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The dyeing of silk Part 1: Low temperature application of solubilised sulphur dyes using sodium thioglycolate

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ABSTRACT

Four C.I. Solubilised Sulphur dyes were applied to cultivated silk fabric using sodium thioglycolate at pH 7, for 30 min at 60 °C in the absence of electrolyte. Medium/deep shades were obtained that displayed good/excellent fastness to washing at 40 °C and little or no sensitivity to oxygen bleach fading. The dry rub fastness of the dyeings ranged from moderate to good whilst the wet rub fastness varied from poor to moderate; light fastness of the 10% omf dyeings varied from low to moderate. The mild application conditions used had little effect on the tensile strength of the fabric.

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1. Introduction

Although silk fibre is synthesised by various organisms (silkworms, spiders, scorpions, etc.) [1,2] the most famous and most characterised is silkworm cocoon silk, as exemplified by 'domestic' or 'cultivated' silk (obtained from the domesticated silkworm, *Bombyx mori*) and 'wild' or 'tussah' silk obtained from the larvae of several species of the *Antheraea* moth [3]. Silk, which has been the most revered and prized of all textile fibres for ~5000 years, is not only the finest and longest of all natural fibres [4], but also is probably the strongest natural fibre with tensile properties comparable to that of synthetic fibres (Table 1) [5]. In this context, interest in the remarkable physical attributes of spider silk continue to attract research attention, as reflected by current interest in the genetic engineering of spider silk proteins by bacteria [6]. Cultivated silk's characteristic soft handle and excellent drape are attributable to the fibre's triangular cross-section, smooth surface and fineness, characteristics that also are responsible for the fibre's unique light reflection and lustre.

Owing to its hydrophilic nature and amphoteric properties, silk displays substantivity towards virtually every dye type [7,8], of which the most commonly used are acid (both non-metallised and metallised variants) and direct dyes; basic dyes are also mainly employed on the basis of their brilliance of shade [8]. However, because of the fineness of cultivated silk fibres (1–2.4 dtexpf; 12–30 μm diameter [9]) and their smooth, triangular section, the dyeing behaviour of such fibres resembles that of microfibre synthetic fibres (0.3–1 dtexpf) [10] insofar as more dye is required to obtain a given depth of shade on cultivated silk than that required for conventional dtex wool or nylon fibres [3] and dyeings display typically low fastness to wet treatments [8]. Many workers, over many decades, have sought to improve/optimise the dyeing of silk by, for example, recourse to optimised dye selection and application methods [8], optimised dye structures [11,12], redox systems [13,14], aftertreatment [15], pre-treatment [16], grafting [17] and dyeing in the presence of supercritical CO_2 [18,19]; in this context, many researchers have focussed on the application of reactive dyes to silk as a means of achieving dyeings of high wet fastness [8,18,20–33].

This paper concerns approaches to furnish moderate/deep shades of good wet fastness on cultivated silk; this first part of the paper describes the application of solubilised sulphur dyes to cultivated silk at low temperature using sodium thioglycolate as reducing agent.

Sulphur dyes are used on cellulosic fibres and their blends to provide economical, mostly black, brown, blue and green shades, in medium/heavy depths. Whilst the fastness properties of sulphur dyes on such fibres can vary, widely, between dyes [34], generally,

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Table 1
Comparison of some physical properties of silk with other fibres [5].

Fibre	Tenacity/N tex^{-1}	Breaking extension/%	Work of rupture/J g^{-1}	Initial modulus/ N tex^{-1}
Silk	0.38	23	60	7.3
Cotton	0.19–0.45	5.6–7.8	5.1–15	3.9–7.3
Wool	0.14	43	38	2.1
Nylon 6/66	0.29–0.84	20–46	77–100	0.6–9
Polyester	0.47–0.82	13–37	60–119	6–9

sulphur dyeings on cotton and other cellulosic fibres display typically moderate to good fastness to light and wet treatments, although they are characteristically offer poor resistant to laundering in the presence of oxygen-based (e.g. sodium perborate or sodium percarbonate) detergent formulations. In terms of their usage on cellulosic fibres, whilst sulphur dyes accounted for only ~7% in terms of market value in 2003 [35], the annual production volume of C.I. Sulphur Black 1 (~80,000 tonnes [36]), in each of its various commercial forms (i.e. C.I Leuco, C.I. Solubilised and C.I. Sulphur) remains one of the world's highest for a single dye, some 110 years after its commercial introduction [37,38]. Although the structure of many sulphur dyes is unknown, it is generally accepted that they comprise macromolecular compounds in which aromatic chromophores are linked via di- and polysulphide bonds ($-S_n-$). In the Colour Index [39], four classes of sulphur dye are identified, although, as *C.I. Condense Sulphur* dyes (Na–*S*-alkyl- or -*S*-arylthiosulfate derivatives) are no longer made, these are not considered here:

- *C.I. Sulphur dye*: as these dyes are water-insoluble and display low substantivity towards cellulosic fibres, they are reduced under alkaline conditions and the resulting, substantive, *leuco* form of the dye is applied to the substrate from alkaline solution.
- *C.I. Leuco Sulphur dye*: these comprise the water-soluble, pre-reduced, leuco form of the parent C.I. Sulphur dye in the presence of a small, stabilising excess of reducing agent.
- *C.I. Solubilised Sulphur dye*: these water-soluble, thiosulfate derivatives ($D-S-SO_3^-$) are applied to cellulosic fibres in the presence of alkali and reducing agent.

For each of these three types of sulphur dye, at the end of dyeing, the leuco derivative is oxidised in situ to reform the parent, insoluble sulphur dye within the fibre. In the Colour Index, C.I. Sulphur dyes and C.I. Leuco Sulphur dyes share the same C.I. Constitution Number whereas a different number is allocated to the related C.I. Solubilised Sulphur dye variant [39]. The advantage of solubilised sulphur dyes compared to the other two types of sulphur dye is that the dyes do not require solubilising prior to dyeing in the presence of reducing agent and alkali.

A variety of reducing systems can be used to apply sulphur dyes to cellulosic fibres [40–42], the most common being Na_2S and NaHS, although alternative reduction systems have been investigated in recent times [41], such as glucose [40] and other reducing sugars [43], as well as thiourea dioxide [44]; electrochemical reduction techniques, including direct cathodic reduction [36,45–47] and electrocatalytic hydrogenation under alkaline conditions [48] have also been described. Oxidation can be undertaken using a variety of oxidants, including traditional types such as $Na_2Cr_2O_7/CH_3COOH$, as well as H_2O_2 and other compounds [34,40].

Sulphur dyes enjoy little, if any, usage on silk as evidenced by the small number of publications in this area [49,50]. This is partly because other dye classes (e.g. acid) provide adequate coloration and, more importantly, as the high temperature, strongly alkaline, reducing conditions that are used for the application of the dyes to cellulosic fibres, impart fibre damage. In this context, Luo [49] observed that the uptake of several C.I. Leuco Sulphur dyes on *B. mori* fabric was not great enough for practical coloration because the dyebath could not be made sufficiently alkaline and the dyeing temperature could not be raised high enough to achieve an adequate level of substantivity without imparting substantial fibre damage. However, this worker proposed that if a dyeing process could be developed that was effective at low temperatures and under weakly alkaline conditions, so as to minimise fibre damage, sulphur dyeing offered potential advantages, in terms of levelness, repeatability and fastness. Wang et al. [50] prepared a water-soluble variant of C.I. Sulphur Brown 10 by its reaction with 3-chloro-2-hydroxypropyltrimethylammonium chloride to overcome the problems of fibre damage posed by the use of alkali and reducing agent. The ensuing, water-soluble, cationic sulphur dye exhibited good uptake on degummed silk when applied in the absence of reducing agent, under neutral pH conditions at 98 °C; 4% omf dyeings displayed good fastness to both rubbing and light. In contrast, very low uptake was observed for the parent sulphur dye (C.I. Sulphur Brown 10) when applied after reduction using Na_2S; the cationic sulphur dye had no adverse effect on the substrate [50].

Sodium thioglycolate ($HSCH_2CO_2Na$) aka sodium salt of mercaptoacetic acid) is a moderate nucleophile [51] and enjoys usage in the pharmaceutical and cosmetic industries. Being a moderate strength reducing agent with relatively good stability to air oxidation, an investigation into its use in the dyeing of silk fabric with solubilised sulphur dyes was undertaken. The effect of the dyeing process on the tensile strength of the fibre was determined.

2. Experimental

2.1. Materials

Degummed *B. mori* silk fabric twill (45 g m^{-2}), obtained from Whaley's (Bradford) Ltd., was scoured prior to use by treatment at 80 °C for 15 min in an aqueous solution (distilled water) comprising 2 g dm^{-3} *Sandozin NIE* using a liquor ratio of 50:1. The scoured fabric was rinsed thoroughly in tap water and allowed to dry in the open air. The four dyes shown in Table 2 were generously provided by DyStar and were selected for use on the basis that they were typical examples of commercial C.I. Solubilised Sulphur dyes. The non-ionic detergent *Lanapex R* (Uniqema) was used to remove surplus dye from the oxidised dyeings. $HSCH_2CO_2Na$ was obtained from Aldrich; all other chemicals used were of general laboratory grade.

McIlvaine buffer solutions [52] were used to control the pH of the dyebaths. For pH values 3–8, the quantities of Na_2HPO_4 and citric acid shown in Table 3 were dissolved in 1 l of distilled water. For pH 9, a solution was made by dissolving Na_2HPO_4 (5 g) and KH_2PO_4 (1 g) in 1 l of distilled water; the pH of the ensuing solution was 7.6, this being adjusted to pH 9 by the addition of an appropriate volume of 0.1 M aq NaOH solution.

Table 2
Dyes used.

Commercial name	C.I. Generic name
Hydrosol Blue R	C.I. Solubilised Sulphur Blue 7
Hydrosol Brown BT	C.I. Solubilised Brown 16
Hydrosol Brilliant Red BCL	C.I. Solubilised Sulphur Red 11
Hydrosol Green GB	C.I. Solubilised Sulphur Green 2

Table 3
pH 3–8 buffer composition [52].

pH	0.2 M Na_2HPO_4	0.1 M Citric acid
3	20.5	79.5
4	38.6	61.4
5	51.5	48.5
6	63.2	36.8
7	82.4	17.6
8	97.3	2.7

2.2. Methods

2.2.1. Dyeing

All dyeings were carried out in sealed, stainless steel dyepots of 300 cm^3 housed in Roaches *Pyrotec 'S'* laboratory-scale dyeing machine, using the method shown in Fig. 1. At the end of dyeing, the samples were removed, rinsed in tap water for 10 min and then oxidised.

2.2.2. Oxidation

The rinsed dyeings were treated in sealed, stainless steel pots of 300 cm^3 capacity, housed in a *Roaches Pyrotec 'S'* laboratory dyeing machine at 60 °C in a bath containing 2 g dm^{-3} 35% H_2O_2 and 1 g dm^{-3} acetic acid (pH 4–5), for 15 min, using a liquor ratio of 50:1. At the end of oxidation, the samples were rinsed in tap water and either were washed-off using the method described below or were allowed to dry in the open air.

2.2.3. Wash-off

The rinsed, oxidised dyeings were treated in sealed, stainless steel pots of 300 cm^3 capacity, housed in a *Roaches Pyrotec 'S'* laboratory dyeing machine using the method shown in Fig. 2, employing a 50:1 liquor ratio. After wash-off, the samples were rinsed in tap water and allowed to dry in the open air.

2.2.4. Colour measurement

The CIE colorimetric co-ordinates and f_k values were calculated from the reflectance values at the appropriate λ_{max} for each dyeing, measured using a *Datacolor Spectroflash 600* spectrophotometer under illuminant D_{65}, employing a 10° standard observer with UV component included and specular component excluded. The samples were folded so as to realise four thicknesses.

2.2.5. Fastness

Wash fastness testing was performed according to both the ISO 105 C06/A2C (40 °C) and UK-TO test (ISO 105 C09) methods [53]. Colour fastness to rubbing was performed according to the ISO 105 X12 test method [53] and the light fastness of the dyeings was determined according to ISO 105 B02 [53].

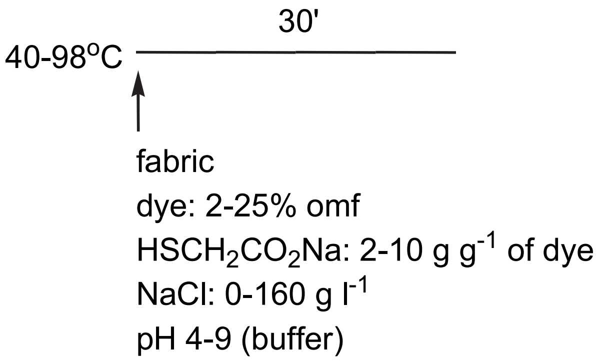

Fig. 1. Dyeing method.

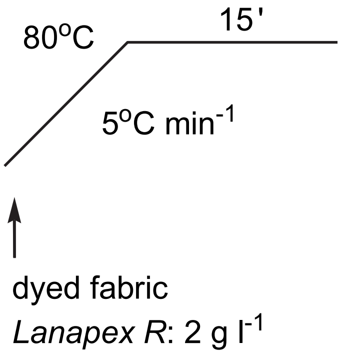

Fig. 2. Oxidation method.

2.2.6. Tensile strength

Tensile strength testing was performed in accordance with ISO 2062 (1995).

2.2.7. Standard deviation

The Microsoft Excel STDEV function was applied to a randomly produced set of washed-off, 10% omf dyeings which had been carried out using 10 g g^{-1} $HSCH_2CO_2Na$, at pH 7 and 60 °C, in the absence of NaCl; the ensuing standard deviations were: L^* 0.0873; a^* 0.3943; b^* 0.6828; C^* 0.6907; $h°$ 0.5951 and f_k 0.8139.

3. Results and discussion

3.1. Effect of reducing agent concentration

In the context of the traditional application of sulphur dyes to cellulosic fibres, for optimum results, a successful reducing agent has to maintain the dye in its reduced form throughout dyeing. An appropriate amount of reducing agent is vital since an insufficient quantity results in off-shades and will lower the overall fastness of dyeings whereas an abundance of reductant can 'over-reduce' the dyes [54]. In addition to that required to reduce the dye, a proportion of the reducing agent will be absorbed by the substrate and a further proportion will be oxidised by air; hence, the reducing agent has to satisfy several criteria in order to be employed successfully in sulphur dyeing.

Table 4 shows the effect of $HSCH_2CO_2Na$ concentration (2–10 g g l^{-1}) on the colorimetric data obtained when 10% omf dyeings of C.I. Solubilised Sulphur Blue 7 had been undertaken at 60 °C and pH 7 in the absence of NaCl. Results are shown for the dyeings both before and, in the cases of 4–10 g g^{-1} $HSCH_2CO_2Na$, after, the dyeings had been washed-off to remove surplus, oxidised dye. In the case of the dyeings obtained prior to wash-off, Table 4 reveals that the lightness, hue and chroma of the two samples which had been obtained using 2 and 2.5 g g^{-1} reducing agent were very similar to each other. Although the hue and lightness of the four dyeings which had been obtained using 3, 4, 5 and 10 g g^{-1} reducing agent were, again, very similar to each other, their chroma varied, but not greatly. It is apparent from the results in Table 4 that, colorimetrically, two sets of dyeing were obtained namely, one that comprised samples obtained when 2 and 2.5 g g^{-1} reductant had been employed and one that included dyeings secured using 3, 4, 5 and 10 g g^{-1} $HSCH_2CO_2Na$. The difference in colour between the two sets of non-washed-off dyeings (i.e. 2, 2.5 vs 3, 4, 5, 10 g g^{-1} $HSCH_2CO_2Na$) is displayed in

Table 4
Effect of pH on colorimetric data obtained using C.I. Solubilised Sulphur Blue 7.

Dye/% omf	Temperature/°C	pH	NaCl/g l^{-1}	$HSCH_2CO_2Na$/g g^{-1} of dye	Wash-off	L^*	a^*	b^*	C^*	$h°$
10	60	7	0	2	Before	24.7	5.5	−12.4	13.6	293.7
				2.5	Before	24.6	5.5	−12.6	13.7	293.5
				3	Before	22.9	6.6	−18.9	20.0	289.2
					After	23.0	8.3	−20.9	22.4	291.6
				4	Before	22.3	6.3	−17.7	18.8	289.7
					After	23.0	8.5	−22.0	23.6	291.0
				5	Before	22.3	6.5	−18.0	19.1	289.9
					After	22.6	8.5	−21.1	22.7	291.9
				10	Before	22.3	6.0	−17.7	18.7	288.7
					After	22.3	6.0	−17.7	18.7	288.7
10	40	7	0	10	After	24.2	6.7	−19.1	20.3	289.4
	60					22.3	6.0	−17.7	18.7	288.7
	80					22.5	6.3	−18.5	19.5	288.7
	98					22.2	5.7	−17.0	18.0	288.5
10	60	4	0	10	After	27.1	5.2	−20.1	20.7	284.5
		5				24.6	5.5	−18.9	19.7	286.1
		6				22.6	5.0	−14.7	15.6	288.8
		7				22.3	6.0	−17.7	18.7	288.7
		8				22.1	5.8	−18.0	18.9	287.8
		9				23.5	5.6	−16.9	17.8	288.4
10	60	7	0	10	After	22.3	6.0	−17.7	18.7	288.7
			10			22.3	5.5	−14.5	15.5	290.7
			20			22.4	5.2	−12.8	13.8	291.9
			40			22.3	5.1	−12.7	13.7	291.8
			80			22.5	5.7	−17.2	18.1	288.5
			160			22.7	5.5	−15.3	16.2	289.7
2	60	7	0	10	After	39.8	4.9	−23.9	24.5	281.6
4						33.4	6.3	−24.4	25.2	284.4
6						27.7	6.7	−23.5	24.4	285.9
8						24.3	6.6	−20.7	21.7	287.7
10						22.3	6.0	−17.7	18.7	288.7
12						20.8	6.2	−15.9	17.1	291.4
15						20.2	4.7	−11.6	12.5	292.2
20						19.4	4.0	−7.8	8.7	297.4
25						19.0	3.0	−3.7	4.8	309.3

the corresponding a^* vs b^* plot of Fig. 3 from which it is apparent that the dyeings obtained using ≥ 3 g g^{-1} reducing agent were bluer and of higher chroma. The lower L^* values observed for the non-washed-off samples obtained using ≥ 3 g g^{-1} $HSCH_2CO_2Na$ (Table 4) are reflected in the corresponding f_k values of the dyeings (Fig. 4) from which it is evident that the colour strength of the samples achieved when 2 and 2.5 g g^{-1} reducing agent had been employed, were virtually identical and that an increase in $HSCH_2CO_2Na$ concentration to 3 g g^{-1} resulted in an increase in f_k; however, colour strength remained almost constant when 4, 5 and 10 g g^{-1} reducing agent had been used. The observed low f_k values achieved using both 2 and 2.5 g g^{-1} reductant can be attributed to low dye exhaustion that resulted from insufficient reduction of the solubilised sulphur dye. The higher colour strength obtained for the 3 g g^{-1} dyeing implies that increased dye reduction and, therefore, higher dye exhaustion occurred; the greater colour strength secured for the 4, 5 and 10 g g^{-1} $HSCH_2CO_2Na$, which also were virtually similar in magnitude for the three concentrations of reductant used, suggest that higher and comparable levels of dye reduction and, thus dye exhaustion, had been achieved at each of the three concentrations of $HSCH_2CO_2Na$ used. However, values of colour strength obtained after the dyeings had been washed-off reveal that this was not the case.

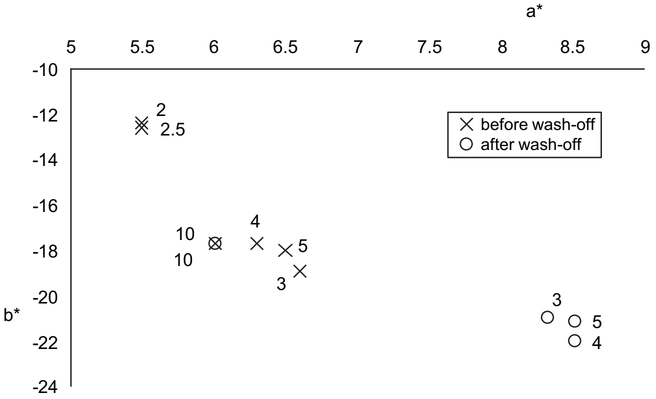

Fig. 3. a^* vs b^* plot for 10% omf C.I. Solubilised Sulphur Blue 7 dyeings obtained using 2, 2.5, 3, 4, 5 and 10 g g^{-1} $HSCH_2CO_2Na$ (60 °C; pH 7; 0 g l^{-1}NaCl).

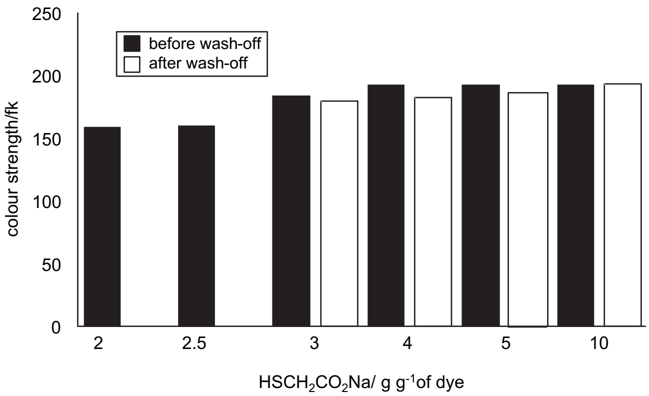

Fig. 4. Effect of $HSCH_2CO_2Na$ concentration on the colour strength of 10% omf C.I. Solubilised Sulphur Blue 7 dyeings (60 °C; pH 7; 0 g l^{-1} NaCl).

As the colour strength of the dyeings which had been obtained using 2 and 2.5 g g^{-1} $HSCH_2CO_2Na$ was markedly lower than that obtained when greater amounts of reducing agent were used and, as the colour of these two particular dyeings was appreciably different to that of their counterparts (Table 4 and Fig. 3), it was decided to not wash-off these particular dyeings. In the case of the washed-off, 3, 4, 5 and 10 g g^{-1} $HSCH_2CO_2Na$ dyeings, Fig. 4 reveals that the colour strength of the washed-off samples gradually increased with increasing amount of reducing agent used over the range 3–5 g g^{-1} reductant. The finding that the f_k values of the washed-off dyeings were lower than those of the corresponding samples prior to wash-off, can be attributed to unreduced dye having been removed from the dyeings during the hot, aqueous wash-off process. Interestingly, only when a concentration of 10 g g^{-1} $HSCH_2CO_2Na$ had been used, did no dye loss occur as a result of wash-off, which implies that such a concentration of reductant was able to fully reduce the dye. Presumably, this is the reason why not only were both the hue and chroma of the non-washed-off and washed-off 10 g g^{-1} dyeings were identical (Table 4 and Fig. 3) but also, why the 10 g g^{-1} washed-off dyeings were different in hue and chroma to that of their washed-off 3, 4 and 5 g g^{-1} counterparts.

Based on the findings discussed above, that concentrations of reductant $<$10 g g^{-1} were unable to fully reduce the dye, subsequent investigations into the effects of pH, temperature and electrolyte concentration on dyeing using C.I. Solubilised Sulphur Blue 7 were carried using 10 g g^{-1} $HSCH_2CO_2Na$.

3.2. *Effect of dyeing temperature*

Fig. 5 and Table 4 show the effect of dyeing temperature on the colour strength and colorimetric data, respectively, for washed-off, 10% omf dyeings of C.I. Solubilised Sulphur Blue 7 obtained using 10 g g^{-1} $HSCH_2CO_2Na$ and pH 7 in the absence of NaCl. An increase in dyeing temperature from 40 to 60 °C increased the colour yield of the dyeings (Fig. 5), which can be explained in terms of the higher temperature having resulted in greater dye reduction and/or penetration of reduced dye in the fibre. Further increase in dyeing temperature from 60 to 98 °C did not result in increased colour strength (Fig. 5), indicating that, under the particular pH and reductant concentration conditions, maximum dye reduction and penetration had been achieved. The effect of temperature on the f_k values obtained for the four dyeings are reflected in the corresponding L^* values (Table 4). In the context of the colorimetric data recorded for the samples, Table 4 shows that both the hue and chroma of each of the four dyeing varied, with the samples becoming progressively duller with increasing temperature; this is clearly evident in the corresponding a^* vs b^* plot (Fig. 6).

3.3. *Effect of pH*

Fig. 7 and Table 4 show the effect of pH on the colour strength and colorimetric data, respectively, of 10% omf dyeings of C.I. Solubilised Sulphur Blue 7 obtained using 10 g g^{-1} $HSCH_2CO_2Na$, at 60 °C and 0 g l^{-1} NaCl. Colour strength progressively increased with increasing pH over the range 4–8 before decreasing at pH 9 (Fig. 7); these results are reflected in the L^* values obtained for the dyeing (Table 4). The findings that the f_k values (and the corresponding L^* values) obtained at pH 6, 7 and 8 were not too dissimilar and that these values were much higher than those secured at pH 4, 5 and 9, suggest that neither high nor low pH favours dye reduction/exhaustion. In terms of the colorimetric data secured for the dyeings, Table 4 and Fig. 8 show that dyeings carried out under acidic conditions were slightly greener than those which had been carried out at pH 7, 8 and 9.

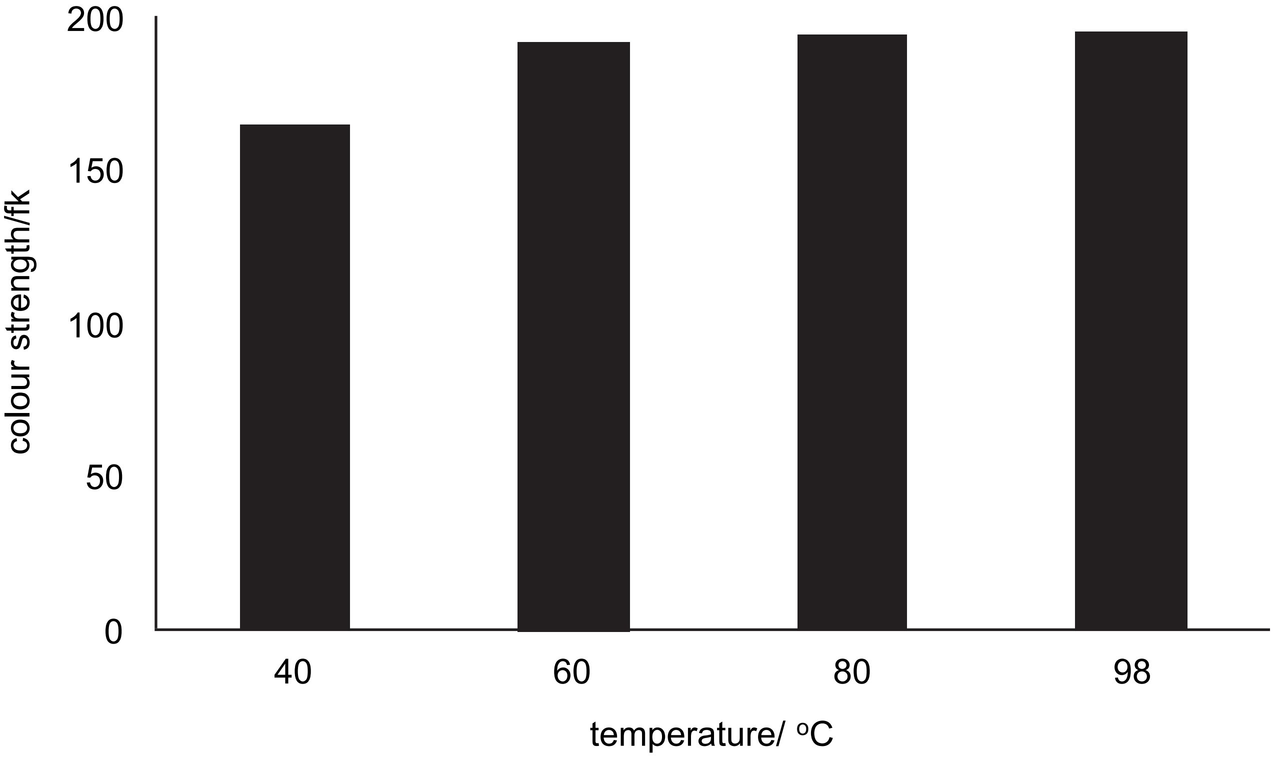

Fig. 5. Effect of temperature on the colour strength of 10% omf C.I. Solubilised Sulphur Blue 7 dyeings (pH 7; 10 g g^{-1} $HSCH_2CO_2Na$; 0 g l^{-1} NaCl).

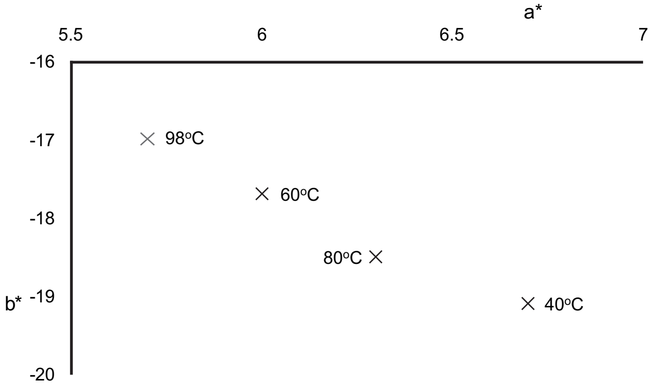

Fig. 6. a^* vs b^* plot for 10% omf C.I. Solubilised Sulphur Blue 7 dyeings obtained at 40, 60, 80 and 98 °C (pH 7; 10 g g^{-1} $HSCH_2CO_2Na$; 0 g l^{-1}NaCl).

3.4. Effect of electrolyte

Table 4 and Fig. 9 show the effect of NaCl concentration on the colorimetric data and colour strength, respectively, of 10% omf dyeings of C.I. Solubilised Sulphur Blue 7 obtained using 10 g g^{-1} $HSCH_2CO_2Na$, at 60 °C and pH 7. Fig. 9 shows that increasing the amount of NaCl used from 0 to 160 g l^{-1} brought about a gradual but not especially large, reduction in colour strength, which may be attributed to electrolyte-induced aggregation of the leuco form of the dye, as is well-known in the case of vat dyes when applied to cellulosic fibres. In terms of the colour of the dyeings, increasing amounts of NaCl markedly reduced chroma (Fig. 10 and Table 4) but had only a comparatively small effect on hue, which can be attributed to dye aggregation.

3.5. Dye build-up

It is apparent from Fig. 11 that the colour strength of washed-off dyeings of C.I. Solubilised Sulphur Blue 7 increased with increasing amount of dye applied over the range 2–25% omf, when dyeing had been carried out at 60 °C and pH 7 in the absence of NaCl, using 10 g g^{-1} $HSCH_2CO_2Na$. The finding that the f_k values increased progressively over the concentration range studied implies that saturation of the fabric was not achieved. The corresponding colorimetric data (Table 4) reveal that on-tone dye build-up occurred insofar as the dyeings became gradually duller with increasing amount of dye applied, this being clearly illustrated in the a^* vs b^* plot (Fig. 12), which is characteristic of dye aggregation.

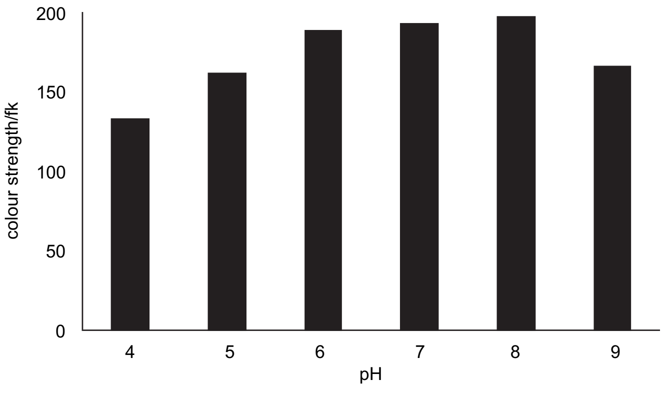

Fig. 7. Effect of pH on the colour strength of 10% omf C.I. Solubilised Sulphur Blue 7 dyeings (10 g g^{-1} $HSCH_2CO_2Na$; 0 g l^{-1}NaCl; 60 °C).

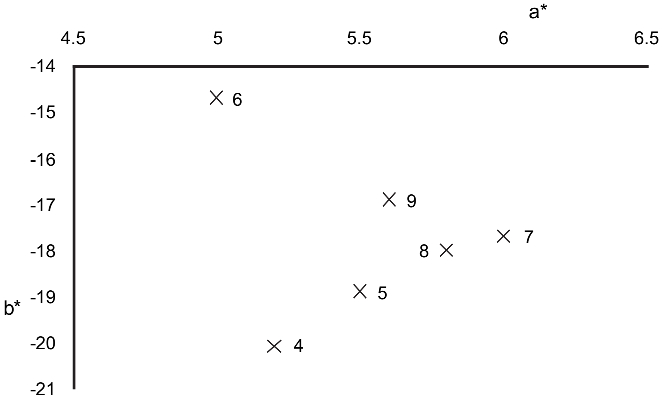

Fig. 8. a^* vs b^* plot for 10% omf C.I. Solubilised Sulphur Blue 7 dyeings obtained using pH 4, 5, 6, 7, 8 and 9 (10 g g^{-1} $HSCH_2CO_2Na$; 0 g l^{-1}NaCl; 60 °C).

3.6. Other dyes

The colour strength of 10% omf dyeings of C.I. Solubilised Sulphur Red 11, C.I. Solubilised Brown 16 and C.I. Solubilised Sulphur Green 2, obtained at pH 7, 60 °C, 10 g g^{-1} $HSCH_2CO_2Na$ and in the absence of NaCl, are displayed in Fig. 13; for comparison, the colour strength of the corresponding dyeing obtained using C.I. Solubilised Sulphur Blue 7 is included. Although dyeings of different colour strength were obtained and, whilst this can be expected for a given range of dyes on a particular substrate, further work is required to identify commercial sulphur dyes that display greater similarity in terms of colour strength when applied to silk using sodium thioglycolate.

3.7. Fastness testing

From a domestic laundering perspective, silk fabrics are considered as ‘delicate’ and, typically, are washed at low temperatures (e.g. 30 or 40 °C) either by hand or, more rarely, by machine, often employing specialised detergent formulations. Accordingly, it was decided to subject 10% omf dyeings to the ISO CO6/A2C wash test, which is carried out at 40 °C. Table 5 shows the fastness results obtained for the four solubilised sulphur dyes to the ISO CO6/A2C test from which it is apparent that each of the dyeings displayed good/excellent fastness insofar as dyeings underwent a relatively modest change in shade as a result of being subjected to the single, standard, 40 °C wash test. The extent of this shade change can be

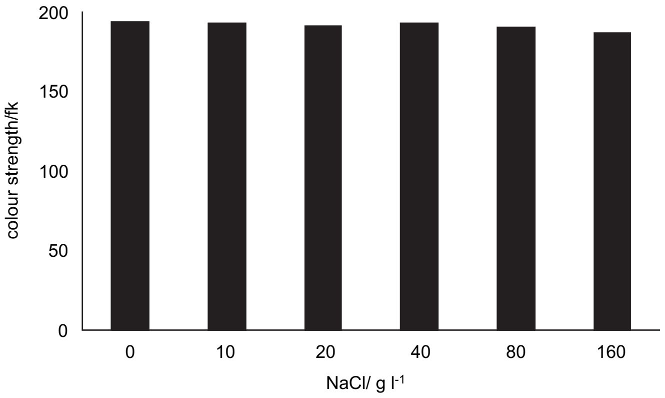

Fig. 9. Effect of NaCl concentration on the colour strength of 10% omf C.I. Solubilised Sulphur Blue 7 dyeings (10 g g^{-1} $HSCH_2CO_2Na$; 60 °C; pH 7).

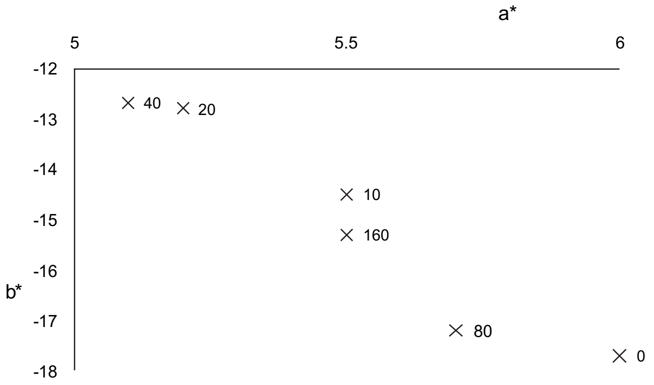

Fig. 10. a^* vs b^* plot for 10% omf C.I. Solubilised Sulphur Blue 7 dyeings obtained using 0, 10, 20, 40, 80 and 160 g l^{-1} NaCl (10 g g^{-1} $HSCH_2CO_2Na$; 60 °C; pH 7).

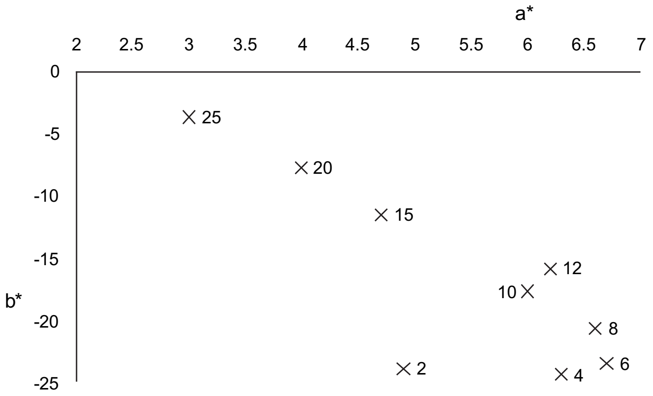

Fig. 12. a^* vs b^* plot for 2, 4, 6, 8, 10, 12, 15, 20 and 25% omf C.I. Solubilised Sulphur Blue 7 dyeings (10 g g^{-1} $HSCH_2CO_2Na$; 60 °C; pH 7; 0 g l^{-1} NaCl).

gauged by the corresponding colour difference (ΔE) values obtained for the dyeings before and after washing (Table 6). The observation (Table 5) that vagrant dye deposited mostly on the adjacent cotton multifibre strip material reflects the inherent substantivity of this particular dye class for cellulosic fibres. As mentioned in the introduction, whilst the structure of many sulphur dyes is unknown, it is generally accepted that they comprise macromolecular compounds in which di- and polysulphide bonds link aromatic chromophores. It is also widely accepted that for each of the three types of sulphur dye available (sulphur, leuco and solubilised), at the end of dyeing, oxidation converts the leuco derivative in situ to the parent, insoluble sulphur dye. Theoretically, if each of the four dyes used in this work were present in the fibre as insoluble macromolecules, the fastness of the dyeings to washing should have been excellent, with little, if any shade change or staining of adjacent materials. However, the results in Tables 5 and 6 clearly show that although the fastness of the dyeings to washing at 40 °C was very good, dye loss nevertheless occurred and vagrant dye was adsorbed onto adjacent material. It is well-known that sulphur dyes are susceptible to oxidative attack with cleavage of the disulphide bond [55] and, despite the fact that little is known of the structure of sulphur dyes, it is suggested [56,57] that some dyes may contain sulfonic acid groups introduced by oxidation; in addition, H_2O_2, which was employed as oxidant in this work, is capable of over-oxidising [58,59] thiolate groups in sulphur dyes, resulting in a degree of water solubility [59] and low wet fastness [56,58] in the case of some dyes. This therefore explains both the shade changes and staining of adjacent materials that were observed as result of wash testing (Tables 5 and 6).

As mentioned earlier, sulphur dyes on cellulosic fibres display generally poor resistance to laundering in the presence of oxygen-based bleaches. The UK-TO test method was introduced to diagnose the susceptibility of dyed substrates to activated, oxygen bleaches that are present in domestic detergents [60,61]. This particular single test is designed to impart colour loss to a dyed sample that is similar to that imparted by 10–15 commercial launderings; according to the test, when the colour difference between a dyed sample before and after testing is <4 ΔE units, the sample is considered to be resistant to oxygen bleach fading whilst a ΔE higher >4 units indicates bleach sensitivity. Table 5 shows the extent of both shade change and staining of adjacent materials that occurred when the 10% omf dyeings were subjected to the UK-TO test method. It is apparent that each of the dyeings underwent a change in shade and vagrant dye was deposited on many of the adjacent multifibre strip materials, especially cotton and nylon. These findings can be explained by assuming that under the reasonably severe, oxidative conditions of the UK-TO method, oxidation of the dyes resulted in lower M_r compounds of increased hydrophilicity/solubility that were able to desorb readily during testing. The observed staining of adjacent materials, which was greatest in the cases of cotton, nylon and wool, can be attributed to the anionicity of such sulphur dye oxidation products coupled with the hydrophilic, absorptive character of the three fibre types. From the corresponding ΔE values obtained for the dyeings before and after UK-TO testing (Table 6), it can be concluded that, according to the assessment criteria of the test method, each of the

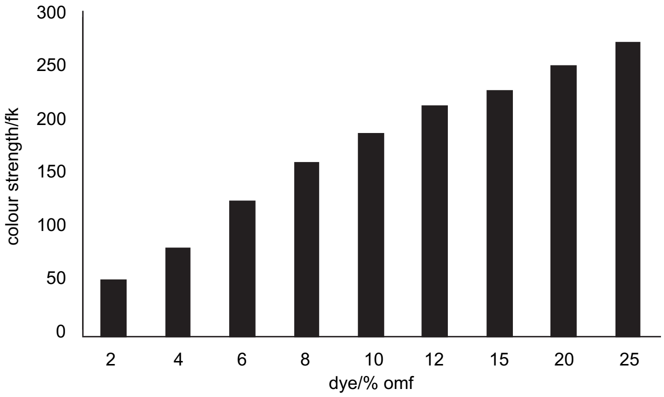

Fig. 11. Build-up obtained for C.I. Solubilised Sulphur Blue 7 (10 g g^{-1} $HSCH_2CO_2Na$; 60 °C; pH 7; 0 g l^{-1} NaCl).

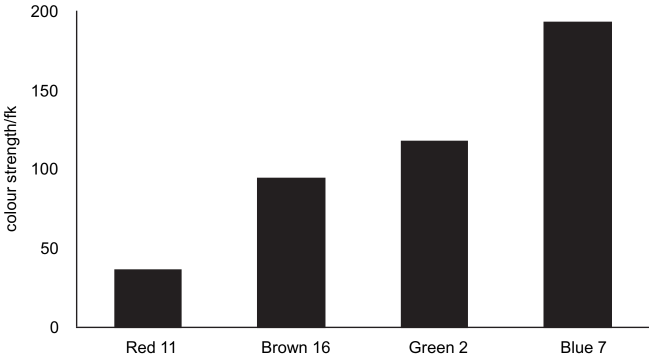

Fig. 13. Colour strength of 10% omf dyeings (10 g g^{-1} $HSCH_2CO_2Na$; 60 °C; pH 7; 0 g l^{-1} NaCl).

Table 5
Fastness of washed-off 10% omf dyeings obtained at 60 °C, pH 7 using 10 g g^{-1} $HSCH_2CO_2Na$ and 0 g l^{-1} NaCl.

C.I. Solubilised Sulphur	ISO CO6/C2							UK-TO						
	Change in shade	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	Change in shade	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Red 11	4/5	5	4/5	5	5	5	5	3/4	4/5	3	3/4	4/5	5	4
Green 2	4/5	5	5	5	5	5	5	4/5	5	4/5	4/5	5	5	5
Blue 7	4/5	5	4/5	5	5	5	5	4/5	5	4	4	4/5	4/5	4
Brown 16	4/5	5	4/5	4/5	5	5	5	4	4/5	4	4	4/5	4/5	4

Table 6
Colorimetric data for washed-off 10% omf dyeings obtained at 60 °C, pH 7 using 10 g g^{-1} $HSCH_2CO_2Na$ and 0 g l^{-1} NaCl.

C.I. Solubilised Sulphur	Test method	L^*	a^*	b^*	C^*	$h°$	f_k	ΔE
Red 11	None	47.2	24.3	−2.5	24.4	354.1	36.5	–
	C06/C2	48.3	25.8	−1.8	25.8	356.0	34.6	1.0
	UK-TO	53.2	21.8	−6.0	22.6	344.6	24.5	4.2
Green 2	None	35.1	−22.3	−7.1	23.4	197.6	117.3	–
	C06/C2	36.4	−22.8	−7.8	24.1	198.9	107.3	0.8
	UK-TO	38.8	−20.6	−11.2	23.4	208.5	87.7	3.7
Blue 7	None	22.3	6.0	−17.7	18.7	288.7	210.6	–
	C06/C2	21.3	7.2	−18.4	19.7	291.4	209.1	1.4
	UK-TO	22.9	8.6	−20.8	22.5	292.6	181.5	3.0
Brown 16	None	35.5	18.4	7.7	19.9	22.7	94.8	–
	C06/C2	36.4	18.3	7.4	19.7	22.1	89.5	0.5
	UK-TO	39.0	16.3	11.9	20.1	36.1	65.7	4.0

Table 7
Fastness of washed-off 10% omf dyeings obtained at 60 °C, pH 7 using 10 g g^{-1} $HSCH_2CO_2Na$ and 0 g l^{-1} NaCl.

C.I. Solubilised Sulphur	Rub		Light
	Dry	Wet	
Blue 7	3–4	2	4–5
Green 2	4–5	3–4	4
Brown 16	4	3	4
Sulphur Red 11	4	3–4	2–3

Table 8
Tensile strength of undyed and washed-off dyeings of C.I. Solubilised Sulphur Blue 7, obtained at 60 °C, pH 7 using 10 g g^{-1} $HSCH_2CO_2Na$ and 0 g l^{-1} NaCl.

Dye/omf (%)	Tensile strength/mN
Nil	152.4 ± 1.3
2	152.8 ± 1.7
5	151.0 ± 2.7
10	149.2 ± 3.2

four dyes can be judged as displaying little or no sensitivity to oxygen bleach fading.

The results shown in Table 7 reveal that the dry rub fastness of washed-off dyeings ranged from moderate to good whilst the wet rub fastness varied from poor to moderate; the light fastness of the 10% omf dyeings varied from low to moderate (Table 7). The findings that the rub and light fastness varied for the four dyes used were not surprising as it is well-known [34] that the fastness properties of sulphur dyes varies, widely between dyes.

3.8. Tensile strength

As mentioned, sulphur dyes enjoy little usage on silk, not only because other dye classes provide acceptable coloration but also because the high temperature, strongly alkaline, reducing conditions that are used for the application of the dyes to cellulosic fibres, damage the delicate silk fibre, which is sensitive to degradation under hot, aqueous, alkaline conditions [9,49]. The results in Table 8 show that dyeing silk with 2, 5 and 10% omf C.I. Solubilised Sulphur Blue 7 at pH 7, 60 °C, using 10 g g^{-1} $HSCH_2CO_2Na$ in the absence of NaCl reduced the tensile strength of the fibre. It is also apparent that this reduction in tensile strength increased with increasing amount of dye applied, as this also increased the amount of reducing agent used. However, the extent of tensile strength reduction was relatively small (Table 8) which can be attributed to the relatively mild dyeing conditions used, namely pH 7 and 60 °C.

4. Conclusions

Medium/deep shades were obtained on cultivated silk fabric by applying the four C.I. Solubilised Sulphur dyes using sodium thioglycolate, at pH 7, for 30 min at low temperature (60 °C), without the need of electrolyte. The relatively mild application conditions used had a small effect on the tensile strength of the fabric. The wash fastness of 10% omf dyeings to washing at 40 °C was good/excellent for all dyeings and the dyes showed little or no sensitivity to oxygen bleach fading. The dry rub fastness of the dyeings ranged from moderate to good whilst the wet rub fastness varied from poor to moderate; light fastness of the 10% omf dyeings varied from low to moderate.

References

[1] Matsumoto A, Kim H, Tsai I, Wang X, Cebe P, Kaplan D. In: Lewin M, editor. Silk. Boca Raton: Taylor & Francis; 2007.
[2] Kaplan D. Silk in Kirk–Othmer encyclopedia of chemical technology. New York: Wiley; 2004.
[3] Das S. The preparation and processing of tussah silk. Journal of the Society of Dyers and Colourists 1992;108:481–6.
[4] Hseih Y-L. Fibers in Kirk–Othmer encyclopedia of chemical technology, Weinham. Wiley-VCH; 2004.
[5] Hearle JWS, Buschow KHJ, Robert WC, Merton CF, Bernard I, Edward JK, et al. Textile fibers: a comparative overview. Oxford: Elsevier; 2001. p. 9100-9116.
[6] Winkler S, Kaplan DL, Buschow KHJ, Robert WC, Merton CF, Bernard I, et al. Silk produced by engineered bacteria. Oxford: Elsevier; 2001. p. 8615-8618.
[7] De Giorgi MR, Cerniani A, Colonna GM, Bianchi AS. Thermodynamic affinity of acid dyes on silk. Dyes and Pigments 1991;15(1):47–55.
[8] Blackburn RS, Burkinshaw SM, Gandhi K. The dyeing of silk with reactive dyes part 1 – Realan dyes. Advances of Colour Science and Technology 1999;2:109–13.
[9] Hatch KL. Textile science. Minneapolis: West Publishing; 1993.
[10] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. Glasgow: Chapman and Hall; 1995.
[11] De Giorgi MR, Carpignano R. Design of dyes of high technical properties for silk by a chemometric approach. Dyes and Pigments 1996;30(1):79–88.
[12] Giorgi MR, Cerniani A, Carpignano R, Savarino P. Design of high fastness acid dyes for silk: a chemometric approach. Journal of the Society of Dyers and Colourists 1993;109(12):405–10.
[13] Burkinshaw SM, Lu JG. Dyeing in the presence of free radical initiators: Part 7: the dyeing of silk fibres. Dyes and Pigments 1994;26(1):1–13.
[14] Luo J. Low-temperature dyeing of real silk fabrics using a redox system. Journal of the Society of Dyers and Colourists 1991;107(3):117–20.
[15] Feiz M, Radfar Z. Improvement of wash fastness of direct and acid dyes applied to silk by aftertreatment with syntan, syntan/cation, and full backtan processes. Iranian Polymer Journal (English Edition) 2006;15(4):299–305.
[16] Weibin X, Jinxin H, Shuilin C, Guoqiang C, Taozhi P. Modification of silk with aminated polyepichlorohydrin to improve dyeability with reactive dyes. Coloration Technology 2007;123(2):74–9.

[17] Prachayawarakorn J, Boonsawat K. Physical, chemical, and dyeing properties of *Bombyx mori* silks grafted by 2-hydroxyethyl methacrylate and methyl methacrylate. Journal of Applied Polymer Science 2007;106(3):1526–34.
[18] Schmidt A, Bach E, Schollmeyer E. The dyeing of natural fibres with reactive disperse dyes in supercritical carbon dioxide. Dyes and Pigments 2003;56 (1):27–35.
[19] van der Kraan M, Fernandez Cid MV, Woerlee GF, Veugelers WJT, Witkamp GJ. Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes. The Journal of Supercritical Fluids 2007;40(3):470–6.
[20] Barker P, Johnson A. The application of monochlorotriazinyl reactive dyes to silk. Journal of the Society of Dyers and Colourists 1973;89(6):203–8.
[21] Meyer U, Wang J-Z, Xia Y, Yang J-Z, Zollinger H. Dye-fibre bond stabilities of some reactive dyes on silk. Journal of the Society of Dyers and Colourists 1986;102(1):6–11.
[22] Agarwal D, Sen K, Gulrajani ML. Formation of crosslinks in silk by bifunctional reactive dyes: effect on solubility and mechanical properties. Journal of the Society of Dyers and Colourists 1996;112(11):321–4.
[23] Agarwal D, Sen K, Gulrajani ML. Application of heterobifunctional reactive dyes on silk. Journal of the Society of Dyers and Colourists 1996;112(1):10–6.
[24] Zhang S, Li J, Yang J. Haloacetyl reactive dyes-synthesis and application to silk. Journal of the Society of Dyers and Colourists 1995;111(6):195–8.
[25] Gulrajani ML. Dyeing of silk with reactive dyes. Review of Progress in Coloration and Related Topics 1993;23(1):51–6.
[26] Dohmyou M, Shimizu Y, Kimura M. Simultaneous dyeing of silk and synthetic fibres with sulphatoethylsulphonyl reactive disperse dyes. Journal of the Society of Dyers and Colourists 1990;106(12):395–7.
[27] Agarwal D, Sen K, Gulrajani ML. Dyeing of silk with bifunctional reactive dyes: the relationship between exhaustion and fixation. Journal of the Society of Dyers and Colourists 1997;113:174–8 (5-6).
[28] Rastogi D, Sen K, Gulrajani M. Photofading of reactive dyes on silk and cotton: effect of dye—fibre interactions. Coloration Technology 2001;117 (4):193–8.
[29] Youssef YA, Mousa AA. Structure-reactivity studies of a new polyfunctional disulphide bis(ES-MCT/SES) reactive dye applied to silk. Coloration Technology 2002;118(6):325–9.
[30] Mousa AA. Synthesis and application of a polyfunctional bis(monochlorotriazine/sulphatoethylsulphone) reactive dye. Dyes and Pigments 2007;75(3):747–52.
[31] Bae J-S, Park J, Koh J, Kim S. Dyeing and fastness properties of a reactive disperse dye on PET, nylon, silk and N/P fabrics. Fibers and Polymers 2006;7(2):174–9.
[32] Mousa AA, Youssef YA. Dyeing of nylon 6 and silk fabrics with a model disulphide bis(ethylsulphone) reactive disperse dye. Coloration Technology 2003;119(4):225–9.
[33] Seu G. The dyeing of silk with heterocyclic disperse azo-dyes. Dyes and Pigments 1993;23(4):267–73.
[34] Senior C. Dyeing with sulphur dyes. In: Shore J, editor. The dyeing of cellulosic fibres. Bradford: Society of Dyers and Colourists; 1995.
[35] Roessler A, Jin X. State of the art technologies and new electrochemical methods for the reduction of vat dyes. Dyes and Pigments 2003;59 (3):223–35.
[36] Bechtold T, Turcanu A, Schrott W. Electrochemical reduction of CI sulphur black 1—correlation between electrochemical parameters and colour depth in exhaust dyeing. Journal of Applied Electrochemistry 2008;38(1):25–30.
[37] Zollinger H. Color chemistry: syntheses, properties and applications of organic dyes and pigments, Weinham. Cambridge: VCH; 1991.
[38] Burkinshaw SM, Collins GW. Aftertreatment to reduce the washdown of leuco sulphur dyes on cotton during repeated washing. Journal of the Society of Dyers and Colourists 1998;114:165–8 (5-6).
[39] Colour Index. Bradford: Society of Dyers and Colourists; 1971.
[40] Shore J, editor. Colorants and auxiliaries, Vol. 2: auxiliaries. 2nd ed. Bradford: Society of Dyers and Colourists; 2002.
[41] Bozic M, Kokol V. Ecological alternatives to the reduction and oxidation processes in dyeing with vat and sulphur dyes. Dyes and Pigments 2008; 76(2):299–309.
[42] Senior C. Chapter 6. In: Shore J, editor. Cellosics dyeing. Bradford: Society of Dyers and Colourists; 1995.
[43] Blackburn RS, Harvey A. Green chemistry methods in sulfur dyeing: application of various reducing d-sugars and analysis of the importance of optimum redox potential. Environmental Science & Technology 2004;38(14):4034–9.
[44] Czajkowski W, Misztal J. The use of thiourea dioxide as reducing agent in the application of sulphur dyes. Dyes and Pigments 1994;26(2):77–81.
[45] Bechtold T, Turcanu A, Burtscher E, Bobleter O. Schwefelfarbstoffe in der Ausziehfarberei – Reduktion durch indirekte Elektrolyse. Textilveredlung 1997;32:204–9.
[46] Bechtold T, Burtscher E, Turcanu A. Direct cathodic reduction of Leuco Sulfur Black 1 and Sulfur Black 1. Journal of Applied Electrochemistry 1998;28 (11):1243–50.
[47] Bechtold T, Turcanu A, Brunner H, Schrott W. Model calculations to optimise multi-cathode flow through electrolysers: direct cathodic reduction of C.I. Sulphur Black 1. Journal of Applied Electrochemistry 2009;39(10):1963–73.
[48] Comisso N, Mengoli G. Catalytic reduction of vat and sulfur dyes with hydrogen. Environmental Chemistry Letters 2003;1(4):229–32.
[49] Luo J, Cao J. Low temperature dyeing of real silk fabrics with liquid sulphur dyes. Journal of the Society of Dyers and Colourists 1997;113(2):67–9.
[50] Wang W, Zhang S, Yang J. A water soluble cationic sulphur dye for the dyeing of silk. Coloration Technology 2005;121(5):245–8.
[51] Jocelyn PC. Biochemistry of the SH group. London: Academic; 1972.
[52] Vogel AI. Textbook of quantitative inorganic analysis. London: Longmans; 1944.
[53] Standard methods for the determination of the colour fastness of textiles and leather. Bradford: Society of Dyers and Colourists; 1990.
[54] Aspland R. Textile dyeing and coloration. Raleigh: AATCC; 1997.
[55] Field L. In: Oae S, editor. Organic chemistry of sulphur. New York: Plenum; 1977.
[56] Burkinshaw SM, Collins GW. Aftertreatments to improve the wash fastness of sulphur dyeings on cotton. Dyes and Pigments 1995;29(4):323–44.
[57] Aspland JR. Textile chemist and colorist. Sulphur Dyes for Cellulosic Fibers 1970;2:229.
[58] Clarke D, Senior C. Dyeing with sulphur dyes. In: Preston C, editor. The dyeing of cellulosic fibres. Bradford: Society of Dyers and Colourists; 1986.
[59] Heid C, Holobek K, Klein R. 100 Jahre Schwefelfarbstoffe. Melliand Textilberichte 1973;54:1314.
[60] Phillips D, Duncan M, Jenkins E, Bevan G, Lloyd J, Hoffmeister J. Development of a test to predict colour fading of cotton fabrics after multi-cycle laundering with a bleach-containing domestic detergent. Journal of the Society of Dyers and Colourists 1996;112(10):287–93.
[61] Phillips D, Taylor J, Lakhanpal R, Scotney J, Bevan G. Colour fastness of optionally aftertreated acid levelling and milling dyes on nylon 6.6 during washing in an activated oxygen-bleach containing detergent. Part 1: fading observed in the UK-TO test and after repeated domestic laundering. Coloration Technology 2001;117(3):147–51.