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Further Studies of the Use of Chitosan in the Dyeing of Full Chrome and Heavily Retanned Leather with Anionic Dyes

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ABSTRACT

Treatment of chrome grain and also heavily retanned leather with three grades of chitosan enhanced the depth of shade of a typical acid and a direct dye on the substrates. For each type of leather, the dyed treated leather was found to be of a similar, but deeper hue and possessed superior fullness and handle to its dyed, untreated counterpart. The extent of shade intensification furnished by pretreatment was greater for the acid dye than the direct dye, possibly due to the greater substantivity of the direct dye for the cationic polymer within the pretreated leathers. Despite their greater colour strength, the wash fastness of the pretreated dyeings was comparable to that of their dyed, untreated counterparts.

INTRODUCTION

Of the various chemical and mechanical processes to which raw hides and skins are subjected during the preparation of leather, the most important is tannage, which involves the introduction of additional cross-links into the hide collagen by means of which the hydrothermal stability of the hide and its resistance to biological and physical agencies are improved. Tannage can be achieved in several ways using, for example, vegetable, mineral or aldehyde tanning agents; chrome tannage is currently the most important and effective tanning method employed.

The retannage of chrome tanned leather, which is carried out to improve, for example, the fullness, softness and handle of the substrate, can be effected using several materials, including vegetable tannins, mineral tanning agents, synthetic tanning agents (syntans) and resins. However, in addition to imparting the desired physical properties to the substrate, retannage of chrome leather also influences the depth, hue and brightness of subsequent dyeings. Characteristically, retanned leather exhibits lower substantivity towards anionic dyes than does its chrome tanned counterpart as a result of the tanning agent physically impeding dye diffusion within the leather, the sulphonate and/or carboxyl groups of the retanning agents repelling incoming dye anions, and also because a proportion of the dye sites within the substrate are occupied by the retanning agents. To enhance the build-up of anionic dyes on retanned leather, several cationic and amphoteric auxiliaries have been developed; in previous work, it was demonstrated that a commercial grade of the naturally-occurring polyaminosaccharide, chitosan, intensified the depth of shade of several classes of anionic dye on chrome tanned hide powder,[1] chrome grain leather[2,3] and heavily retanned leather[3–5] as well as crusted and dyed-through leather.[6] The present study concerns the effects of three grades (high, medium and low viscosity) of chitosan on the build-up and wash fastness properties of an acid dye and a direct dye on both chrome grain and heavily retanned leather.

EXPERIMENTAL

Materials

Leather
Samples (measuring approximately 30 × 22 cm) of locally processed, British bovine, wet-blue leather with a shaved thickness of between 1·4 and 1·5 mm were used. The mass of each sample was recorded and all processing variables were based on this shaved mass.

Dyes
Both the acid dye (CI Acid Yellow 83) and direct dye (CI Direct Black 155) used were selected on the basis of their widespread use on leather and were commercial samples kindly supplied by Yorkshire Chemicals Plc; the dyes were used without purification. The structure of neither dye has been disclosed in the Colour Index.[7]

Chitosan
Three commercial grades of chitosan (Table 1) were kindly supplied by Rigest Trading Ltd. Stock aqueous solutions (2·5 and 10 g l^{-1}) of each of the three grades of chitosan were prepared by dissolution of the appropriate amount of the polyaminosaccharide in 1 litre of aqueous formic acid

TABLE 1
Grades of Chitosan Used

Grade	*Source*	*Viscosity (cps)*	*Deacetylation (%)*
Low viscosity	Shrimp	49	76·4
Medium viscosity	Crab	410	86·9
High viscosity	Shrimp	2920	85·6

(10 g l^{-1}) solution at room temperature by stirring (magnetic stirrer and follower) for 24 h. The pH of the chitosan treatment bath was adjusted to 4 using aqueous ammonium hydroxide solution.

Syntans
The following commercial products were generously supplied by Yorkshire Chemicals Plc:

Paralene PWG: replacement syntan
Parvol G: auxiliary syntan
Parvol PRA: auxiliary syntan.

Natural tanning agent
A sample of Mimosa extract was generously provided by Yorkshire Chemicals Plc.

Resin
A commercial sample of Paramel PA (Yorkshire Chemicals Plc) was used.

Fat liquor
A commercial sample of Paradol HIR was kindly supplied by Yorkshire Chemicals Plc.

Procedures

Processing methods
All wet processing was carried out using a Beamhouse Engineering four-drum laboratory cabinet. The methods employed for the processing of the chrome grain (wet-blue) and heavily retanned leathers are shown in Appendices 1 and 2, respectively.

Colour measurement

The reflectance values of both the flesh and grain sides of dyed, untreated and chitosan pretreated leather samples were measured, using a Colorgen CS 1100 reflectance spectrophotometer interfaced to an Amstrad personal computer, under illuminant D_{65}, using a 10° standard observer with UV component excluded and specular component included. Each leather sample was measured four different times and the average reflectance calculated. The CIElab colour difference (ΔE) between the pretreated and untreated dyed samples was calculated from the L^*, a^* and b^* coordinates of the respective samples (by subtraction of the L^*, a^* and b^* values of the pretreated samples from those of the untreated samples). The K/S values were calculated from the reflectance values at the λ_{max} of the dyeings, and the percentage enhancement of colour strength ($\%E$) achieved by pretreatment with the polyaminosaccharide was calculated using eqn (1).

$$\%E = \frac{K/S_C - K/S_U}{K/S_U} \times 100 \quad (1)$$

where K/S_U and K/S_C are the colour strengths of the dyed untreated and dyed chitosan-pretreated sample, respectively.

Wash fastness

The fastness of untreated and chitosan pretreated, dyed leather samples was determined using the UK-LE: 1978 test method.[8]

RESULTS AND DISCUSSION

It was found that all dyeings were uniform and that chitosan pretreatment neither enhanced nor impaired the levelness of dyeings secured on both full chrome and heavily retanned leather; furthermore, each of the dyed, chitosan pretreated samples was found to be considerably smoother and fuller than their corresponding dyed, untreated counterparts. These findings concurred with those observed in previous studies of the effect of the polyaminosaccharide on the dyeing of chrome grain and heavily retanned leather.[2–5]

The two concentrations of each of the three grades of chitosan employed in the work, namely 200% omf of a 2·5 g l^{-1} solution in the case of chrome grain leather and 10% omf of a 10 g l^{-1} aqueous solution for retanned leather, were used as these particular concentrations had been observed in previous studies to impart inhanced dyeability to the two types of leather.[2–5]

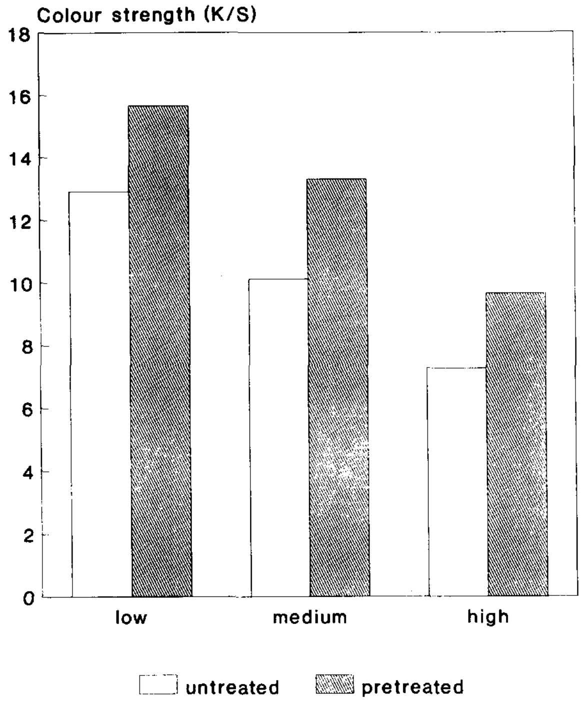

Fig. 1. The effect of chitosan viscosity (200%; 2·5 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Acid Yellow 83 on the grain side of chrome grain leather.

CI Acid Yellow 83

Figures 1 and 2 show the colour strength (*K/S*) achieved using 0·5% omf CI Acid Yellow 83 on the grain and flesh sides of both untreated chrome grain leather and also chrome grain leather which had been pretreated with 200% omf of a 2·5 g l^{-1} solution of each of the three grades of chitosan. Clearly, pretreatment with the polyaminosaccharide enhanced the colour strength of the dyeings on both the grain and flesh sides of the substrate. The enhanced colour strength of the dyeings imparted by pretreatment with chitosan is reflected in the lower lightness (L^*) values of the pretreated dyeings as shown in the corresponding colorimetric data (Table 2); these data also reveal that pretreatment with each of the three grades of chitosan resulted in dyeings that were slightly duller and redder than the corresponding dyeings of the untreated substrate (as evidenced by the lower c^* values and the lower a^* and H° values, respectively, of the pretreated dyeings). Table 2 also shows that the extent of intensification of shade furnished by chitosan treatment ranged from over 4 to nearly 7 ΔE units. The enhancement of dye uptake imparted by the polyaminosaccharide

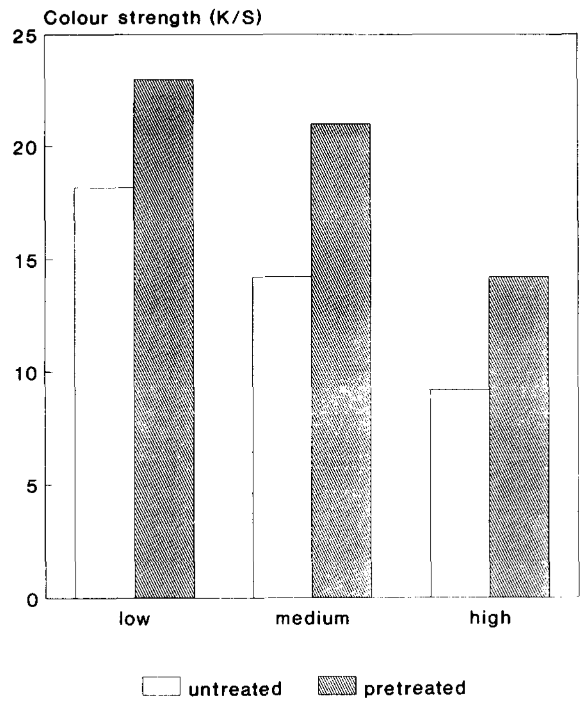

Fig. 2. The effect of chitosan viscosity (200%; 2·5 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Acid Yellow 83 on the flesh side of chrome grain leather.

TABLE 2
Colorimetric Data for Untreated and Chitosan Formate (200%; 2·5 g l^{-1}) Pretreated Chrome Grain Leather Dyed with CI Acid Yellow 83

Chitosan viscosity	*Surface*	*Treatment*	L^*	a^*	b^*	c^*	$H°$	ΔE
Low	grain	nil	52·7	21·6	46·3	51·1	65·0	6·2
		chitosan	48·3	24·9	43·4	50·0	60·2	
	flesh	nil	42·4	19·3	35·6	40·5	61·5	4·9
		chitosan	38·6	21·3	33·3	39·5	57·5	
Medium	grain	nil	56·3	20·0	47·2	51·2	67·0	4·4
		chitosan	53·1	22·9	47·2	52·5	64·1	
	flesh	nil	47·7	19·1	39·0	43·4	64·0	5·6
		chitosan	42·6	21·1	37·7	43·2	60·7	
High	grain	nil	57·8	16·8	43·4	46·5	68·8	4·4
		chitosan	54·5	19·6	43·1	47·3	65·5	
	flesh	nil	50·9	17·5	37·6	41·4	65·1	6·8
		chitosan	45·0	20·1	35·5	40·8	60·4	

can, as previously suggested,[1–6] be attributed to the provision, by chitosan, of additional protonated amino groups within the pretreated substrate.

Figures 1 and 2 also show that the colour strength of the three dyeings of untreated chrome grain leather differed, despite the fact that the dyeings had been carried out under identical conditions using the same substrate. This observed difference in *K/S* of the untreated dyeings was expected and can be attributed to the fact that the dyeing behaviour of leather varies, not only between different hides of the same breed of animal, but also between different portions of the same hide, as was the case for the results displayed in Figs 1 and 2. Thus, in order to ascertain whether one of the three particular grades of chitosan employed was more effective than any other in intensifying the depth of shade, the percentage enhancement of colour strength (%*E*) achieved by pretreatment with the cationic polymer was determined using eqn (1). The %*E* values secured for the dyed chrome grain samples under consideration (Table 3) reveal that of the three ranges of the polyaminosaccharide used, low viscosity chitosan imparted the lowest intensification of shade and that the remaining two viscosity grades were similar in the extent to which they enhanced dye uptake.

Figures 3 and 4 show the colour strength achieved using 0·5% omf of the dye on the grain and flesh sides of both untreated retanned leather and also retanned leather which had been pretreated with 10% omf of a

TABLE 3

Percentage Enhancement (%*E*) of Colour Strength Achieved for Chitosan Formate Pretreated Leather

Chitosan viscosity	*Surface*	*Treatment*	*%E*	
			CI Acid Yellow 83	*CI Direct Black 155*
Low	grain	chrome	21·5	8·2
		retanned	2·4	−6·2
	flesh	chrome	25·0	26·5
		retanned	11·3	2·5
Medium	grain	chrome	31·2	1·8
		retanned	136·9	105·7
	flesh	chrome	46·4	−1·7
		retanned	170·8	92·5
High	grain	chrome	31·2	12·4
		retanned	120·8	100·9
	flesh	chrome	52·2	32·8
		retanned	109·9	103·4

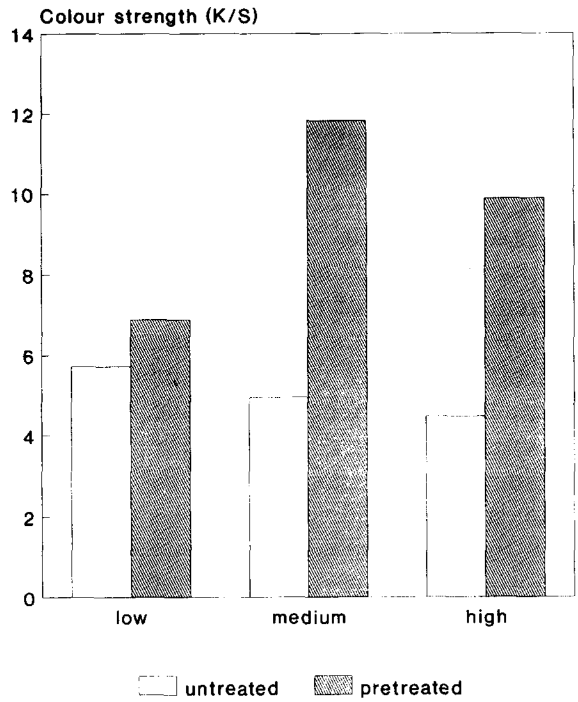

Fig. 3. The effect of chitosan viscosity (10%; 10 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Acid Yellow 83 on the grain side of retanned leather.

10 g l^{-1} solution of each of the three grades of chitosan. It is evident that pretreatment enhanced the colour strength of the dyeings on both the grain and flesh sides of the substrate, this being reflected in the lower L^* values recorded for the pretreated dyeings (Table 4). The corresponding colorimetric data (Table 4) reveal that pretreatment resulted in dyeings that were brighter and slightly redder than the corresponding dyeings of the untreated substrate (as evidenced by the higher c^* values and the lower a^* and $H°$ values, respectively, of the pretreated dyeings). Table 4 also shows that the extent of intensification of shade furnished by chitosan treatment ranged from 0·5 to over 12 ΔE units. In terms of the relative effectiveness of the three grades of the cationic polymer in enhancing dye uptake, the $\%E$ values displayed in Table 3 demonstrate that low viscosity chitosan imparted considerably lower intensification of shade than either the medium or high viscosity grades and that of these latter two forms of the polyaminosaccharide, the medium viscosity grade product imparted greatest intensification of shade.

As mentioned earlier, anionic dyes exhibit lower substantivity towards retanned chrome grain leather than its chrome tanned counterpart; the

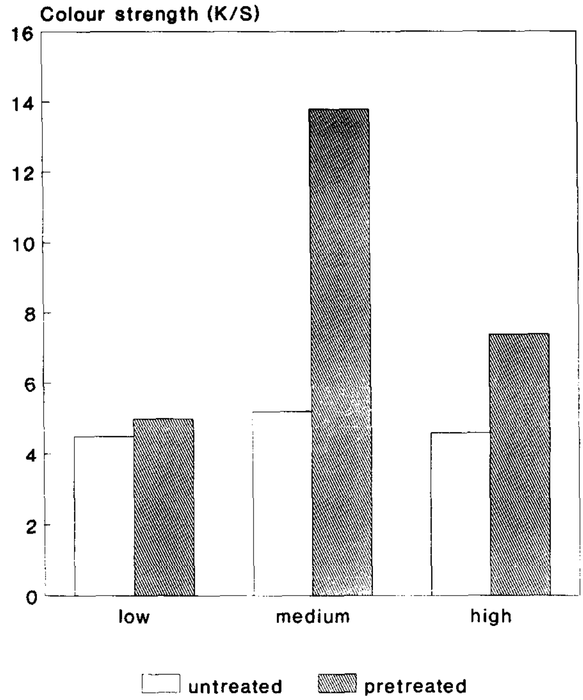

Fig. 4. The effect of chitosan viscosity (10%; 10 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Acid Yellow 83 on the flesh side of retanned leather.

TABLE 4
Colorimetric Data for Untreated and Chitosan Formate (10%; 10 g l^{-1}) Pretreated Heavily Retanned Leather Dyed with CI Acid Yellow 83

Chitosan viscosity	*Surface*	*Treatment*	L^*	a^*	b^*	c^*	$H°$	ΔE
Low	grain	nil	54·2	17·8	36·2	40·4	63·7	0·5
		chitosan	53·1	18·0	36·1	40·4	63·5	
	flesh	nil	55·8	11·2	28·6	30·7	68·7	1·3
		chitosan	54·7	11·7	29·1	31·3	68·2	
Medium	grain	nil	58·9	15·4	36·9	40·0	67·3	11·8
		chitosan	49·4	21·8	39·5	45·1	61·1	
	flesh	nil	56·1	12·1	32·1	34·3	69·3	12·3
		chitosan	45·2	17·4	34·7	38·8	63·4	
High	grain	nil	59·6	15·1	35·8	38·9	67·2	10·4
		chitosan	53·3	20·3	42·3	46·9	64·4	
	flesh	nil	58·5	11·6	29·9	30·3	67·5	9·9
		chitosan	53·0	16·0	34·9	38·5	65·4	

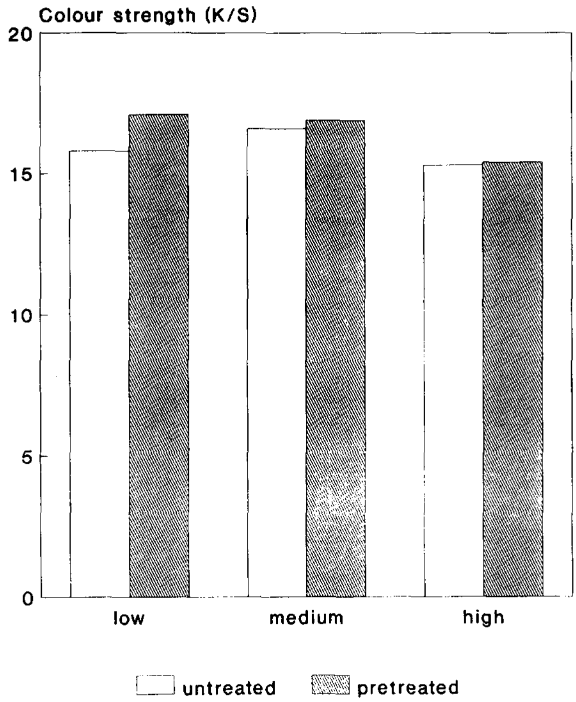

Fig. 5. The effect of chitosan viscosity (200%; 2·5 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Direct Black 155 on the grain side of chrome grain leather.

results obtained (Figs 1–4 and Tables 2 and 4) support this statement, insofar as uptake of CI Acid Yellow 83 on both the grain and flesh sides of untreated retanned leather was considerably lower than that achieved on untreated chrome grain leather. The reduced dyeability of the untreated retanned leather with the anionic dye can, as proposed earlier, be attributed to the greater anionicity of the retanned leather resulting from the presence of anionic (sulphonate and carboxyl) groups in the retanning agent. It was, therefore, not surprising to observe that the effectiveness of the three grades of the polyaminosaccharide in enhancing dye uptake was, with the exception of low viscosity chitosan, much greater in the case of retanned leather than for chrome grain leather, this being attributable to the adsorbed cationic polymer having not only provided additional dye sites (protonated amino groups) within the retanned substrate but also having reduced the anionicity of the substrate. The results (Figs 1–4 and Tables 2–4) also show that whilst each of the three different grades of the polyaminosaccharide enhanced uptake of the dye on to both chrome grain and heavily retanned leathers, the low viscosity grade product was considerably less effective than either the medium or high viscosity products. As the number of amino groups in the polyaminosaccharide will increase

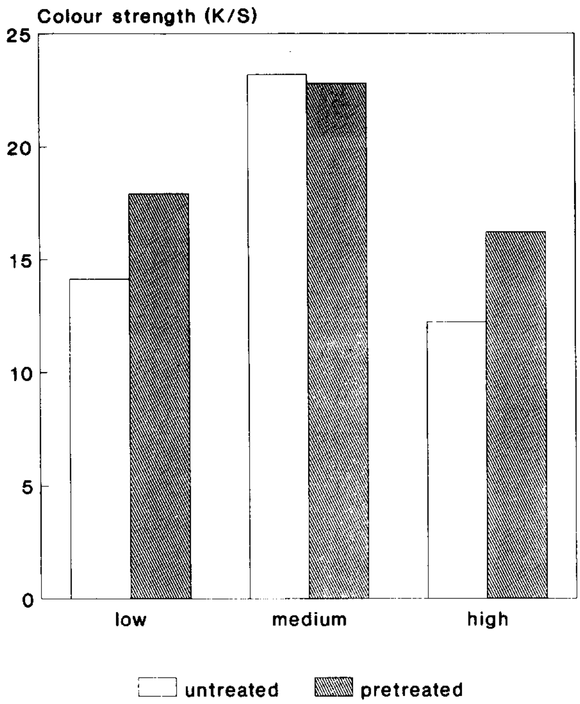

Fig. 6. The effect of chitosan viscosity (200%; 2·5 gl^{-1}) on the colour strength of 0·5% omf dyeings of CI Direct Black 155 on the flesh side of chrome grain leather.

with increasing degree of deacetylation, and as the enhancement of dye uptake imparted by the polyaminosaccharide can be attributed to the provision, by chitosan, of protonated amino groups within the pretreated substrate, it seems reasonable to propose that the low effectiveness of the low viscosity chitosan can be attributed to its degree of deacetylation (76·4%) being lower than that of its medium and high viscosity counterparts (86·9% and 85·6%, respectively) (Table 2). Furthermore, the combination of the finding that there was relatively little difference between the effectiveness of the medium and high grade chitosan products in enhancing dye uptake (Table 3) and that the two forms of the polyaminosaccharide had very similar degrees of deacetylation, adds support to the proposal that the extent to which the three grades of chitosan enhance dye uptake was related to the degree of their deacetylation.

CI Acid Black 155

Figures 5 and 6 show the colour strength (*K/S*) achieved using 0·5% omf CI Direct Black 155 on the grain and flesh sides of both untreated chrome grain leather and also chrome grain leather which had been pre-

TABLE 5
Colorimetric Data for Untreated and Chitosan Formate (200%; 2·5 g l^{-1}) Pretreated Chrome Grain Leather Dyed with CI Direct Black 155

Chitosan viscosity	*Surface*	*Treatment*	L^*	a^*	b^*	c^*	H°	ΔE
Low	grain	nil	20·7	2·9	−3·5	4·6	310·1	0·9
		chitosan	19·9	2·8	−2·9	4·1	313·1	
	flesh	nil	22·1	1·9	−3·5	4·0	298·7	2·8
		chitosan	19·3	2·2	−3·7	4·2	300·6	
Medium	grain	nil	20·3	2·7	−3·3	4·2	309·1	0·3
		chitosan	20·1	2·8	−3·2	4·3	310·8	
	flesh	nil	16·6	2·8	−4·3	5·1	302·6	1·2
		chitosan	16·7	2·7	−4·3	5·1	302·2	
High	grain	nil	21·2	2·9	−2·8	4·1	316·6	2·3
		chitosan	21·7	2·8	−0·6	2·8	348·2	
	flesh	nil	23·9	1·9	−2·8	3·4	305·6	3·2
		chitosan	20·9	2·2	−1·9	2·9	319·9	

treated with 200% omf of a 2·5 g l^{-1} solution of each of the three grades of chitosan, from which it is evident that, with the exception of medium grade chitosan on the grain side of the substrate, pretreatment enhanced the colour strength of the dyeings on both the grain and flesh sides of the substrate. The enhanced colour strength of the dyeings imparted by pretreatment with chitosan is reflected in the lower lightness (L^*) values of the pretreated dyeings (Table 5); the colorimetric data displayed in Table 5 also shows that in the case of medium grade chitosan on the flesh side of the substrate, there was very little difference in colour between the untreated and pretreated dyeings. It is evident from Table 5 that pretreatment with each of the three grades of chitosan resulted in dyeings that were generally redder than the corresponding dyeings of the untreated substrate (as evidenced by the higher H° values of the pretreated dyeings); the extent of intensification of shade secured by chitosan pretreatment ranged from 0·3 to 3·2 ΔE units (Table 5). The $\%E$ values displayed in Table 3 reveal that medium viscosity chitosan imparted considerably lower intensification of shade than either the low or high viscosity grades and, that of these latter two grades of the polyaminosaccharide, the high viscosity variant imparted greatest intensification of shade.

Figures 7 and 8 show that, with the exception of the low grade chitosan on the grain side of the substrate, pretreatment using 10% omf of a 10 g l^{-1} solution of each of the three grades of the cationic polymer enhanced the colour strength of 0·5% omf dyeings on both the grain and flesh sides of heavily retanned leather, this being reflected in the lower L^* values

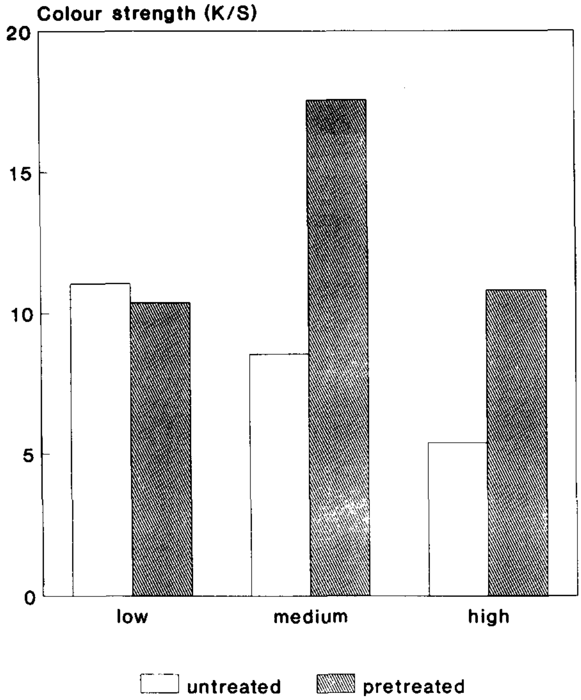

Fig. 7. The effect of chitosan viscosity (10%; 10 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Direct Black 155 on the grain side of retanned leather.

TABLE 6
Colorimetric Data for Untreated and Chitosan Formate (10%; 10 g l^{-1}) Pretreated Heavily Retanned Leather Dyed with CI Direct Black 155

Chitosan viscosity	*Surface*	*Treatment*	L^*	a^*	b^*	c^*	$H°$	ΔE
Low	grain	nil	29·0	−0·2	−10·0	10·0	268·7	0·5
		chitosan	29·9	−0·3	−10·1	10·1	267·8	
	flesh	nil	36·1	−1·4	−7·1	7·3	258·5	0·6
		chitosan	35·8	−1·4	−7·5	7·7	259·6	
Medium	grain	nil	32·4	−0·7	−9·1	9·2	265·5	12·0
		chitosan	20·7	1·9	−7·8	8·1	284·2	
	flesh	nil	31·5	−0·9	−6·8	6·8	262·3	10·2
		chitosan	21·5	0·8	−5·7	5·7	278·5	
High	grain	nil	38·7	−1·4	−7·4	7·5	259·3	10·9
		chitosan	27·9	0·5	−7·7	7·8	343·3	
	flesh	nil	41·4	−1·2	−7·1	7·2	260·4	10·9
		chitosan	30·5	−0·1	−7·3	7·3	269·3	

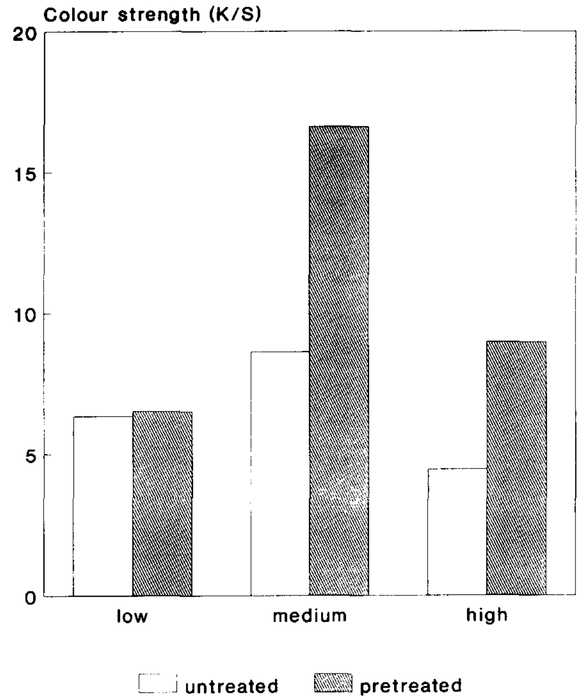

Fig. 8. The effect of chitosan viscosity (10%; 10 g l^{-1}) on the colour strength of 0·5% omf dyeings of CI Direct Black 155 on the flesh side of retanned leather.

recorded for the pretreated dyeings (Table 6). The colorimetric data displayed in Table 6 also shows that in the case of low grade chitosan on both the grain and flesh sides of the substrate, there was very little difference in colour between the untreated and pretreated dyeings. The pretreated dyeings were slightly redder than the corresponding untreated dyeings (as evidenced by the higher H° values of the pretreated dyeings) and the extent of intensification of shade furnished by chitosan pretreatment ranged from 0·5 to over 12 ΔE units. The $\%E$ values shown in Table 3 demonstrate that low viscosity chitosan imparted much lower intensification of shade than either the medium or high viscosity grades and that there was little difference between these latter two grades of the polyaminosaccharide in terms of the extent of intensification of shade achieved.

The enhanced uptake of the direct dye imparted by the polyaminosaccharide can, as previously suggested, be attributed to the provision, by chitosan, of additional protonated amino groups within the pretreated substrate. However, the results show that in the cases of medium viscosity chitosan on the flesh side of chrome grain leather and low viscosity chitosan on the grain side of heavily retanned leather, pretreatment with the cationic polymer reduced the colour strength of the dyeing. Furthermore, it is apparent (Table 3) that the extent of the intensification of shade imparted by the cationic polymer to the dyeings of CI Direct Black 155 was, for both chrome grain and heavily retanned leathers, much lower than that obtained for dyeings of CI Acid Yellow 83. These findings may be explained in terms of the effect of the cationic polymer on the diffusional behaviour of the dyes within the pretreated substrates. In view of the very high M_r of the polyaminosaccharide, it can be proffered that its rate and extent of diffusion within both the chrome grain and heavily retanned leathers will be low, which, in turn, will result in the polymer being situated mainly at the periphery of the substrates. Consequently, when the chitosan pretreated leathers are subsequently dyed, it can be suggested that owing to a combination of the high substantivity of the two anionic dyes for the polyaminosaccharide and its physical presence as a 'layer' at the surface of the substrate, the diffusional power of the dyes within the pretreated substrate will be reduced. Further, it can be argued that the direct dye will exhibit higher substantivity towards the polyaminosaccharide treated leathers than the acid dye employed, with the effect that the diffusional behaviour of the direct dye within the pretreated substrate would be lower than that of the acid dye. If such a suggestion were correct then it follows that chitosan pretreatment of chrome grain and retanned leathers should have imparted lower shade intensification to the direct dye, as was indeed found to be the case.

The finding (Table 3) that the intensification of shade furnished by the polyaminosaccharide was greater on the flesh side than the grain side for both of the dyes used on each of the two substrates under consideration can, in view of the well known structural difference between the two sides, be attributed to the chitosan having been adsorbed to a greater extent on the flesh side. Further work is required to determine the relative uptake of the polyaminosaccharide on the flesh and grain sides of the chrome grain and heavily retanned types of leather.

Table 7 reveals that, generally, the wash fastness of both CI Acid Yellow 83 and CI Direct Black 155 on untreated chrome grain leather was higher than on untreated heavily retanned leather; this can be attributed to the fact that in the case of the retanned leather, the extent of diffusion of the dye within the substrate was lower owing to the presence of the anionic retanning agents, with the result that the dye could more easily diffuse out of the dyed, retanned leather than out of the dyed, chrome grain leather during washing. The results in Table 7 also show that the wash fastness of the chitosan pretreated dyeings was, for each dye on both types of leather, identical to that secured for the corresponding dyeings of both types of untreated leather. Thus, with the exception of medium viscosity chitosan on the flesh side of chrome grain leather and low

TABLE 7
Fastness of Dyeings to UK-LE Wash Test

Chitosan viscosity	*Substrate*	*Treatment*	*CI Acid Yellow 83*			*CI Direct Black 155*		
			Ch	*c*	*w*	*Ch*	*c*	*w*
Low	chrome grain	nil	3	4	5	3	3	5
		chitosan	3	3	5	3	3	5
	retanned	nil	5	2–3	5	5	2–3	5
		chitosan	5	2–3	5	5	2–3	5
Medium	chrome grain	nil	3	3–4	5	3	3–4	5
		chitosan	3	3–4	5	3	3–4	5
	retanned	nil	5	3–4	5	5	4	5
		chitosan	5	3–4	5	5	4	5
High	chrome grain	nil	3	4	5	3	3–4	5
		chitosan	3	4	5	3	3–4	5
	retanned	nil	3	3	5	4	3	5
		chitosan	3	3	5	4	3	5

Ch: change in shade of original grain side; *c*: staining of cotton adjacent; *w*: staining of wool adjacent.

viscosity chitosan on the grain side of retanned leather in the case of CI Direct Black 155, although pretreatment with the polyaminosaccharide had increased the colour strength of the dyeings and in the majority of cases the extent of this enhanced colour strength was over 100% (Table 3), the wash fastness of the pretreated dyeings was comparable to that of the untreated dyeings.

CONCLUSIONS

Pretreatment with each of the three grades of chitosan enhanced the smoothness and fullness of both chrome grain and heavily retanned leather and intensified the depth of shade of CI Acid Yellow 83 and also CI Direct Black 155 on both substrates, the latter effect being attributable to the polyaminosaccharide having provided additional dye sites within the leather. The extent of shade intensification furnished by pretreatment was greater for the acid dye than the direct dye, possibly due to the greater substantivity of the direct dye for the cationic polymer within the pretreated leathers. Despite their much greater colour strength, the wash fastness of the pretreated dyeings was comparable to that of their dyed, untreated counterparts.

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APPENDIX 1: PROCESSING OF CHROME GRAIN LEATHER

Wash	Water		35°C	5 min
Drain				
Neutralisation[a]	Water	150%	35°C	40 min
	Parvol PRA	2%		
	Na_2CO_3	0·75%		
Drain				
Rinse			40°C	5 min
Drain				
Pretreatment[b]	Chitosan formate (2·5 g l^{-1}; pH 4)	200%	40°C	30 min
Drain				
Rinse			60°C	10 min
Dye	Water	150%	60°C	
	Dye	0·5%		30 min
	Formic acid (10%)	0·25%		20 min
Drain				
Rinse	Water		60°C	5 min
Fat liquor	Water	150%	60°C	
	Paradol HIR	4%		40 min
Rinse				
Horse-up				
Toggle				
Condition				
Stake/dry				

[a] Final pH 6·0.
[b] Another sample processed without this stage.

APPENDIX 2: PROCESSING OF RETANNED WET-BLUE LEATHER

Wash	Water		35°C	5 min
Drain				
Neutralisation[a]	Water	150%	35°C	40 min
	Parvol PRA	2%		
	Na_2CO_3	0·75%		
Drain				
Rinse			40°C	5 min
Drain				
Retan[b]	Water	100%	40°C	
	Paralene PWG	5%		20 min
	Paramel PA	5%		20 min
	Parvol G	2%		10 min
	Mimosa powder	3%		10 min
Pretreatment[c]	Water	190%	40°C	
	Chitosan formate (10 g l^{-1}; pH 4)	10%		30 min
Drain				
Rinse			60°C	10 min
Dye	Water	150%	60°C	
	Dye	2%		30 min
	Formic acid (10%)	1%		20 min
Drain				
Rinse	Water		60°C	5 min
Fat liquor	Water	150%	60°C	
	Paradol HIR	4%		40 min
Rinse				
Horse-up				
Toggle				
Condition				
Stake/dry				

[a] Final pH 6·0.
[b] Another sample processed without this stage.
[c] Final pH 5·0.