ELSEVIER

Dyes and Pigments, Vol. 31, No. 1, pp. 35–52, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/96 $15.00 + 0.00

0143-7208(95)00094-1

The Use of Chitosan in the Dyeing of Full Chrome Leather with Reactive Dyes

S. M. Burkinshaw & A. N. Jarvis

Specialty Chemical Group, Department of Colour Chemistry, The University,
Leeds LS2 9JT, UK

(Received 18 September 1995; accepted 17 October 1995)

ABSTRACT

Treatment of chrome grain leather with two grades of chitosan enhanced the depth of shade obtained using three difluorochloropyrimidine and three β-sulphatoethylsulphone reactive dyes. The pretreated leather was found to be of a deeper and similar hue to that of its dyed untreated counterpart and, despite its greater colour strength, the wash fastness of the pre-treated dyeings was comparable to that of its dyed untreated counterpart. The greater colour strength of the dyed, pre-treated leather was attributed to increased dye-leather substantivity arising from the presence of the cationic polymer at the surface of the leather. The application of an unreactive, hydrolysed version of one of the dyes to chitosan-treated leather revealed that polyaminosaccharide pretreatment also imparted to the leather additional nucleophilic groups that were available for covalent attachment of the reactive dyes. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The substantivity of anionic dyes towards leather accrues from reversible, non-specific forces such as Van der Waals and ion–ion interaction. However, once the dye molecule has been adsorbed on to the fibrous hide matrix, two options become available depending upon the particular type of anionic dye used. Traditional anionic dyes for leather, such as those represented in the acid and direct application classes, will also subsequently bind to the hide fibres by means of the above general, non-specific and fully reversible forces of interaction; however, as these binding forces are relatively weak and reversible, adsorbed dye molecules in the peripheral regions of the dyed leather will readily diffuse out of the substrate during wet processing giving rise to the dyeings exhibiting only low to moderate wash fastness. Alternatively, anionic reactive dyes will bind covalently to nucleophilic groups within the collagen so that the resultant dyeings display very good to excellent wash fastness properties on leather.

Although reactive dyes generally possess superior wash fastness on leather to that of their non-reactive anionic counterparts, they enjoy relatively little use in the dyeing of chrome leather owing to the constraints imparted by the substrate, namely that the temperature of dyeing is commonly limited to 60°C and the pH of dyeing is limited to between 7 and 8.

Various approaches have been developed to improve the uptake of anionic dyes on leather, the most common being to increase the cationicity of the surface of the leather and thereby enhance the electrostatic attraction operating between the dye and the substrate. Previous papers by one of the present authors demonstrated that the uptake of several non-reactive anionic dyes on to chrome tanned hide powder,[1] chrome grain and heavily retanned leather,[2–6] as well as crusted and dyed-through leather,[7] was increased by pretreating the substrate prior to dyeing with the naturally occurring polyaminosaccharide, chitosan. In this previous work,[1–7] the enhanced substantivity of the anionic dyes towards the pretreated leather was attributed to the presence in chitosan of primary amino groups, which, under the acidic dyeing conditions used, were protonated and thereby provided additional cationic sites for the adsorption and binding of anionic dyes.

In the case of anionic reactive dyes, the colour yield of a dyeing on leather might also be improved by the introduction of additional nucleophilic groups within the substrate that serve as additional binding sites for the reactive dye. As primary amino groups, under aqueous conditions, yield the following equilibria, the exact position of which depends upon the pK_a of the amino group and the pH of the aqueous environment, it was considered that both enhanced cationicity and nucleophilicity might simultaneously be imparted to leather by introducing primary amino groups within the hide:

$$-NH_2 \quad \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \quad -NH_3^+$$

According to the above equilibrium, the protonated amino groups would, under acidic conditions, provide cationic sites that would increase the substantivity of the anionic dyes for the leather, whilst under alkaline conditions the non-protonated amino groups would provide additional nucleophilic groups with which the reactive dyes could react.

In view of the well-known ability of chitosan to enhance the substantivity of anionic, non-reactive dyes on various types of leather[1–7] which accrues from the presence of primary amino groups (of pK_a 6·2[8]) in the polyaminosaccharide, it was decided to investigate the use of chitosan as a means of improving both the extent of uptake and fixation of reactive dyes on chrome grain leather.

EXPERIMENTAL

Materials

Leather

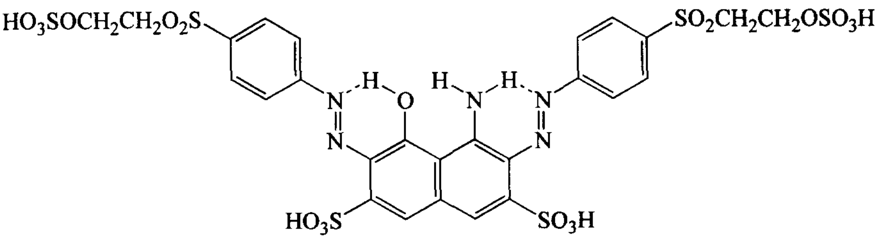
Samples (measuring approximately 10 × 10 cm) of locally processed British bovine, 'wet-blue' leather with a shaved thickness of between 1·4 and 1·5 mm were used. All experiments were performed using samples from the same hide so as to reduce the likelihood of obtaining inconsistant results by using different hides, as leather is notorious for its greatly varying dyeing behaviour.

Cotton

A sample of scoured and bleached, fluorescent-brightener-free, unmercerised cotton fabric (145 g m^{-2}) was used.

Dyes

Six reactive dyes were used, namely three difluorochloropyrimidine *Drimarene* (Sandoz) dyes and three β-sulphatoethylsulphone *Remazol* (Hoechst) dyes (Table 1); all six dyes were commercial samples, kindly supplied by the respective manufacturer. The hydrolysed derivative of CI Reactive Orange 64, prepared as detailed below, was also used. Of the six dyes employed, the structure of only one, namely CI Reactive Black 5 (I) is disclosed in the Colour Index.[9]



I

Chitosan

Two commercial grades of chitosan (Table 2) were kindly supplied by Rigest Trading Ltd. Stock aqueous solutions (2·5 and 10 g $litre^{-1}$) of each of the two grades of chitosan were prepared by dissolution of the appropriate amount of the polyaminosaccharide in 1 litre of aqueous formic acid solution (10 g $litre^{-1}$) at 25°C by stirring (magnetically) for 24 h at room temperature.

TABLE 1
Dyes Used

Commercial name	*CI generic name*
Drimarene Brilliant Orange K-3R	CI Reactive Orange 64
Drimarene Brilliant Red 4BL-CDG	CI Reactive Red 147
Drimarene Brilliant Green K-5BL	CI Reactive Green 21
Remazol Brilliant Blue FB	None ascribed[9]
Remazol Red RB	CI Reactive Red 198
Remazol Black B	CI Reactive Black 5

TABLE 2
Grades of Chitosan Used

Grade	*Source*	*Viscosity (cps)*	*Deacetylation (%)*
Low Viscosity	Shrimp	49	76·4
High Viscosity	Shrimp	2920	85·6

The pH of the resulting chitosan solution was then raised to 4 prior to its application to leather, using 35% aqueous ammonium hydroxide solution.

Fat liquor

A commercial sample of Paradol IG (Yorkshire Chemicals Plc) was employed.

Syntan

A commercial sample of the auxiliary syntan Parvol PRA (Yorkshire Chemicals plc) was used.

Other reagents

Sandozin NIE was obtained from Sandoz UK and 1,4-diazabicyclo[2.2.2]octane (DABCO) from Aldrich.

All other reagents were of general purpose grade.

Procedures

Processing methods

Each of the six reactive dyes (0·5% omf) was applied to untreated and pretreated leather using a Beamhouse Engineering four-drum laboratory cabinet. The methods employed for the application of the six reactive dyes to the 'wet-blue' chrome grain leather are shown in Appendix 1. The hydrolysed derivative of CI Reactive Orange 64 was applied to the wet-blue leather using the method described in Appendix 2.

Preparation of the hydrolysed derivative of CI Reactive Orange 64

CI Reactive Orange 64 (1·0 g), potassium hydroxide (1·00 g) and DABCO (0·1 g) were dissolved in 100 cm^3 of distilled water at room temperature. The solution was then refluxed at 98°C for 12 h and then cooled to room temperature. The extent of hydrolysis was followed using TLC analysis; an aliquot of the dye was spotted on to plastic-backed silica gel sheets and eluted using a mixture of propan-2-ol/butanone/35% aqueous ammonia solution (1 : 1 : 1). At the end of 12 h, the R_f of the hydrolysed derivative was 0·45 compared to the value of 0·6 obtained for the reactive dye prior to hydrolysis. The hydrolysed dye was finally obtained by neutralising the aqueous, alkaline reaction liquor to pH 7 using concentrated hydrochloric acid and adjusting the volume of the solution to 100 cm^3 using distilled water.

Further evidence that the hydrolysed derivative of the dye had been obtained was secured by the following study. Both the parent reactive dye and the hydrolysed derivative (each at 0·5% omf) were applied to cotton using the method shown in Appendix 3. At the end of dyeing, each dyed sample was removed and washed-off using a solution (50 : 1 liquor ratio) of 2 g $litre^{-1}$ Sandozin NIE and 5 g $litre^{-1}$ sodium carbonate at 98°C for 15 min, followed by thorough rinsing in tap water. The ensuing washed-off dyeings were then extracted with 30% aqueous pyridine under reflux for 60 min after which time it was observed that whilst the depth of shade of the sample which had been dyed with the reactive dye was little different to that of the dyed sample prior to 'stripping' with pyridine, the sample which had been dyed with the hydrolysed dye was completely uncoloured. Thus, treatment with aqueous pyridine had completely 'stripped' the hydrolysed dye from the cotton but had removed very little of the reactive dye from the substrate. It was therefore concluded that the above hydrolysis reaction had been successful and that the desired hydrolysed derivative of CI Reactive Orange 64 had been obtained.

Colour measurement

The reflectance values of both the grain and flesh sides of dyed, untreated and dyed, chitosan-pretreated leather samples were measured using a Colorgen CS1100 reflectance spectrophotometer interfaced to an Amstrad personal computer. The viewing conditions used were illuminant D_{65}, 10° standard observer with UV component excluded and specular component included. Each leather sample was measured four times and the average reflectance calculated. The K/S values were calculated from the reflectance values at the λ_{max} of the dyeing and the percentage enhancement of colour strength (%E) achieved by the chitosan pretreatment was calculated using eqn (1) where K_c/S_c and K_u/S_u are the colour strengths of dyed chitosan-pretreated and dyed untreated samples respectively:

$$\%E = \frac{(K_c/S_c - K_u/S_u)}{K_u/S_u} \times 100 \qquad (1)$$

Wash fastness

The fastness of the dyed samples to the UK-LE wash fastness method was determined according to the standard method.[10]

RESULTS AND DISCUSSION

It was found that all chitosan-pretreated samples were considerably smoother and fuller than their corresponding dyed, untreated counterparts; this result concurs with those obtained using non-reactive anionic dyes on chrome grain and heavily retanned leather.[1-7] However, it was also observed that pretreatment with the 10 g litre^{-1} solution of the high viscosity sample of polyaminosaccharide resulted in a deterioration in the levelness of the dyeings.

Difluorochloropyrimidine dyes

Figures 1–3 show the colour strength (K/S) obtained for 0·5% omf dyeings of the grain and flesh sides of untreated leather as well as 2·5 and 10 g litre^{-1} chitosan-formate-pretreated chrome grain leather. Clearly, for each of the three dyes used, 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 (Tables 3–5). It is also evident from Tables 3–5 that chitosan pretreatment yielded dyeings that were, in general, yellower (greener) than those secured without chitosan pretreatment. Tables 3–5 also show that the extent of intensification of shade furnished by chitosan treatment ranged from over 2·7 to nearly 25·9 ΔE units. One factor thought to be responsible for this enhancement of dye uptake imparted by the polyaminosaccharide can, as previously suggested,[1-7] be the provision, by chitosan, of additional amino groups within the pretreated substrate, which, under the acidic conditions (pH 5·5) prevalent during the exhaustion stage of dyeing, would be protonated and thereby result in increased ion–ion interaction operating between the anionic dyes and the pretreated leather.

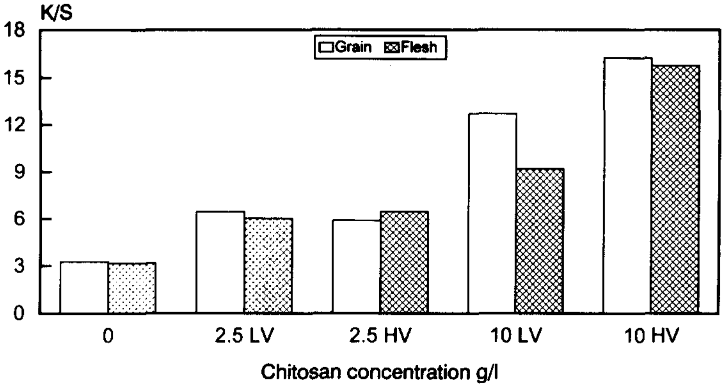


Fig. 1. Colour strength obtained for 0·5% omf dyeings of CI Reactive Orange 64 on untreated and chitosan-formate-pretreated (LV; low viscosity; HV; high viscosity) chrome grain leather.

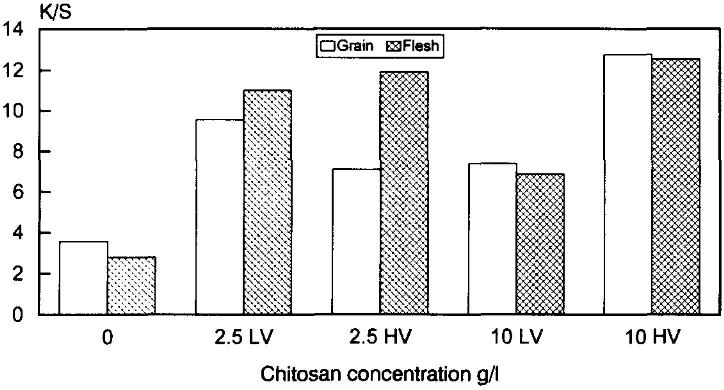


Fig. 2. Colour strength obtained for 0·5% omf dyeings of CI Reactive Red 147 on untreated and chitosan-formate-pretreated (LV; low viscosity; HV; high viscosity) chrome grain leather

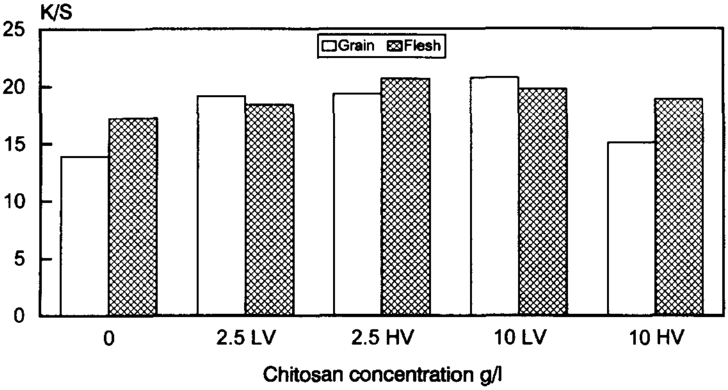


Fig. 3. Colour strength obtained for 0·5% omf dyeings of CI Reactive Green 21 on untreated and chitosan-formate-pretreated (LV; low viscosity, HV; high viscosity) chrome grain leather.

TABLE 3

Colorimetric Data for Untreated and Chitosan-Format-Pretreated Chrome Grain Leather Dyed with CI Reactive Orange 64

Conc (g litre^{-1}) /side	*L**	*a**	*b**	*C*	*h°*	*DE*
Nil / Grain	58·22	24·21	17·37	29·80	35·66	—
2.5 LV / Grain	53·16	32·65	25·30	41·30	37·77	12·64
10 LV / Grain	44·80	24·38	22·07	32·88	42·15	14·22
2.5 HV / Grain	49·32	29·85	21·96	37·06	36·34	11·49
10 HV / Grain	45·47	37·87	35·24	51·73	42·93	25·86
Nil / Flesh	53·94	19·56	12·39	23·15	32·34	—
2.5 LV / Flesh	50·58	26·95	19·08	33·02	35·29	10·52
10 LV / Flesh	44·14	20·14	17·08	26·41	40·30	10·88
2.5 HV / Flesh	46·20	23·68	14·36	27·70	31·23	9·00
10 HV / Flesh	39·01	28·57	21·35	35·67	36·77	19·61

TABLE 4

Colorimetric Data for Untreated and Chitosan-Formate-Pretreated Chrome Grain Leather Dyed with CI Reactive Red 147

Conc (g litre^{-1}) /side	*L**	*a**	*b**	*C*	*h°*	*DE*
Nil / Grain	51·67	26·72	-7·96	27·88	343·42	—
22·5 LV / Grain	40·29	44·44	-4·86	44·71	353·76	21·29
10 LV / Grain	42·63	42·13	-7·39	42·77	350·05	17·87
2·5 HV / Grain	41·98	36·67	-7·83	37·50	347·94	13·89
10 HV / Grain	36·59	46·84	-3·11	46·94	356·20	25·61
Nil / Flesh	52·11	19·31	-8·75	21·20	335·62	—
2·5 LV / Flesh	39·73	31·82	-5·57	32·30	350·07	17·88
10 LV / Flesh	40·86	31·60	-7·00	32·37	347·51	16·76
2·5HV / Flesh	41·38	27·83	-6·78	28·64	346·31	13·84
10 HV / Flesh	32·66	31·41	-4·51	31·73	351·82	23·29

The percentage enhancement of colour strength (%*E*) achieved by pretreatment with the cationic polymer was determined using eqn (1). The %*E* values secured (Tables 6 and 7) for the three difluorochloropyrimidine dyes reveal that of the two types of polyaminosaccharide used, the low viscosity type generally imparted slightly lower intensification of shade than the higher viscosity grade. This can be attributed to the number of amino groups in the polyaminosaccharide increasing with increasing degree of deacetylation, as the higher viscosity grade of chitosan had been deacetylated to a further extent than the lower viscosity, grade (85·6 to 76·4% respectively) (Table 2).

TABLE 5

Colorimetric Data for Untreated and Chitosan-Format-Pretreated Chrome Grain Leather Dyed with CI Reactive Green 21

Conc (g litre^{-1}) /side	*L**	*a**	*b**	*C*	*h°*	*ΔE*
Nil / Grain	42·91	-27·03	-15·83	31·33	210·36	—
2·5 LV / Grain	38·53	-29·73	-17·19	34·34	260·04	5·32
10 LV / Grain	33·81	-25·84	-16·49	30·65	212·54	9·20
2·5 HV / Grain	38·25	-29·66	-17·43	34·40	210·44	5·58
10 HV / Grain	38·06	-32·65	-14·79	35·84	204·36	7·50
Nil / Flesh	39·27	-21·21	-15·83	26·46	216·73	—
2·5 LV / Flesh	38·42	-23·50	-14·60	27·66	211·85	2·73
10 LV / Flesh	37·29	-24·33	-16·02	29·12	213·36	3·70
2·5 HV / Flesh	32·09	-22·28	-12·57	25·58	209·43	7·96
10 HV / Flesh	36·21	-24·39	-14·59	28·42	210·89	4·58

TABLE 6

Percentage Enhancement (%*E*) of Colour Strength Achieved for Difluorochloropyrimidine Dyes, Low Viscosity Chitosan-Formate-Pretreated Leather

Conc. (g litre^{-1}) /side	*CI Reactive Orange 64 147*	*CI Reactive Red 21*	*CI Reactive Green*
2·5 / Grain	95·83	164·9	37·91
10 / Grain	286·7	104·6	49·28
2·5 / Flesh	79·17	276·7	10·65
10/ Flesh	173·0	134·6	18·89

TABLE 7

Percentage Enhancement (%*E*) of Colour Strength Achieved for Difluorochloropyrimidine Dyes, High Viscosity Chitosan-Formate-Pretreated Leather

Conc. (g litre^{-1}) /side	*CI Reactive Orange 64*	*CI Reactive Red 147*	*CI Reactive Green 21*
2·5 / Grain	81·94	101·0	391·4
10 / Grain	401·9	261·8	8·560
2·5 / Flesh	117·9	346·6	16·00
10/ Flesh	433·3	369·8	5·839

β-Sulphatoethylsulphone dyes

Figures 4–6 show the colour strength (K/S) achieved using 0·5% omf of each of the three dyes on the grain and flesh sides of untreated and 2·5 and

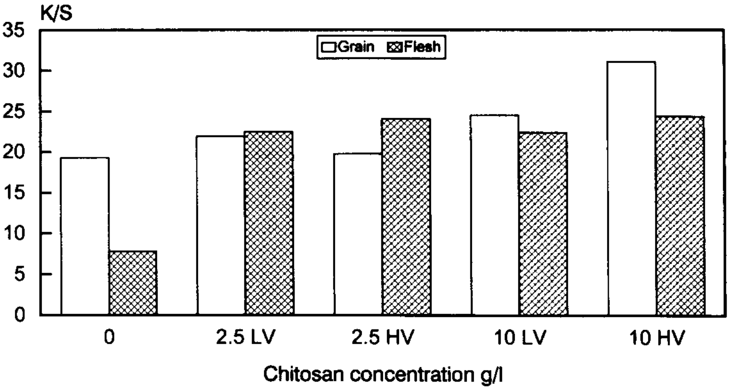


Fig. 4. Colour strength obtained for 0·5% omf dyeings of Remazol Brilliant Blue FB on untreated and chitosan-formate-pretreated (LV; low viscosity; HV; high viscosity) chrome grain leather.

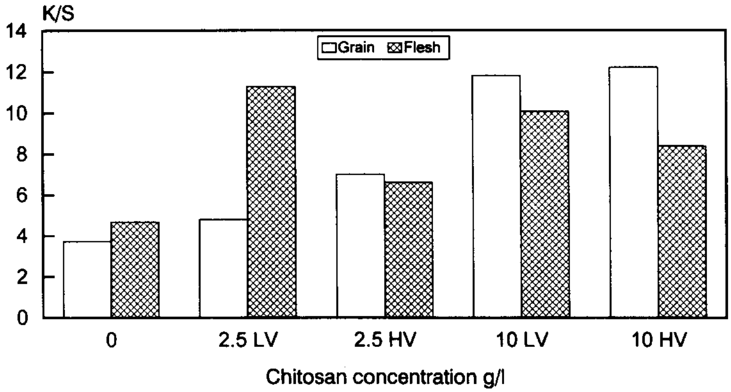


Fig. 5. Colour strength obtained for 0·5% omf dyeings of CI Reactive Red 198 on untreated and chitosan-formate-pretreated (LV; low viscosity, HV; high viscosity) chrome grain leather.

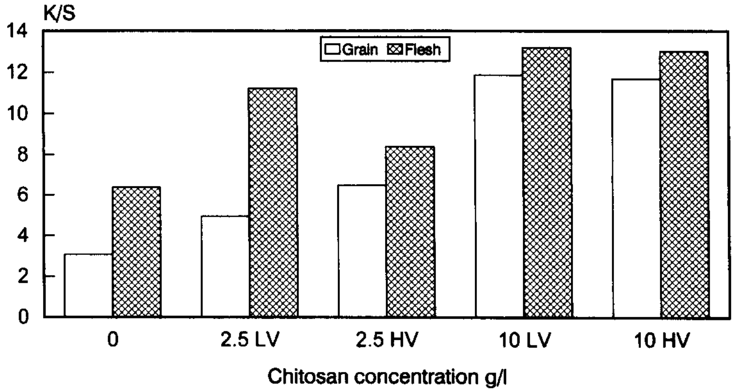


Fig. 6. Colour strength obtained for 0·5% omf dyeings of CI Reactive Black 5 on untreated and chitosan-formate-pretreated (LV; low viscosity, HV; high viscosity) chrome grain leather.

10 g litre^{-1} chitosan-formate-pretreated chrome grain leather. As was observed for the the three difluorochloropyrimidyl dyes, pretreatment with the polyaminosaccharide enhanced the colour strength of the dyeings on both the grain and flesh sides of the substrate; this is reflected in the lower lightness (L*) values of the pretreated dyeings as shown the corresponding colorimetric data (Tables 8–10). It is also evident from Tables 8–10 that chitosan pretreatment yielded dyeings, in the cases of the blue and black dyes, that were bluer than the corresponding dyed, untreated samples and, in the case of the red dye, that were redder than the untreated dyeings. Tables 8–10 also reveal that pre-treatment with the polyaminosaccaride resulted in an intensification of shade that ranged from 3·8 to over 22·5 ΔE units. Unlike the difluorochloropyrimidyl dyes, there appeared to be little difference in the ability of the two grades of chitosan to intensify the depth of shade of

TABLE 8

Colorimetric Data for Untreated and Chitosan-Formate-Pretreated Chrome Grain Leather Dyed with Remazol Brilliant Blue FB

Conc (g litre^{-1}) /side	L^*	a^*	b^*	C	h°	ΔE
Nil / Grain	27·38	27·38	-33·39	33·65	277·12	—
2·5 LV / Grain	24·27	5·45	-29·62	30·12	290·42	5·06
10 LV / Grain	20·51	9·95	-29·85	31·46	288·43	9·65
2·5 HV / Grain	24·58	6·59	-32·23	32·90	281·55	3·88
10 HV / Grain	20·97	10·32	-32·98	34·55	287·38	8·89
Nil / Flesh	34·41	-0·95	-29·16	29·18	268·14	—
2·5 LV / Flesh	24·19	3·56	-23·37	23·64	278·66	16·89
10 LV / Flesh	21·15	7·52	-26·04	27·11	286·11	20·37
2·5 HV / Flesh	29·98	3·03	-27·36	27·53	276·32	10·39
10 HV / Flesh	22·46	7·06	-26·88	27·79	284·71	18·88

TABLE 9

Colorimetric Data for Untreated and Chitosan-Formate-Pretreated Chrome Grain Leather Dyed with CI Reactive Red 198

Conc (g litre^{-1}) /side	L^*	a^*	b^*	C	h°	ΔE
Nil / Grain	49·09	27·46	-4·39	27·81	350·91	—
2·5 LV / Grain	43·08	40·58	-1·28	40·61	358·19	14·77
10 LV / Grain	39·78	40·28	-0·87	40·29	358·76	16·23
2·5 HV / Grain	43·86	42·39	-2·26	42·45	356·95	15·97
10 HV / Grain	37·04	46·10	-0·46	46·10	359·42	22·54
Nil / Flesh	44·52	18·67	-6·12	19·65	341·86	—
2·5 LV / Flesh	36·11	28·69	-1·91	28·76	356·19	13·74
10 LV / Flesh	37·42	30·04	-3·18	30·21	353·96	13·72
2·5 HV / Flesh	40·12	27·51	-3·17	27·69	353·43	10·30
10 HV / Flesh	36·54	28·27	-3·11	28·44	353·72	12·84

TABLE 10
Colorimetric Data for Untreated and Chitosan-Formate-Pretreated Chrome Grain Leather Dyed with CI Reactive Black 5

Conc (g litre^{-1}) /side	L^*	a^*	b^*	C	$h°$	ΔE
Nil / Grain	47·74	–5·43	–8·94	10·46	238·74	—
2·5 LV / Grain	37·46	–3·88	–12·13	12·74	252·26	10·86
10 LV / Grain	25·12	–4·73	–13·26	14·08	250·37	18·55
2·5 HV / Grain	36·30	–5·38	–13·40	14·44	248·12	12·28
10 HV / Grain	29·89	–3·95	–14·07	14·62	254·33	18·64
Nil / Flesh	39·74	–3·63	–8·91	9·62	247·81	—
2·5 LV / Flesh	29·99	–1·67	–9·20	9·35	259·73	9·95
10 LV / Flesh	33·96	–3·43	–9·33	9·94	249·81	5·80
2·5 HV / Flesh	35·93	–2·92	–10·00	10·42	253·71	4·02
10 HV / Flesh	29·99	–1·98	–9·68	9·88	258·46	9·92

the dyeings, as reflected in the very similar percentage colour enhancement (%E) values obtained (Tables 11 and 12).

The results obtained using all six reactive dyes demonstrate that the intensification of shade furnished by the polyaminosaccharide was greater on the flesh side than on the grain side of the leather. This can be attributed to the

TABLE 11
Percentage Enhancement (%E) of Colour Strength Achieved for β-Sulphatoethylsulphone Dyes, Low Viscosity Chitosan-Formate-Pretreated Leather

Conc. (g litre^{-1}) /side	*Remazol Brilliant Blue FB*	*CI Reactive Red 198*	*CI Reactive Black 5*
2·5 / Grain	8·383	32·19	76·58
10 / Grain	21·93	225·4	323·8
2·5 / Flesh	197·8	138·0	76·28
10 / Flesh	192·5	112·7	108·3

TABLE 12
Percentage Enhancement (%E) of Colour Strength Achieved for β -Sulphatoethylsulphone Dyes, High Viscosity Chitosan-Formate-Pretreated Leather

Conc. (g litre^{-1})/side	*Remazol Brilliant Blue FB*	*CI Reactive Red 198*	*CI Reactive Black 5*
2·5 / Grain	6·984	83·94	94·53
10 / Grain	68·16	220·5	251·0
2·5 Flesh	79·10	32·56	31·64
10 Flesh	210·2	68·00	103·9

chitosan having been adsorbed to a greater extent on the flesh side than the grain owing to the well-known structural differences between the two sides.

In order to determine whether chitosan pretreatment had provided not only increased dye substantivity but also increased dye fixation, the dyed samples were subjected to the UK-LE wash fastness test. If chitosan pretreatment had imparted increased colour yield to the dyeings solely due to increased electrostatic interaction operating between the anionic dyes and the protonated amino groups in the polymer and this additionally adsorbed dye was not covalently bound, the dye would readily be removed during washing, with the result that the pretreated dyeings would exhibit lower wash fastness than their corresponding dyed, untreated counterparts. Alternatively, if the additionally adsorbed dye was covalently bound to the pretreated leather, the resulting dyeings would display similar wash fastness to that of their dyed, untreated counterparts. It is evident from the results presented in Tables 13 and 14 that, in general, the wash fastness of the pretreated dyeings was not lower than that of the corresponding untreated dyeings, which indicates that the additionally adsorbed reactive dye was covalently bound to the pretreated substrate.

TABLE 13

Fastness of Dyeings to UK-LE Wash Test, Difluorochloropyrimidine Dyes

Sample	*Ch*		*c*		*w*	
	G	*F*	*G*	*F*	*G*	*F*
Orange [a]	3/4	4	4	3/4	5	5
Red [a]	4	5	5	5	5	5
Green[a]	3	4	4	4	5	5
Orange[b]	3/4	3/4	4	3	5	5
Red[b]	3	4	5	5	5	5
Green[b]	3/4	4	4	4	5	5
Orange[c]	4	4/5	4	3/4	5	5
Red[c]	5	4	5	5	5	5
Green[c]	3/4	4/5	4/5	4	5	5
Orange[d]	3	4	3/4	3	5	5
Red[d]	3/4	4	5	4/5	5	5
Green[d]	4/5	4/5	4/5	4/5	5	5
Orange[e]	4	4/5	4	3/4	5	5
Red[e]	4	4	5	5	5	5
Green[e]	4/5	4/5	4/5	4	5	5

Ch: change in shade of original grain or flesh side; c: staining of cotton adjacent; w: staining of wool adjacent; G: grain layer; F: flesh layer;

[a] Nil chitosan.

[b] 2·5 litre^{-1} low viscosity chitosan.

[c] 10 litre^{-1} low viscosity chitosan.

[d] 2·5 litre^{-1} high viscosity chitosan.

[e] 10 litre^{-1} high viscosity chitosan.

TABLE 14

Fastness of Dyeings to UK-LE Wash Test Ab-sulphatoethylsulphone Dyes

Sample	*Ch*		*c*		*w*	
	G	*F*	*G*	*F*	*G*	*F*
Red[a]	3/4	4	4	3/4	5	5
Blue[a]	4	5	5	5	5	5
Black[a]	3	4	4	4	5	4
Red[b]	3/4	3/4	4	3	5	5
Blue[b]	3	4	5	5	5	5
Black[b]	3/4	4	4	4	5	5
Red[c]	4	4/5	4	3/4	5	5
Blue[c]	5	4	5	5	5	5
Black[c]	3/4	4/5	4/5	4	5	5
Red[d]	3	4	3/4	3	5	5
Blue[d]	3/4	4	5	4/5	5	5
Black[d]	4/5	4/5	4/5	4/5	5	5
Red[e]	4	4/5	4	3/4	5	5
Blue[e]	4	4	5	5	5	5
Black[e]	4/5	4/5	4/5	4	5	5

For explanations see Table 13.

In order to further examine whether the additionally adsorbed reactive dye was bound to the pretreated leather, the hydrolysed derivative of CI Reactive Orange 64 was applied at 0·5% omf to both untreated and pretreated hide, initially using the method described in Appendix 1. However, it was observed that although the samples after dyeing were of reasonable colour strength, all the dye was removed from the dyeings during subsequent rinsing and fat-liquoring. This was not entirely surprising in view of the fact that the hydrolysed version of the reactive dye will be an 'acid' dye that will be bound to the fibre by means of reversible forces of interaction, namely ion–ion forces. Although the structure of CI Reactive Orange 64 has not been disclosed in the Colour Index,[9] the finding that rinsing and fat-liquoring removed all the dye from the dyed substrate implies that in its hydrolysed form, the dye has insufficient wet fastness for use as an 'acid' dye for leather. A further range of dyeings was carried out using the hydrolysed derivative of CI Reactive Orange 64, but, in this case, rather than subjecting the dyeings to rinsing and fat-liquoring after dyeing, the dyed samples were removed from the dyebath at the end of dyeing and allowed to dry in the open air, as described in Appendix 2. The colour strength (*K/S*) values of the dyeings are displayed in Fig. 7, from which it is apparent that pretreatment with chitosan increased the extent of dye uptake on to the substrate. Table 15 shows that the extent of this enhancement in dye uptake secured

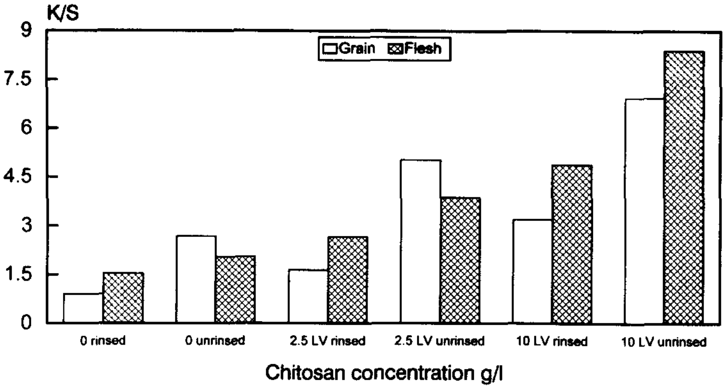


Fig. 7. Colour strength obtained for 0·5% omf dyeings of hydrolysed CI Reactive Orange 64 on untreated and chitosan-format-pretreated (LV; low viscosity; HV; high viscosity) chrome grain leather.

TABLE 15
Percentage Enhancement (%*E*) of Colour Strength Achieved for Chitosan-Formate-Pretreated Leather dyed using 0·5% omf Hydrolysed CI Reactive Orange 64

Sample	*Grain*	*Flesh*
2·5 LV Cht	170·3	146·4
10 LV Cht	509·6	411·9

TABLE 16
Colorimetric Data for Untreated and Chitosan-Format-Pretreated Chrome Leather Dyed with the Hydrolysed CI Reactive Orange 67

Conc (g litre ^{1}) /side	L^*	a^*	b^*	C	h°	ΔE
Nil / Grain	61·42	22·84	19·11	29·78	39·92	—
2·5 LV / Grain	56·55	35·94	34·99	5–0·17	44·23	21·15
10 LV / Grain	50·35	42·43	45·17	61·97	46·79	34·43
Nil / Flesh	63·49	15·99	12·22	20·12	37·39	—
2·5 HV / Flesh	58·93	29·62	24·00	38·12	39·02	18·58
10 HV / Flesh	52·69	36·10	32·67	48·69	42·15	30·65

by pretreatment ranged from slightly under 150% to over 500%, this corresponding to between just over 18 and slightly under 35 ΔE units (Table 16). Table 17 shows that the dyeings of the hydrolysed reactive dye exhibited very low wash fastness and that the fastness of the pretreated dyeings was lower than that of their untreated counterparts. Thus, whilst pretreatment with the polyaminosaccharide enhanced the uptake of the hydrolysed reactive

TABLE 17
Fastness of 0·5% omf Dyeings of Hydrolysed CI Reactive Orange 64 to UK-LE Wash Test

Sample	*Ch* *G / F*	*c* *G / F*	*w* *G / F*
No Cht	2 3	2/3 2/3	5 5
2·5 LV	2 2	2 2	5 5
10 LV	1/2 2	2 2	5 5

For explanations see Table 13.

dye, it can be proffered that the additionally adsorbed dye was bound to the fibre only by reversible forces of interaction, such as ion–ion forces, and, consequently, the dyeings exhibited only poor fastness to washing.

CONCLUSIONS

Pretreatment with each of the two grades of chitosan enhanced the smoothness and fullness of the chrome grain leather and intensified the depth of shade of the three difluorochloropyrimidine and the three β-sulphatoethylsulphone reactive dyes on the substrate. The latter finding can be attributed to the polyaminosaccharide having provided both additional cationic sites for adsorption of the anionic reactive dyes as well as nucleophilic sites for covalent attachment of the dyes. Despite their much greater colour strength, the wash fastness of the pretreated dyeings was comparable to that of their dyed, untreated counterparts.

REFERENCES

1. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **75** (1991) 203.
2. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **76** (1992) 11.
3. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **76** (1992) 54.
4. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **76** (1992) 132.
5. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **76** (1992) 205.
6. Burkinshaw, S. M. & Kitching L., *Dyes and Pigments*, **27** (1995) 17.
7. Burkinshaw, S. M. & Karim, M. F., *J. Soc. Leath. Tech. Chem.*, **77** (1993) 14.
8. Karim, M. F., *PhD Thesis*, Leeds University, 1989.
9. *Colour Index*, Society of Dyers and Colourists, Bradford, 1975.
10. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th edn. Society of Dyers and Colourists, Bradford, 1990.

APPENDIX 1

Processing of 'wet-blue' chrome grain leather with the six reactive dyes

Wash	Water		25°C	5 min
Drain				
Neutralisation[a]	Water	150%	35°C	40 min
	Parvol PRA	2%		
	Na_2CO_3	0·75%		
Drain				
Rinse				
Drain				
Pre-treatment[b]	Water	190%	40°C	
	Chitosan formate	10%		30 min
	(2·5 and 10 g litre^{-1}; pH 4)			
Drain				
Rinse			60°C	5 min
Dye exhaustion[c]	Water	150%	60°C	
	Dye	0·5%		
	NaCl	5%		30 min
	(Drimarenes only)			
Dye-fixation[d]	Na_2CO_3	0·5%	60°C	60 min
Drain				
Rinse			60°C	5 min
Fat liquor	Water	150%	60°C	
	Paradol IG	5%		20 min
Drain				
Rinse				
Horse-up				
Toggle				
Condition				
Stake / dry				

[a] Final pH 6·0.
[b] Another sample processed without this stage.
[c] pH 5·5.
[d] To give a pH of 8.

APPENDIX 2

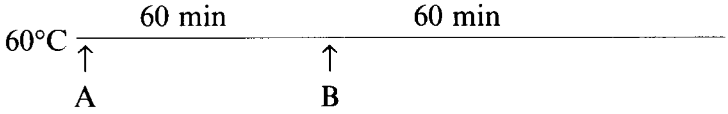
Processing of 'wet-blue' chrome grain leather with hydrolysed form of CI Reactive Orange 64

Wash	Water		25°C	5 min
Drain				
Neutralisation[a]	Water	150%	35°C	40 min
	Parvol PRA	2%		
	Na_2CO_3	0·75%		
Drain				
Rinse				
Drain				
Pre-treatment[b]	Water	190%	40°C	
	Chitosan formate (2·5 and 10 g litre^{-1}; pH 4)	10%		30 min
Drain				
Rinse			60°C	5 min
Dye exhaustion[c]	Water	150%	60°C	
	Dye	0·5%		
	NaCl	5%		30 min
Dye-fixation[d]	Na_2CO_3	0·5%	60°C	60 min
Drain				
Dry				

[a] Final pH 6·0.
[b] Another sample processed without this stage.
[c] pH 5·5.
[d] To give a pH of 8.

APPENDIX 3

Application method for the dyeing of cotton with the hydrolysed form of CI Reactive Orange 64



A 0·5% omf dye
80 g litre^{-1} NaCl

B 10 g litre^{-1} 0·1 M aqueous NaOH solution