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The dyeing of silk: Part 3 the application and wash-off of modified vinyl sulfone dyes

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Silk was dyed using three modified vinyl sulfone reactive dyes designed for use on nylon fibres. The extents of exhaustion and fixation of the dyes were markedly dependent on pH and temperature; low application pH (pH 3 and 4) favoured dye exhaustion but disfavoured dye fixation whilst the use of pH 9 resulted in low fixation and exhaustion. Optimum dye fixation was obtained at pH 7–8, as a corollary of the presence of nucleophilic $-NH_2$ groups in the substrate and conversion of the masked dyes to the corresponding reactive vinyl sulfone variant. The marked temperature-dependence of dye exhaustion and fixation observed at pH 5–9 was considered to be indicative of a rate-determined, kinetic effect that was fixation-related rather than exhaustion-driven. Of the four wash-off methods examined, none removed sufficient dye from the dyeings and, although two commercial detergent formulations were most effective for the first few wash tests, this advantage decreased with increasing number of wash tests.

1. Introduction

Cultivated silk, obtained from the domesticated silkworm, *Bombyx mori*, is arguably the most prized of all textile fibres. The fibre's characteristic soft handle and excellent drape are attributable to its triangular cross-section, smooth surface and fineness, characteristics that also are responsible for the fibre's unique lustre. However, because of these unique physical characteristics, the dyeing behaviour of silk fibre resembles that of microfibre synthetic fibres [1], as large amounts of dye are required to achieve moderate/deep shades and such dyeings display typically low fastness to wet treatments. Considerable efforts have been extended over many decades to optimise/improve the dyeing of silk [2] and much attention has focussed on the use of reactive dyes as a means of obtaining dyeings of high wet fastness. However, as no exclusive reactive dye range has been developed for silk, the various publications pertaining to the dyeing and printing of silk with reactive dyes therefore relate to the use of reactive dyes intended for other fibres. In this context, whilst the commercial introduction of reactive dyes for cellulosic fibres in the mid 1950's spawned a bewildering array of commercial dye ranges for such fibres, in comparison, very few commercial reactive dye ranges have been marketed for use on wool and even less focus has attended the development of commercial reactive dye ranges for polyamide fibres. In the latter context, the *Eriofast* (Huntsman) [3] and the *Stanalan* (DyStar) ranges [4] of dyes for nylon fibres are relatively recent introductions.

This paper concerns approaches to achieve dyeings of good wet fastness on cultivated silk. The first part of the paper [2] showed that four C.I. Solubilised Sulphur dyes displayed good/excellent fastness to washing at 40 °C whilst the second part described the effects of various aftertreatments on the fastness, to repeated washing at 40 °C, of both non-metallised and pre-metallised acid dyes on silk. This part of the paper concerns the application of *Stanalan* (DyStar) modified vinyl sulfone dyes to silk.

Although vinylsulfone (VS) reactive dyes, in the form of the sulphuric acid esters of β-hydroxyethylsulfone (ie the β-sulfatoethylsulfone derivative: $-SO_2CH_2CH_2OSO_3H$) first appeared commercially in 1952 as two members of the *Remalan* (Hoechst) range of dyes for wool [5], the commercial and technological exploitation of VS dyes really only began in earnest in 1958, with the introduction of the *Remazol* (Hoechst) range of dyes for cellulosic fibres. Usually, VS dyes are marketed as *blocked* or *masked* VS derivatives (**1**), which, under appropriate conditions during dyeing, gradually activate to the reactive VS form (**2**) which then undergoes reaction with suitable nucleophiles within the substrate. VS dyes are commonly sold [6] in the β-sulfatoethylsulfone form (**1**; $X = OSO_3Na$) which, under the action of OH- in the case of

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Table 1
pH 3–8 buffer composition.

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

cellulosic fibre dyeing, eliminates bisulphate, generating the VS variant. The use of appropriate masking groups for VS dyes is advantageous as it not only prolongs storage life and dye solubility [6] but also determines the conditions (eg pH and temperature) under which the elimination step proceeds, which, in turn, influence dye exhaustion, levelness, fixation, etc. One such masking group that has been employed in the *Hostalan* (Hoechst) range of VS dyes for wool is *N*-methyltaurine (**1**; X = $N(CH_3)CH_2CH_2OSO_3H$) [7]. The *Stanalan* (DyStar) range of modified vinyl sulfone dyes is a component of a dyeing system that utilises a modified nylon 6,6 fibre [8] and has been shown to provide both dyeings [8] and prints [9] of high wet fastness on both conventional decitex and microbre nylon 6,6.

$$\underset{\mathbf{1}}{\text{D-SO}_2\text{CH}_2\text{CH}_2\text{-X}} \longrightarrow \underset{\mathbf{2}}{\text{D-SO}_2\text{CH=CH}_2}$$

This paper describes concerns not only the exhaustion and fixation characteristics of members of the *Stanalan* (DyStar) range of modified vinyl sulfone dyes on silk, but also considers the effectiveness of four different wash-off methods in terms of the change in depth of shade during repeated washing at 40 °C.

2. Experimental

2.1. Materials

The, degummed, scoured, *B. mori* silk fabric twill described previously [2] was used. The three dyes used namely, *Stanalan Yellow MFFR*, *Stanalan Dark Red MFFN* and *Stanalan Brilliant Blue MFFR* (no C.I. Generic Names ascribed [10]) were generously provided by DyStar. The two non-ionic detergents, *Sandozin NIE* (alkylene oxide [11]; Clariant) and *Lanapex R* (a mixture of modified phosphate esters with polyphosphates [12]; Uniqema) were kindly provided by the respective maker. All other chemicals used were of laboratory grade purity.Table 1

McIlvaine buffer solutions [13] were used to control the pH of the dyebaths. For pH values 3 to 8, the quantities of Na_2HPO_4 and citric acid shown in Table 2 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.

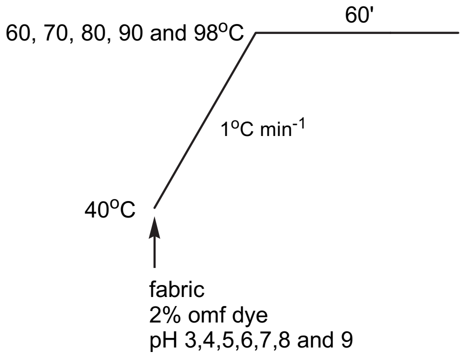


Fig. 1. Dyeing method.

2.2. Methods

2.2.1. Dyeing

All dyeings (2% omf) were carried out in sealed stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec 'S'* laboratory dyeing machine using a liquor ratio of 40:1 using the method shown in Fig. 1.

2.2.2. Dye exhaustion

The extent of dye exhaustion that occurred as a function of both dyeing temperature (60, 70, 80, 90 and 98 °C) and pH (3, 4, 5, 6, 7, 8 and 9) was determined by measuring the absorbance of an appropriately diluted aliquot of cool dye solution, using a *Phillips PU 8700* spectrophotometer equipped with a 1 cm path length quartz cell, at the λ_{max} of the dye. By reference to an appropriate calibration curve, the percentage exhaustion of the dyebath (%E) was calculated using Eq (1) where C_0 is the concentration of the dye solution prior to dyeing and C_t the concentration of the dye solution at time, t minutes.

$$\%E = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

2.2.3. Determination of dye fixation

The extent of covalent dye fixation to the silk fibre was determined by stripping unfixed dye using 20% aqueous pyridine solution, following the procedure described by Anthoulias [8]. The extent of fixation (%F) was calculated using Eq (2) where the subscripts $_1$ and $_2$ represent, respectively, the fk values before and after stripping.

$$\%F = \frac{fk_2}{fk_1} \times 100 \qquad (2)$$

The overall fixation efficiency (%T), which describes the amount of exhausted dye (%E) that has been fixed (%F), was calculated using Eq (3).

Table 2
Effect of wash-off method on colour.

Wash-off method	*Blue MFFN*					*Red MFFR*					*Yellow MFFN*				
	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
None	50.1	0.2	−39.1	39.1	270.3	44.3	39.9	−18.4	43.9	335.2	81.3	8.7	71.5	72.1	83.1
Water	50.6	0.3	−40.3	40.3	270.4	44.8	39.1	−18.3	43.2	334.9	83.3	5.9	74.5	74.7	85.5
Na_2CO_3	50.9	−0.4	−40.1	40.1	269.5	45.2	39.4	−17.4	43.1	336.2	83.2	5.5	74.0	74.3	85.8
Lanapex R	51.3	−0.4	−39.9	39.9	269.4	45.3	39.5	−18.1	43.4	335.4	83.2	5.5	73.1	73.4	85.7
Sandozin NIE	51.1	−0.3	−39.6	39.6	269.6	44.9	39.4	−18.5	43.5	334.8	83.6	5.7	73.3	73.4	86.3
aq pyridine	55.3	−2.2	−35.9	36.0	266.6	45.7	40.1	−16.9	43.5	337.1	85.2	2.4	65.9	66.0	87.9

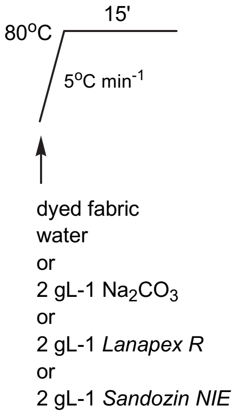


Fig. 2. Wash-off methods.

$$\%T = \frac{\%E \times \%F}{100} \tag{3}$$

2.2.4. Wash-off

Dyeings were washed-off in sealed, stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec 'S'* laboratory dyeing machine using a liquor ratio of 50:1 using the method shown in Fig. 2. Four different wash-off media were employed, namely water, Na_2CO_3, *Lanapex R* and *Sandozin NIE.*

2.2.5. Colour measurement

The equipment and techniques described previously [2] were used.

2.2.6. Effect of repeated wash fastness on depth of shade

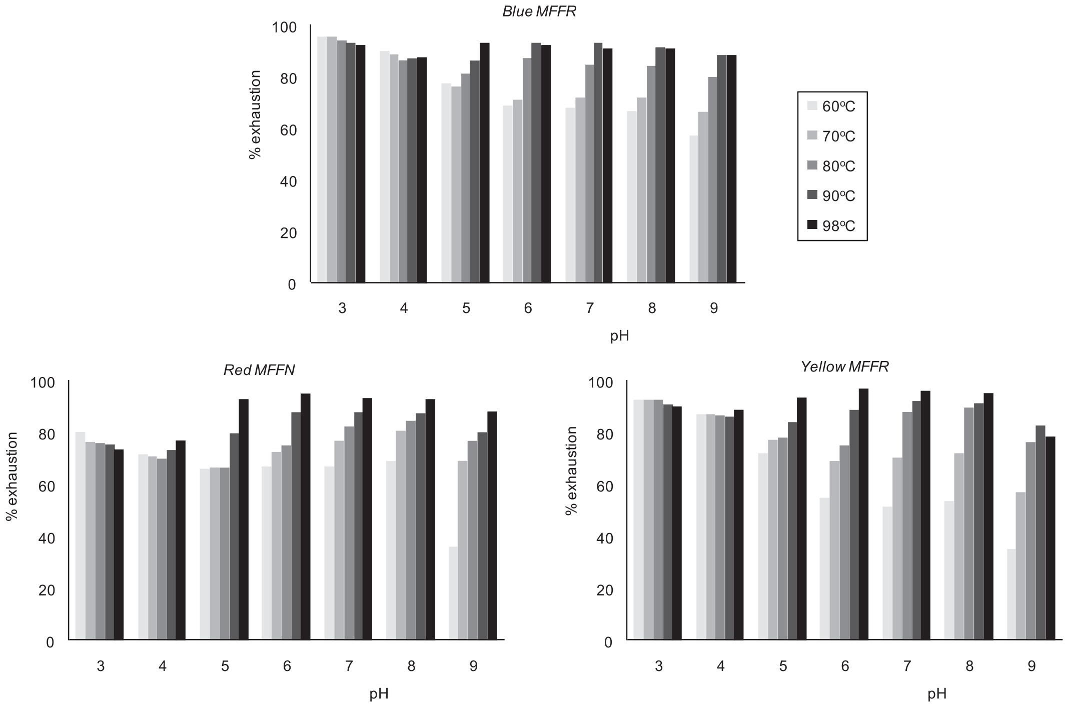
The dyeings were subjected to ten, consecutive ISO C06/A2C (40 °C) [14] wash tests. At the end of each wash test, the sample was rinsed thoroughly in tap water; a fresh sample of SDC multifibre strip used for each of the five wash tests. The extent to which repeated wash testing reduced the depth of shade of the dyeings was determined using Eq (4) where the subscript $_u$ refers to the colour strength of the untreated dyeing before washing and the subscript $_a$ refers to the colour strength of respective dyeings obtained after either the wash-off process or wash test #1, #2, ... #10.

$$\%\text{colour loss} = \left(\frac{fk_u - fk_a}{fk_u}\right) \times 100 \tag{4}$$

3. Results and discussion

3.1. Dye exhaustion and fixation

Fig. 3 shows that when the three dyes had been applied at 60 °C and 70 °C, dye exhaustion decreased as dyeing pH was raised from 3 to 9. As silk contains various amino-containing residues [15] the observed higher dye exhaustion at pH 3 and 4 can be attributed to electrostatic attraction operating between the sulfonated dye molecules and such protonated amino groups in the fibre. The observed decrease in dye uptake that accompanied an increase in dyeing pH from 5 to 9 at 60 °C and 70 °C can be attributed not only to a decrease in the extent of such amino group protonation, but, as the substrate also contains OH-containing amino acid residues [15], to a corresponding increase in repulsive, negative charge development that accrued from ionisation of OH-containing residues. However, in contrast, Fig. 3 also shows that over the range 80 °C–98 °C, temperature had relatively little effect on dye exhaustion in the cases of pH 3 and 4, whilst over the pH range 5–9, dye exhaustion increased markedly, with increasing application temperature. For each of the three dyes used, Fig. 3 shows that a clear difference exists between the trends in dye exhaustion secured at pH 3 and 4 compared to that obtained in the pH region 5 to 9. This difference may be related to the isoelectric point (pI) of the substrate, for which published values vary, typically between


Blue MFFR

Red MFFN

Yellow MFFR

Fig. 3. % Dye exhaustion as a function of pH and temperature.

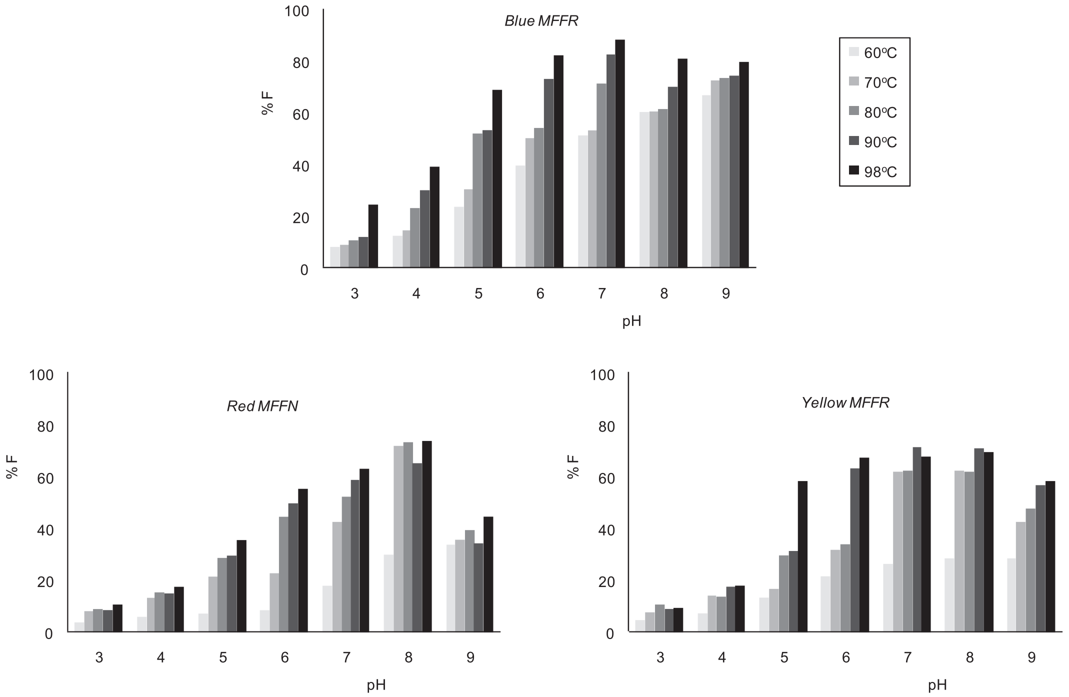


Fig. 4. Dye fixation (%F) as a function of pH and temperature.

3.6 and 5.2 [16], depending on the method of measurement used, the conditions employed for determination and the type of silk involved; a value of 3.8 has recently been reported for pI in the case of the dyeing of silk with acid dyes [17].

The %E results (Fig. 3), which clearly show that the exhaustion of the three dyes onto silk was both pH- and temperature-dependant, can perhaps best be explained by reference to the corresponding extents of covalent dye fixation (%F) obtained (Fig. 4), as VS dye exhaustion on silk is considered to be primarily a function of reaction with the fibre rather than the number of protonated groups in the fibre [18]. It is evident that %F increased with increasing pH over the range pH 3–7 or 8 depending on dye and, thereafter, dye exhaustion decreased at pH 9. In addition, at each pH value used, %F generally increased with increasing temperature over the range 60–98 °C. Whilst the extent of total fixation (%T) achieved (Fig. 5) followed the same pattern as that of dye fixation (%F), the %T values emphasise the marked temperature-dependence of dye fixation for each pH value used.

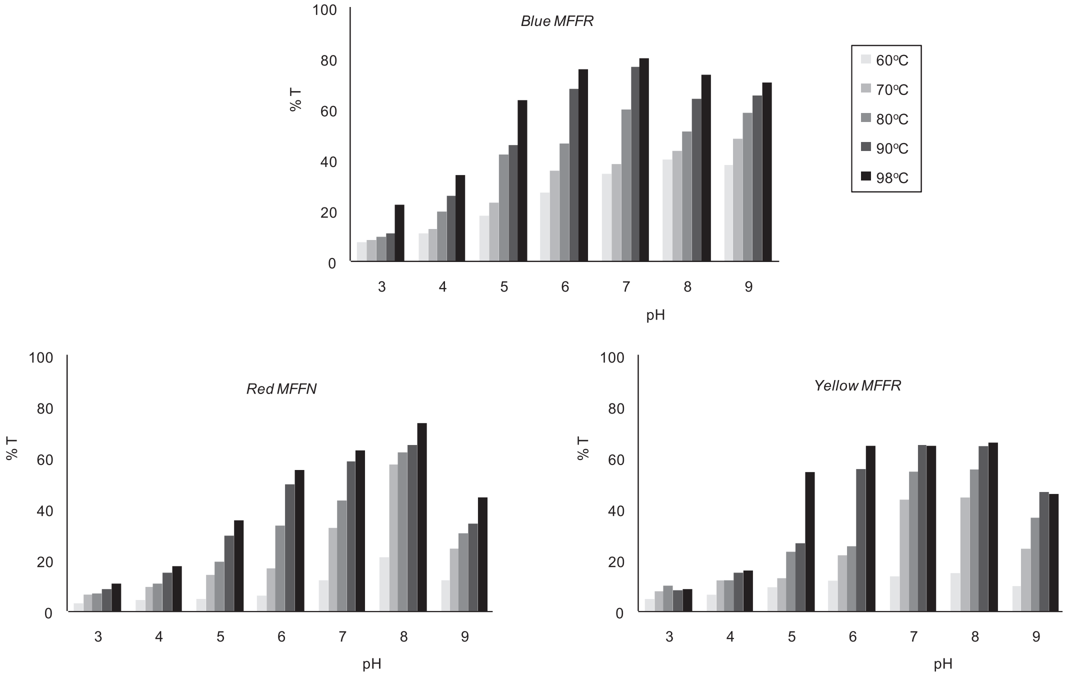


Fig. 5. Dye fixation (%T) a function of pH and temperature.

The %F and %T results (Figs. 4 and 5) agree with those obtained for the dyeing of silk with VS dyes [19] insofar as maximum dye fixation occurs typically at pH 7–8; it is believed that reaction involves the amino groups of glycine, alanine, serine, histidine and lysine [19]. Furthermore, optimum dyeing pH values of 6–7 have been reported for the *N*-methyltaurine-ethylsulfone derivative and pH 7–8 in the case of the β-sulfatoethylsulfone form of VS dyes on silk [15]. Under the alkaline conditions used in this work (ie pH 8 and 9), it is also possible that reaction with OH-containing side chains such as serine and tyrosine [15,20,21] may well have taken place. The importance of the role of the amino groups in terms of both the uptake and fixation of the three modified VS dyes on silk can be explained in the context of the exhaustion (Fig. 3) and fixation (Figs. 4 and 5) results obtained. Protonation of the amino groups in silk is an equilibrium situation (Scheme 1) that depends on pH insofar as, the equilibrium depicted in Scheme 1 will move to the right with decreasing pH. As the three modified VS dyes can react only with nucleophilic (ie non-protonated) amino groups, it follows that as protonation of the amino groups increases with decreasing dyeing pH, the number of nucleophilic amino groups in the substrate available for reaction with the dyes will decrease with decreasing pH. In addition, as the conversion of the β-sulfatoethylsulfone form to the reactive VS form has been shown to be very low under acidic conditions [18,22] but very high at pH 7–8 [22] and, as it is considered that VS dye exhaustion on silk is primarily a function of reaction with the fibre rather than the number of protonated groups in the fibre [18], the dye exhaustion and fixation results displayed in Figs. 3 to 5 can be explained as follows:

- *high dye exhaustion but low dye fixation at* pH *3 and 4*: whilst such acidic conditions favour dye exhaustion, owing to adsorption of the anionic dyes onto the protonated amino groups, these conditions disfavour dye fixation owing to the comparatively small number of available nucleophilic amino groups;
- *low dye exhaustion and low dye fixation at* pH *9*: whereas dye fixation should be high because of the large number of nucleophilic $-NH_2$ groups in the fibre, dye exhaustion will be low owing to the few available protonated amino groups; in addition, dye hydrolysis can be expected to be higher at pH 9 than at other pH values used for dyeing.
- *maximum dye fixation at* pH *7–8*: a combination of an adequate number of available nucleophilic $-NH_2$ groups in the fibre and high conversion of the masked form to the VS form of the dye.

The observed, temperature-dependence of both dye exhaustion and fixation observed at pH 5–9 (Figs. 3 to 5) is indicative of a rate-determined, kinetic effect and seems likely to be fixation-related rather than exhaustion-driven, in view of the proposal that VS dye exhaustion on silk is a function of reaction with the fibre rather than protonated groups in the fibre [18].

3.2. Wash-off

At the end of dyeing, it is routine practice for all dye/substrate combinations, to remove surplus dye and dyeing auxiliaries (electrolyte, levelling agents, etc.) from the dyeing, so as to enable the correct shade and optimum fastness to be achieved. This usually hot, aqueous process, which is generically referred to as 'wash-off', typically employs specific auxiliaries (eg surfactants). In the case of reactive dyes, as their application to cellulosic, wool and nylon fibres is always accompanied by dye hydrolysis, an appropriate wash-off of this hydrolysed dye, as well as any unreacted dye and dyeing auxiliaries, is required at the end of the dyeing process [23]. In the case of the *Stanalan* range of reactive dyes applied to nylon fibres, Du Pont and DyStar recommend the use of either one or two 15 min water rinses at 60 °C, depending on the depth of shade [8]. To secure optimum wet fastness, Du Pont also recommends an aftertreatment of washed-off dyeings with a commercial syntan in the case of ≥1.5% omf depths of shade [8]. As mentioned, since no exclusive reactive dye range has been developed for silk and, as the *Stanalan* dye range is intended for application to nylon fibres, no 'standard' wash-off method is available for reactive dyes on silk. Hence, in this work, it was decided to examine the effectiveness of four different wash-off methods which used (Fig. 2) namely water, as employed in the case of the wash-off of *Stanalan* dyes on nylon [5], two non-ionic surfactants and Na_2CO_3, on the basis that each has previously been used in the wash-off of reactive dyes from nylon [9,24,25]. To determine the effectiveness of each wash-off process, the dyeings were subjected to ten, repeated wash fastness tests at 40 °C and the colorimetric parameters and colour strength of the dyeings were measured at the end of each wash test. In addition, the extent to which dye was removed from the dyeings as a result of both wash-off and repeated wash testing was quantified by determining % colour loss (Eq (4)).

$$-NH_2 + H^+ \rightleftharpoons -\overset{+}{N}H_3$$

Scheme 1. Protonation of amino groups.

Table 2 shows the colorimetric parameters obtained for the three dyes used, both prior to wash-off and after each of the four wash-off methods; the corresponding colour strength values (fk) are shown in the respective 'before washing' columns in Fig. 6. It is evident that for each of the three dyes used, wash-off increased the lightness (L^*) (Table 2) and reduced the colour strength (Fig. 6) of the dyeings. These findings clearly demonstrate that each of the four wash-off methods removed surplus dye, which, in turn, indicates that dye–fibre reaction was incomplete and that either/both unfixed (reactive) and hydrolysed forms of the dyes were present on the dyed substrates at the end of dyeing. Table 2 and Fig. 6 reveal that of the wash-off methods employed, water alone was least effective in removing surplus dye (as measured by increases in L^* and reductions in colour strength) and, generally, the effectiveness of the other wash-off methods increased in the order: Na_2CO_3 < *Sandozin NIE* < *Lanapex R*. The dashed lines in Fig. 6 denote the fk values of the dyeings which had been subjected to the aq pyridine extraction method that was used to determine the extent of dye fixation. As this 'stripping' treatment removed all unfixed and hydrolysed dye from the dyeings, it follows that an fk value greater than that of the stripped dyeing indicates that surplus, unfixed/hydrolysed dye was still present within the dyed fabric. In this context, a comparison of the fk values obtained for dyeings which had been washed-off (the respective 'before washing' columns in Fig. 6) and those secured for the corresponding stripped dyeings (the dashed lines in Fig. 6) gives an indication of the ability of the four wash-off methods to remove surplus dye from the dyeings.

A measure of the extent of the reduction in depth of shade that was imparted by wash-off is given by the 'before washing' % colour loss values in Fig. 7, from which it is apparent that the two surfactant compositions, *Lanapex R* and *Sandozin NIE*, removed much more dye than either the water or Na_2CO_3 wash-off treatments. The dashed lines in Fig. 7 denote the % colour loss values obtained for the dyeings which had been subjected to aq pyridine stripping. Comparison of the % colour loss values for dyeings which had been washed-off (the respective 'before washing' columns in Fig. 7) and those obtained for the corresponding stripped dyeings (the dashed lines in Fig. 7) shows how relatively little unfixed/hydrolysed dye was removed by each of the four wash-off methods used.

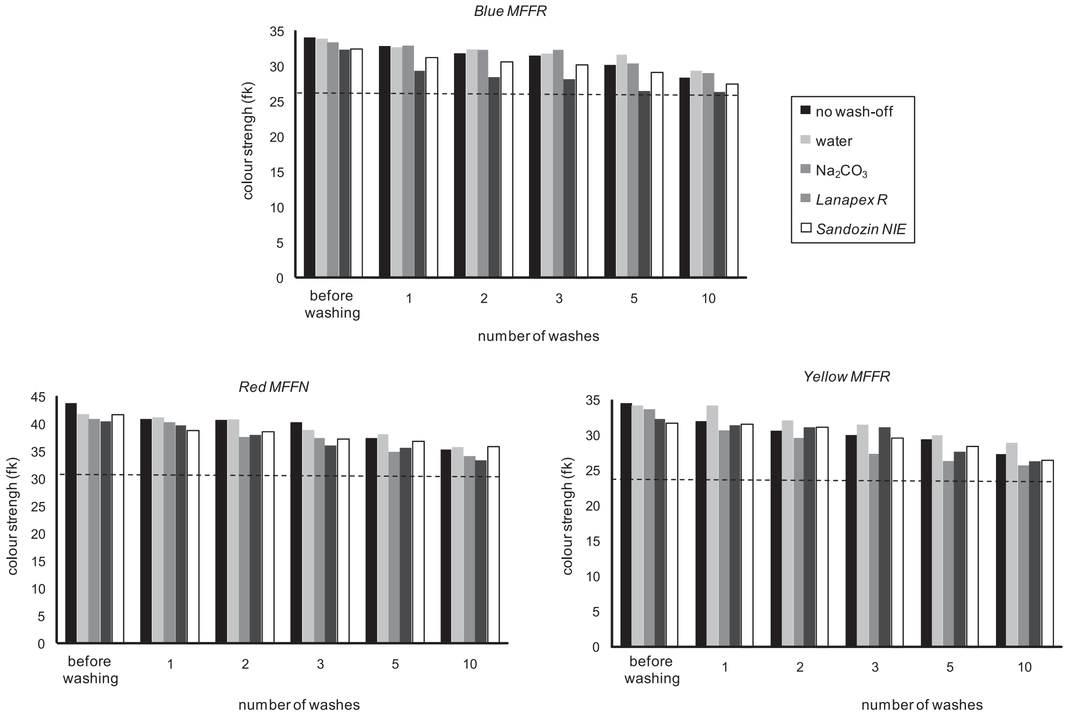


Fig. 6. Colour strength as a function of number of washes.

Comparison of the colorimetric data obtained for the unwashed-off dyeings with those of dyeings which had been subjected to the four wash-off processes (Table 2) shows that there was little difference in the colour of the respective dyeings. However, it is apparent that the aq pyridine stripping treatment not only reduced the lightness of the dyeings markedly but also reduced the chroma of, and imparted a yellow hue to, the dyeings, this being attributable to discoloration of the silk fabric.

3.3. Repeated wash testing

The colorimetric data obtained for the dyeings before (Table 2) and after (Table 3) wash testing show that repeated washing had little effect on the colour (hue, ho and chroma, C*) of the dyeings.

Fig. 6 shows the colour strength of 2% omf dyeings which had been washed-off and subjected to ten, repeated wash tests at 40 °C. It is evident that for each of the three dyes used, fk decreased with

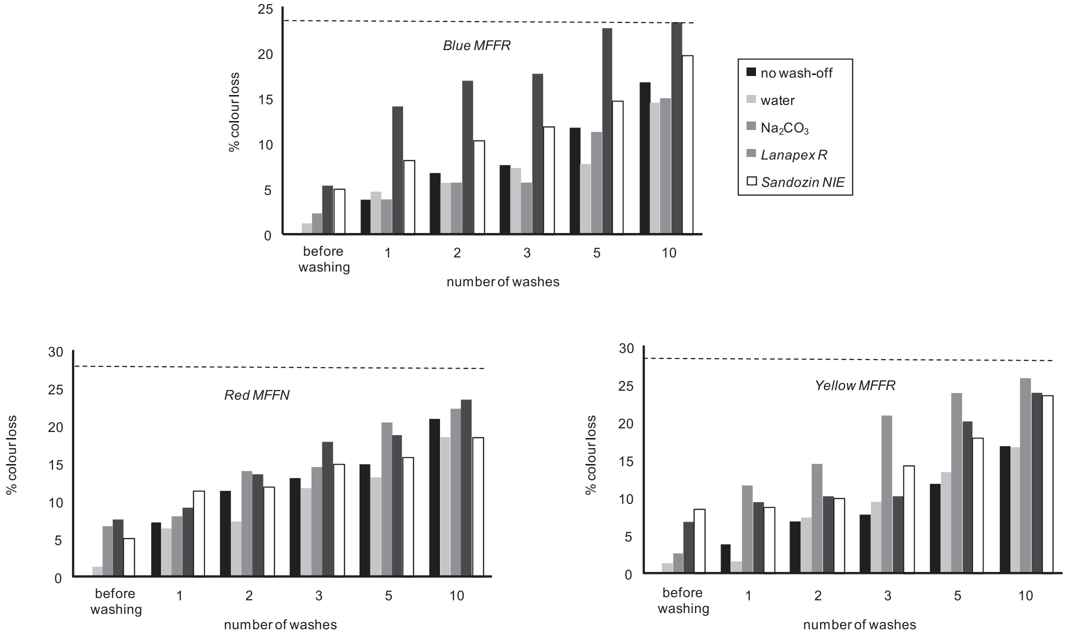


Fig. 7. Cumulative colour loss a function of number of washes.

Table 3
Effect of repeated wash testing on colour.

Wash-off method	Number of washes	*Blue MFFN*					*Red MFFR*					*Yellow MFFN*				
		L*	a*	b*	C*	h°	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
None	1	51.0	−0.3	−39.7	39.7	269.6	45.3	39.3	−17.5	43.0	336.0	81.8	7.7	70.8	71.2	83.8
	2	51.5	−0.6	−39.6	39.6	269.2	45.4	39.6	−17.7	43.4	335.9	82.2	7.7	70.3	70.7	83.7
	3	51.7	−0.7	−39.7	39.7	269.1	45.5	39.7	−17.8	43.5	335.8	82.1	7.7	69.9	70.4	83.7
	5	52.2	−0.8	−39.0	39.0	268.9	46.4	38.9	−17.4	42.7	335.9	82.3	7.6	69.8	70.2	83.8
	10	52.8	−1.2	−37.7	37.8	268.2	47.2	38.4	−17.2	42.1	335.8	82.3	8.0	68.4	68.9	83.3
Water	1	51.1	−0.2	−39.8	39.8	269.8	45.2	39.7	−18.0	43.6	335.6	83.3	5.7	74.8	75.0	85.6
	2	51.3	−0.6	−39.7	39.7	269.1	45.4	40.0	−17.6	43.7	336.2	83.4	5.5	73.4	73.6	85.7
	3	51.6	−0.5	−39.7	39.7	269.2	46.0	39.5	−17.6	43.2	336.0	83.6	5.7	73.3	73.5	85.6
	5	51.5	−0.6	−38.9	38.6	269.2	46.2	39.0	−17.4	42.7	336.0	83.7	5.7	72.6	72.8	85.5
	10	52.4	−1.0	−38.0	38.0	268.5	47.0	38.3	−17.4	42.1	335.6	83.1	6.8	71.1	71.5	84.6
Na_2CO_3	1	51.0	−0.6	−39.6	39.6	269.1	45.3	39.0	−18.0	43.0	335.2	84.0	4.9	73.3	73.5	86.2
	2	51.3	−0.6	−39.7	39.7	269.1	46.3	39.0	−18.0	43.0	335.3	83.9	4.7	72.3	72.4	86.3
	3	51.3	−0.3	−39.8	39.9	269.6	46.4	39.3	−17.8	43.2	335.7	84.2	4.0	70.9	71.1	86.8
	5	52.1	−0.8	−39.0	39.0	268.8	47.4	38.6	−17.2	42.3	336.0	83.9	5.6	70.1	70.3	85.4
	10	52.5	−1.1	−38.0	38.0	268.3	47.6	37.8	−16.8	41.4	336.0	84.2	4.4	69.6	69.7	86.4
Lanapex R	1	52.7	−1.2	−38.9	38.9	268.2	45.7	39.6	−17.5	43.3	336.2	83.9	4.9	73.6	73.8	86.2
	2	53.2	−1.5	−38.9	38.9	267.9	46.3	39.5	−17.9	43.4	336.0	83.9	5.6	73.6	73.8	85.7
	3	53.2	−1.1	−38.5	38.5	268.3	47.0	38.9	−17.3	42.6	336.0	83.9	5.5	73.5	73.7	85.8
	5	54.0	−1.5	−38.0	38.0	267.8	47.0	38.8	−17.4	42.5	335.8	84.0	5.1	71.0	71.2	85.9
	10	53.9	−1.5	−37.0	37.0	267.6	47.9	38.0	−17.1	41.6	335.8	83.9	5.6	70.1	70.3	85.4
Sandozin NIE	1	51.8	−1.0	−39.4	39.4	268.6	46.0	39.6	−18.1	43.5	335.4	83.3	4.5	72.5	72.6	86.5
	2	51.9	−0.8	−38.8	38.8	268.8	46.0	39.5	−18.0	43.4	335.5	83.4	5.0	72.7	72.9	86.1
	3	52.2	−0.8	−38.9	38.9	268.8	46.4	38.7	−17.6	42.6	335.6	83.8	5.0	72.4	72.6	86.1
	5	52.7	−1.1	−38.7	38.7	268.3	46.6	39.1	−17.3	42.7	336.2	83.4	4.8	70.6	70.7	86.0
	10	53.3	−1.3	−38.0	38.0	268.0	47.0	38.1	−16.7	41.6	336.3	83.5	6.0	70.0	69.8	85.1

increasing number of washes which can be attributed to unfixed/hydrolysed dye having been removed during wash testing; this reduction in fk is confirmed by the corresponding increase in lightness of the dyeings that accompanied repeated washing (Table 3). The dashed lines in Fig. 6 mark the fk values of the dyeings which had been subjected to aq pyridine stripping, from which it is apparent that, even after ten wash tests, surplus dye remained within the dyed silk in the cases of each of the four wash-off methods used, with the exception of the blue dye which had been washed-off using *Lanapex R*. In this context, the % colour loss values displayed in Fig. 7 show the cumulative reduction in depth of shade that occurred as a result of dye loss during repeated wash fastness testing. Whilst colour loss increased with increasing number of washes, clear differences exist between the four wash-off methods used in terms of their effects on depth of shade reduction. As mentioned, the dashed lines in Fig. 7 denote the % colour loss values obtained for the dyeings which had been subjected to aq pyridine stripping. Comparison of the % colour loss values for dyeings which had been washed-off and those obtained for the corresponding stripped dyeings (the dashed lines in Fig. 7) clearly shows the gradual nature of dye loss and suggest that many more wash tests at 40 °C will be required to fully remove the fairly substantial amounts of unfixed/hydrolysed dye that still remain in the substrate after ten washes.

In terms of the differences between the four wash-off methods, Fig. 7 shows that for the red and yellow dyes, *Lanapex R* and Na_2CO_3 were more effective than water and *Sandozin NIE* whereas for the blue dye, the two surfactant compositions were most effective. Interestingly, only in the case of the blue dye which had been washed-off using *Lanapex R* was the extent of colour loss after ten washes equivalent to that achieved for the stripped dyeing (Fig. 7). Furthermore, for all three dyes, the difference in % colour loss obtained for dyeings which had been washed-off and those which had received no wash-off appeared to decrease with increasing number of washes. These findings suggest that whilst the use of detergent formulations in wash-off may be advantageous in terms of the first few wash tests, thereafter, such compounds may offer little advantage over water or Na_2CO_3.

4. Conclusions

Both the exhaustion and fixation of the three members of the *Stanalan* dye range were pH- and temperature-dependent. Low application pH (pH 3 and 4) favoured dye exhaustion but disfavoured dye fixation whilst the use of pH 9 resulted in low fixation and low exhaustion. Optimum dye fixation occurred at pH 7–8, as a consequence of a combination of sufficient numbers of available nucleophilic $-NH_2$ groups in the fibre and high conversion of the masked form of the dye to the reactive VS variant. The temperature-dependence of dye exhaustion and dye fixation at pH 5 to 9 is indicative of a rate-determined, kinetic effect and is probably fixation-related rather than exhaustion-driven, as VS dye exhaustion on silk is a function of reaction with the fibre rather than protonated groups in the fibre. Of the four wash-off methods examined, none removed sufficient amounts of dye from the silk fabric and, whilst the two detergent formulations were most effective in terms of the first few wash tests, this advantage decreased with increasing number of wash tests.

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