. A.T. Peters, whose approach and learning was an inspiration to his undergraduate and Ph.D. student Martin Bide

Abstract

The rheology of binary mixtures of three anionic thickeners, alginate, carboxymethyl starch (CMS) and a modified polyacrylic acid has been measured. Two reactive dyes were printed from pastes based on these mixtures. The printing (amount applied, penetration, fixation) and the final print (colour yield, levelness, fabric stiffening) were assessed. Several of the mixtures showed dye-dependent behavior, and evidence suggests that the CMS undergoes interactions with one of the dyes used. In small amounts alginate and CMS seem effective as a rheology modifiers, with CMS avoiding dye-dependent rheology changes and providing high colour yields. Other parameters are dye-dependent. While the study does not include the thickeners used singly, the most advantageous mixture seems to be a modified polyacrylic acid with a small addition of CMS. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Printing; Mixed thickeners; Rheology; Carboxymethyl starch; Alginate

1. Introduction

Textile printing is an important method of decorating textile fabric. The coloration is achieved either with dyes or pigments in a printing paste. Printing pastes are viscous liquids and thickeners provide the viscosity. A successful print involves correct colour, sharpness of mark, levelness, good hand and efficient use of dye ("colour yield"): all of these factors depend heavily on the type of thickener used and the resulting print paste rheology. When using dyes the paste also has to include all necessary wetting, dispersing and fixing agents. The thickener must be stable and compatible with all these components: the use of an anionic thickener with a cationic dye, for example, would be a printer's nightmare. In addition, the solids content of the thickener must provide sufficient adhesion of the dye on the fabric between printing and fixation.

Cellulose fibers form the most commonly printed substrate, and reactive dyes are the most commonly use dyes in textile printing. Sodium alginate, a derivative of seaweed, is widely used for reactive dye printing. The hydroxy groups of most other carbohydrates are capable of reacting with the dye giving low colour yields or unsatisfactory fabric handle because of the insolubilisation of the thickener. Sodium alginate contains hydroxyl groups, but the reaction between alginate and dye is limited by mutual anion repulsion of the alginate's carboxyl

* Corresponding author. Tel.: +44-113-233-3777; fax: +44-113-233-3704.
E-mail address: mbide@uri.edu (M. Bide).

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groups and the dye's sulfonic acid groups. The repulsion additionally promotes migration of dye from the thickener into the fabric during steaming [1].

The relatively high cost and limited supply of alginates has spurred efforts to find alternatives. Synthetic thickeners of polyacrylic acid can be produced in many forms. They predominate in the printing of pigments where their low solids content and low VOC content are important. They additionally offer advantages over natural thickeners in quick and easy paste preparation and viscosity adjustment, and consistency of quality and supply. As used, polyacrylic acid is anionic (the carboxylic acid groups are neutralized, typically with ammonia) and does not react with typical reactive dyes, and many efforts have been made to adopt them for reactive dye printing.

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 other chemicals in the paste, so it is difficult to control the viscosities of print pastes. Calcium and magnesium ions, commonly found in hard water, may form insoluble salts with polyacrylic acid and cause washing off problems and the fabric hand to be impaired. The lower solids content also provides for a thinner film of thickening agent after the print is dried: while this may promote a greater transfer of dye from the film to the fiber in steaming, problems of dry dye flaking off before fixation may occur.

A direct comparison of synthetic and alginate thickeners in reactive dye printing has been published [2]. In that work it was observed that the amount of dye applied to the fabric in the printing step remained reasonably constant for a given thickener, even when its concentration (and thus the viscosity of the paste) varied. More dye was applied from the synthetic thickener. The penetration of the synthetic thickener pastes was greater, so (given comparable percent fixation values) the colour yield (K/S) from the two pastes was broadly comparable, despite the greater amount originally applied from the synthetic thickener paste. The horizontal spread of pastes was also constant for each thickener over a range of concentrations, and greater for the synthetic material. Thus with a sharper mark, and more economical use of dye, additional reasons for the continued preference for alginates were suggested. Research to overcome these problems has continued, modified polyacrylic acids have been developed, and their use in printing reactive dyes continues to be promoted [3].

Starch is a cheap and readily available polysaccharide with a long history in textile printing. It suffers from a number of disadvantages and to overcome these, it may be subject to chemical modification. Modifications that provide anionic character are of interest, and among the various starch ethers that have been produced the carboxymethyl ether is potentially useful to the reactive dye printer. They have been recommended for use in mixtures with alginate to increase colour yield. However, modified starch still includes the groups that can react with reactive dyes, particularly dyes of high reactivity or large molecular size. The situation is thus that alginates, polyacrylic acids, or carboxymethyl starches each have advantages and disadvantages for the printing of reactive dyes: none is ideal.

The use of mixed thickeners is not new. Indeed, the mixture of starch and gum tragacanth was very widely used when natural thickeners were the norm. In an era before the development of reactive dyes, Zonnenberg [4] 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.

Today the pressure to print reactive dyes economically with high quality has led to the commercial development of mixed thickeners in this application. Such mixtures have not been examined in detail. The aim of this work is to examine the rheology and printing properties of a series of reactive dye pastes based on mixtures of the three most common anionic thickeners, and to determine if such mixing is able to overcome disadvantages, while not losing the advantages for which each is known. There are many variables that might be examined, but generally a printer is looking for a paste that is simple to prepare, stable in its rheology, prints level and sharp, minimizes the use of dye and auxiliaries such as urea, and is easy to remove.

2. Experimental

2.1. Fabric

Scoured 100% spun rayon challis.

2.2. Thickeners

Lamitex H (sodium alginate high viscosity type, Pronova Biopolymer), “alginate” Carbopol 2491 (modified polyacrylic acid, B.F. Goodrich), “synthetic” Supergum S-600 (carboxymethyl starch, B.F. Goodrich), “CMS” A conventional polyacrylic acid synthetic thickener for pigment printing “conventional synthetic”.

2.3. Dyes

Procion Turquoise PX-GR 50 LIQ., (BASF Corp.). Procion Red PX-4B 33 LIQ (BASF Corp.).

2.4. Procedures

Following initial trials, stock paste concentrations of 40 g/kg for the alginate, 100 g/kg for the synthetic and 80 g/kg for the CMS were determined to be suitable. Stock pastes of each thickener were prepared as shown in Table 1. Each was mixed for 5 min with a hand-held electric mixer at maximum speed and allowed to stand 24 h. For comparison purposes, a paste was made of a conventional synthetic polymer thickener of the type used for pigment printing at 100 g/kg concentration.

The rheology of each stock paste was measured with the same rheometer using #sc4-14 spindle at increasing and decreasing shear rates.

Printing pastes were prepared from those stock pastes according to the formulas of Table 2.

Mixtures of pairs of the main stock pastes formed the thickener in the above recipe. There were, therefore, three series of mixtures (alginate/synthetic, alginate/CMS, and synthetic/CMS). Each series was printed with each of the two dyes in the study. The ratio of the thickeners in each series was 100/0, 80/20, 65/35, 50/50, 35/65, 20/80, 0/100. Rheologies of the printing pastes were measured under the same conditions as the stock pastes.

The pastes were printed through a 150-mesh screen engraved with a blotch and a line element on a lab print table using a magnetic squeegee. The magnet force was 85%. Printed fabrics were dried. A sample was removed for the determination of the amount of dye applied. The remainder was fixed using dry heat at 150°C for 5 min. The prints were washed once in cold and twice in hot water, soaped (CNC Detergent E, 1 g/l) for 15 min at the boil, then rinsed, dried and ironed.

The amount of dye on the fabric, both before and after fixation, was determined spectrophotometrically. Pieces of printed fabric (unfixed and fixed/washed) were weighed accurately and dissolved overnight in 70 ml of 70% w/w sulfuric acid at 4°C. The samples were stirred occasionally during the first 2 h. The resulting clear solutions were diluted with deionised water to 250 ml. Two spectrophotometric readings at the appropriate

Table 1
Stock paste recipes

	A	B	C
Calgon T (g)	5	5	5
Lamitex H (g)	40	–	–
Carbopol 2491 (g)	–	100	–
Supergum S-600 (g)	–	–	80
Water (g)	955	895	915
Total	1000	1000	1000

Table 2
Print paste recipes

Ingredient	Amount (g)
Water	205
Sodium bicarbonate	15
Ludigol F	10
Urea	150
Thickener	600
Total	1000

λ_{max} were taken from each solution. Concentration/absorbancy plots of the same dyes dissolved in a rayon/sulfuric acid solution allowed the concentration of dye in solution to be determined, and hence the amount of dye on the fabric was calculated. The amount of the dye originally applied (g/kg) and the amount of dye fixed (g/kg) was used directly. Percentage fixations were calculated from the amounts of applied and fixed dye.

The reflectance of printed fabrics was measured on a Datacolor CS-5 spectrophotometer. The values of K/S at the wavelength of maximum absorption were calculated and were used as a measure of colour value. K/S values of the non-print side of the textile were measured and, using Eq. (1), a value for the percent penetration of the paste into the fabric was obtained [2]:

$$\%\ \text{Penetration} = \frac{100(K/S)_b}{0.5[(K/S)_f + (K/S)]_b} \tag{1}$$

where $(K/S)_f$ and $(K/S)_b$ are the K/S values for the face and back of the fabric respectively.

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

Levelness was assessed visually. Unlevelness in prints is referred to either as pinney, 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.

3. Results and discussion

The results of all the experiments performed are given in graphical form in Figs. 1–8. Fig. 1 shows the rheological profiles of the thickeners (stock pastes without dye). For comparison, a conventional synthetic thickener (for pigment printing) was included.

All of the thickeners are pseudoplastic and they show decreasing viscosity with increasing shear rate. The data in Fig. 1 suggest that they are all similarly shear-thinning: the curves follow a similar path.

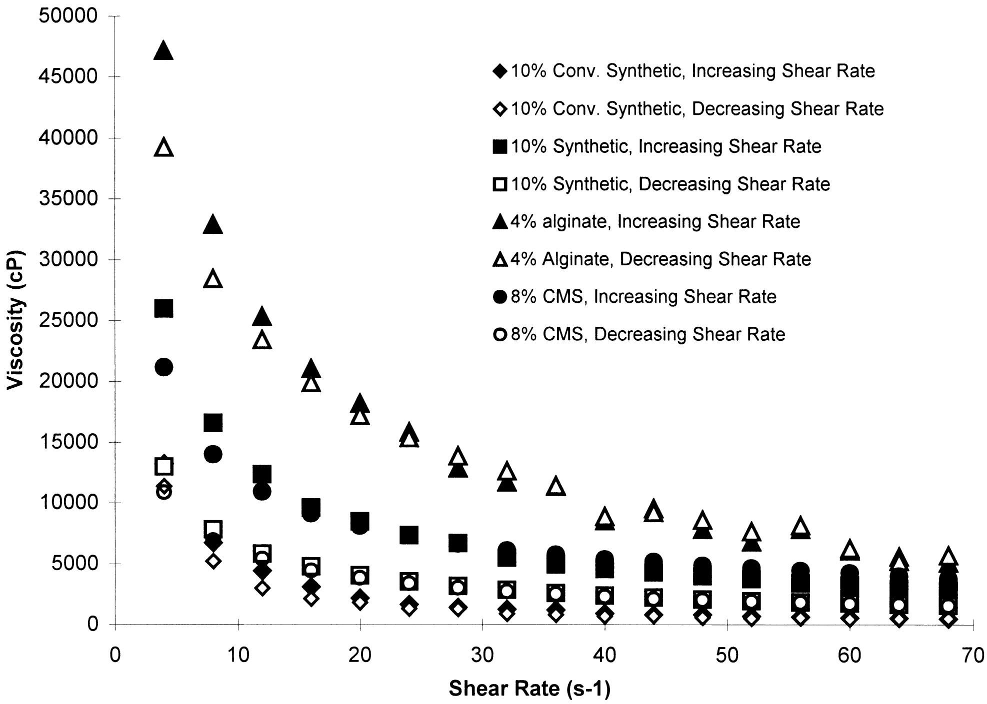

Fig. 1. Rheological profiles of a conventional synthetic thickener, Carbopol, alginate and CMS.

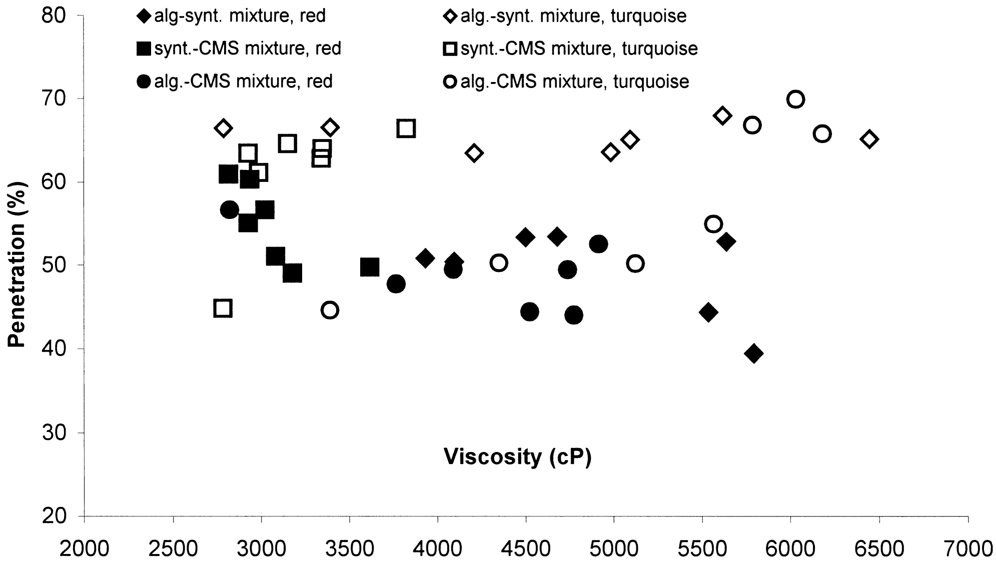

Fig. 2. Penetration vs. viscosity at shear rate 14 s^{-1}.

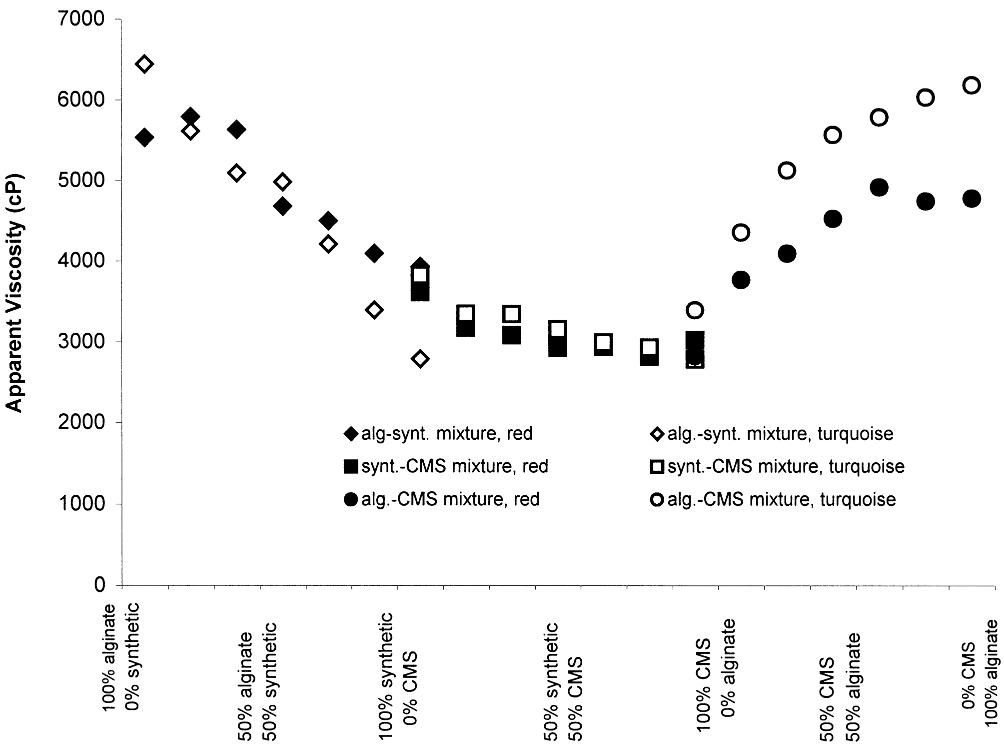

Fig. 3. Viscosity vs. mixture ratio at 14 s^{-1} shear rate.

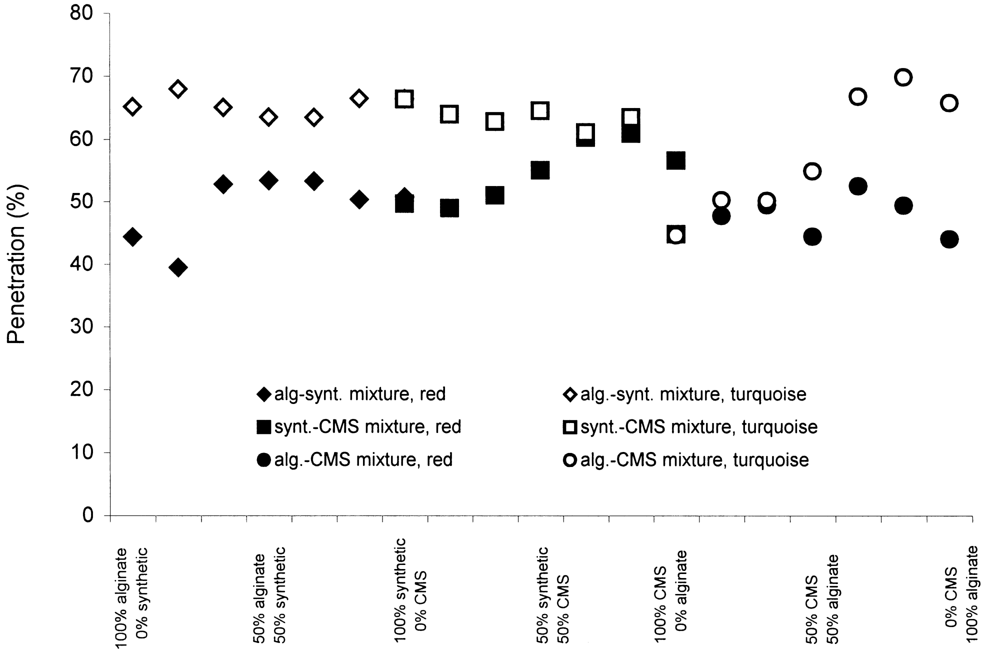

Fig. 4. Penetration vs. mixture ratio.

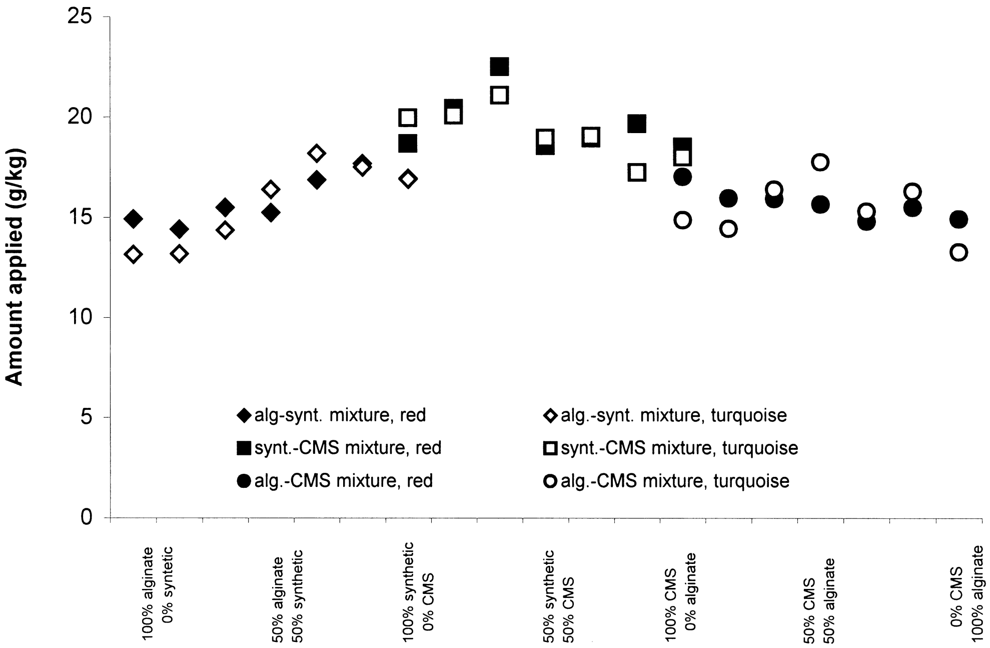

Fig. 5. Amount applied vs. mixture ratio.

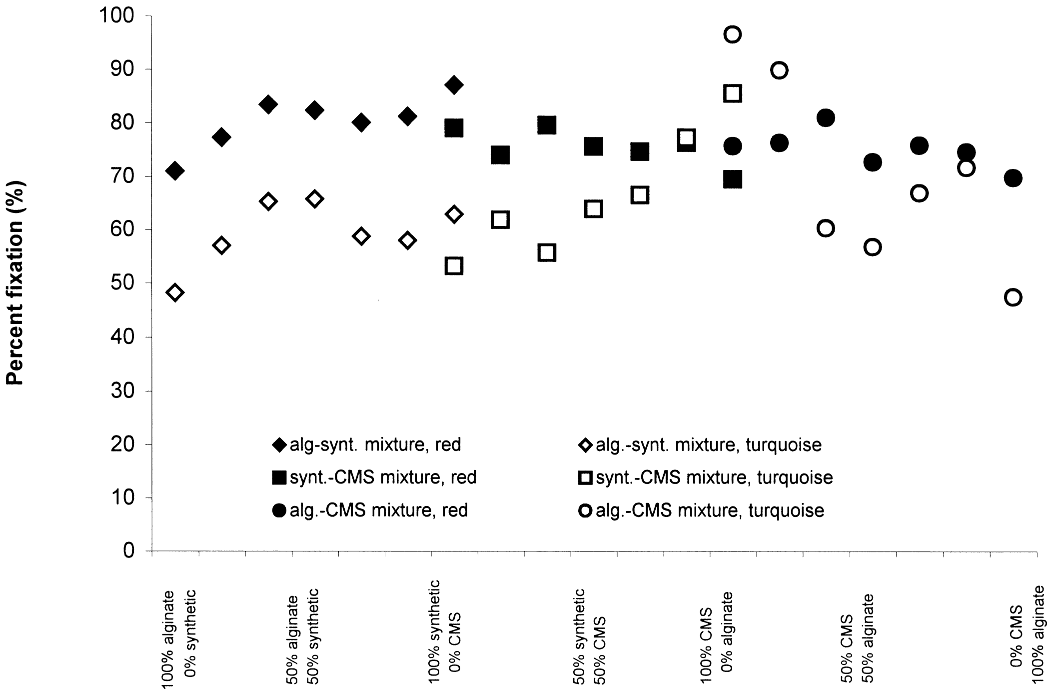

Fig. 6. Percentage fixation vs. mixture ratio.

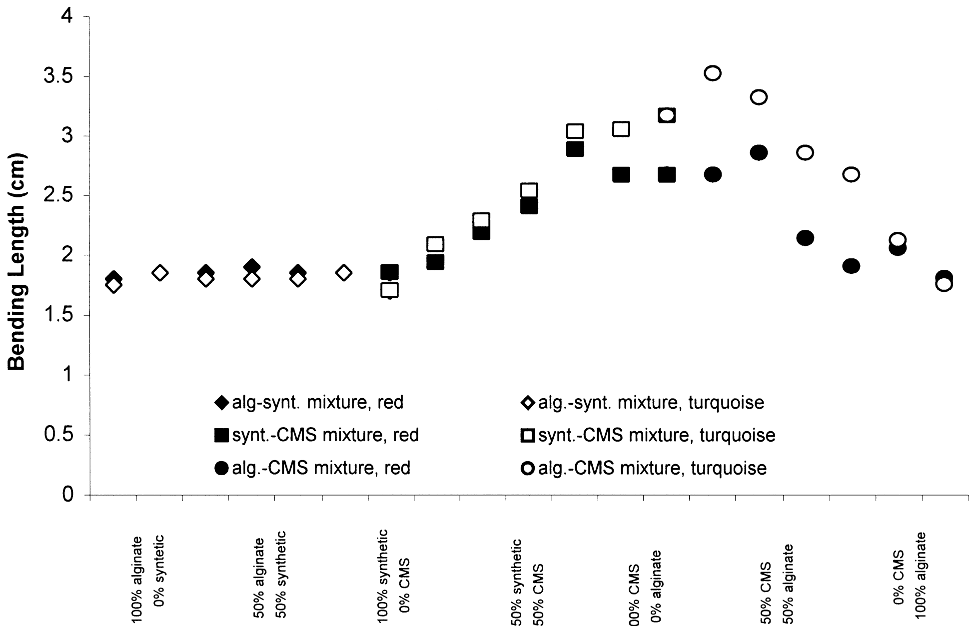

Fig. 7. Bending length vs. mixture ratio.

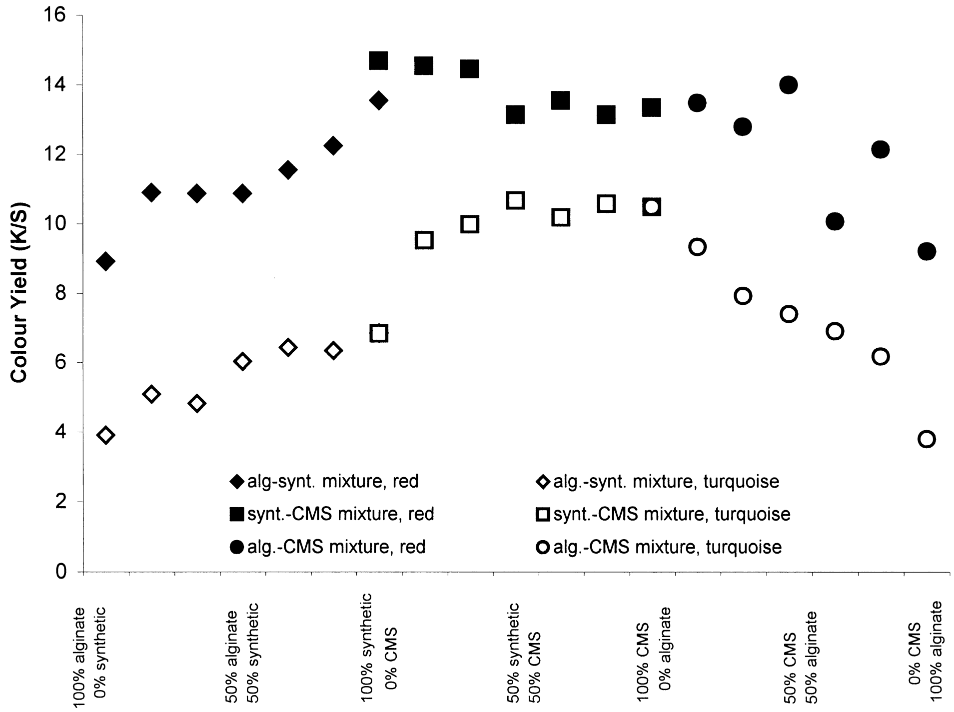

Fig. 8. K/S vs. mixture ratio.

However, the synthetic thickeners (conventional *and*, to a slightly lesser extent, modified) are more shear thinning: they have very high apparent viscosities at low shearing rates, these data are omitted from Fig. 1 to allow the remainder to be seen more clearly.

The rheological profiles of Figure 1 indicate that the alginate and conventional synthetic stock pastes follow the same profile with increasing and decreasing shear rate. For the synthetic (Carbopol) and CMS, however, there is a difference between the increasing and decreasing shear rate curves, especially at low shear rate. This is indicative of a measure of thixotropy, and such a time-dependence might indicate a slow return to an original apparent viscosity after the shear thinning effected during the printing operation, and thus an increase of flow at this time. This might suggest increased penetration and increased spread beyond the printed mark. However, the results (Fig. 2) bear out the earlier findings [2] that within the normal range of apparent viscosities, apparent viscosity has little effect on penetration or line spread for a given thickener. The nature of the thickener itself is the major factor.

Fig. 3 shows viscosity vs. mixture ratio at a shear rate of 14 s^{-1} for pastes containing dye. Most importantly, they show little if any of the interactions noted by Zonnenberg [4] leading to drastically different viscosities of the mixtures when compared to the individual materials. Those observations were attributed to a coacervation effect of one thickener on another and a resulting interference in the water "sheath" around the polymer chains. Here, with all-anionic materials, the interaction is presumably minimized. Overall, for the alginate-synthetic mixtures, as the amount of synthetic thickener increases, the viscosity decreases, the effect becoming more marked as the proportion of synthetic thickener increases. Increasing proportions of CMS with the synthetic thickener have little effect on viscosity, while the addition of small amounts of alginate to CMS results in a rapid increase of viscosity, the effect slowing as the proportion increases. The overall suggestion is that small amounts of alginate are effective as a viscosity modifier for both synthetic and CMS pastes. Fig. 3 also indicates the effects of the two different dyes on the apparent viscosities of these pastes. There is a distinct difference between the red and turquoise dyes in the alginate-CMS mixtures, the turquoise pastes having consistently higher apparent viscosities, and the difference increasing with higher proportions of alginate. The addition of synthetic to alginate rapidly overcomes this effect and at high synthetic/low alginate proportions, the effect is apparently reversed. Synthetic/CMS mixtures show little if any dye-related variation.

Fig. 4 shows the penetration of pastes as the thickener ratio changes. Broadly speaking the average penetration for the two dyes varies little, although in alginate/CMS mixtures, the penetration is high with a high proportion of alginate, and low when CMS is in the majority. It has been suggested [1] that CMS gives lower penetration and thus tends to increase colour yield, and that the lack of penetration (with its lack of flow) can result in pinniness. That unlevelness was indeed noted here. For all except the pastes containing approximately 50% or higher concentrations of CMS, the turquoise dye pastes have higher penetration. The relatively lower penetration of these CMS turquoise pastes may be ascribed to the possibility of interaction of CMS with the turquoise dye discussed in more detail below. The penetration of the red dye is, conversely, highest with pastes containing a high proportion of CMS.

Fig. 5 shows the amount of paste applied from each of the thickener mixtures. This is lowest with pastes thickened with a predominance of alginate, and highest with CMS/synthetic pastes in which the synthetic component is present in the majority. (It is possible that the pastes containing higher proportions of CMS may be involved with the dye interactions discussed above, even before fixation, thus reducing the amount applied). Overall the larger amount applied from CMS/synthetic mixtures correspond with their apparent viscosity (Fig. 3). In contrast to other properties measured, there is little difference noted between the behaviour of pastes containing different dyes. Since both penetration and volume applied involve paste flow, such a contrast is surprising.

Fig. 6 shows the percent fixation of dye printed from the various mixtures of thickeners. Pastes containing a high proportion of alginate show lower fixations. For most mixtures, the fixation is lower for the turquoise dye, presumably a function of its lower substantivity or reactivity. As with penetration, however, an exception is noted for the pastes containing a high proportion of CMS, whether mixed with alginate or synthetic. This again suggests the likelihood of an interaction occurring between CMS and the turquoise dye. Reactive dyes may undergo a reaction with CMS depending on the degree of substitution (DS) of CMS [1,5]. Other dye–fibre type interactions may also occur, particularly with dyes of a large molecular size such as this phthalocyanine turquoise. It is thus possible that the dye measured as "fixed" is in reality held on the fiber as a thickener/dye complex. The suggestion of an interaction between CMS and the turquoise dye is borne out by the increased stiffness of these fabrics shown in Fig. 7. Unremoved thickener can cause stiff hand in the final fabric, and this was observed in these experiments. As the proportion of CMS increased in the mixtures the bending length of the printed fabrics increased, lending support to the supposition of a difficulty in removing dye/thickener interaction products.

Fig. 8 shows the K/S values of the printed fabrics as the thickener mixture ratios change. An increase of K/S can be caused by a lack of penetration (typically associated with higher viscosity), a higher amount applied (associated with lower viscosity), or a greater fixation. In general, a decreasing proportion of alginate in the mixtures resulted in higher colour yield. This occurs despite the higher apparent viscosities found for pastes containing a high proportion of alginate, so the effect is not based on a higher viscosity giving a higher proportion of colour at the surface as discussed above, and found previously [2]. Instead, the higher K/S values of CMS/synthetic mixtures seem directly attributable to the greater amount applied from these pastes and the higher fixations (Figs. 5 and 6). In the CMS/synthetic mixtures containing a majority of CMS, there is a question of how much of the colour yield obtained is derived from thickener/dye complex discussed above, rather than dye fixed by reaction with cellulose. For alginate-synthetic mixtures it is noted that the pastes containing a high proportion of the synthetic thickener are transferred to a greater degree, and fix slightly better: they thus show a significantly greater colour yield. This suggests economic benefit, both of reduced dye consumption and reduced dye waste to cause environmental impact. The stiffness of the prints (Fig. 7) does not change as the proportions of alginate and synthetic change.

Two other items of data were collected that are not presented in graphical form. Prints were examined for levelness. All the red prints and most of the turquoise prints were level. However, all pastes containing a high proportion of CMS, whether with synthetic or with alginate, showed a pinney appearance. The width of the line elements in each print was measured. The spread of a line beyond the printed width is an indication of leveling ability of the pastes, (or the lack of spread would indicate sharpness of mark). Line widths measured here were virtually constant, and thus give no opportunity for conclusions to be drawn.

4. Conclusions

These experiments have examined binary mixtures of three thickeners, each of which is supposedly suitable for printing reactive dyes. Only one concentration of each was examined and it is very possible that at different concentrations, other conclusions might be drawn. Certain factors that were not examined here might prove decisive for the printer, especially cost. The effect of handling on a dried print before fixation was not studied and is commonly given as a reason for maintaining at least a proportion of natural thickener in reactive dye print pastes. The value of mixed thickeners is the maximization of beneficial behaviors and the minimization of disadvantages. The relative value of benefits and disadvantages is a commercial matter, and not examined here, nor is this a comparison of single thickeners against each other.

Some broad statements about the behaviour of these mixtures can be made. In mixtures, alginate seems effective as a rheology modifier, its initial effect being greater than its proportion would suggest. Pastes of high alginate concentration have stable viscosities little affected by other thickeners. Synthetic/alginate mixtures suffer dye-dependent changes of rheology that affect penetration when one is in the majority, but equal mixtures of the two show this least. The same dye-dependence is true for CMS alginate mixtures containing a majority of alginate. Mixtures containing a majority of CMS (with alginate or synthetic) tend to lack this dependency and indicate the value of CMS as a modifier for these pastes. Synthetic/CMS pastes showed least viscosity variation overall, and least dye-dependent variation in viscosity. When CMS is present in small proportions the mixtures give the highest colour yields, avoids CMS/dye interaction, (i.e. does not stiffen the fabric), and for the two dyes examined here, shows little viscosity dependence on the dye present. Penetration, fixation and K/S are, however, still dye dependent, and the high colour yields are caused in part by a greater use of dye. Penetration, stiffness and fixation data suggest strongly that an interaction takes place between the CMS paste and the turquoise reactive dye used here. Such an interaction may also be responsible for the pinney unlevelness noted for CMS based pastes.

For a single thickener alginate may be most suitable for reasons suggested elsewhere [2] and based on market share. However, if a mixture is to be used the results presented here suggest that the most advantageous would appear to be the synthetic material modified with a small amount of CMS.

Acknowledgements

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