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The dyeing of silk: Part 4 heterobifunctional dyes

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ABSTRACT

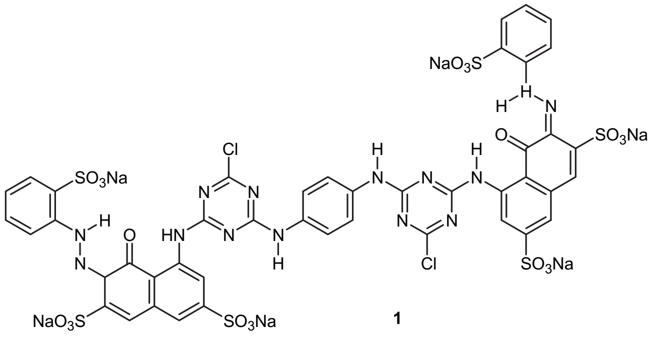
The exhaustion and fixation of three, commercial aminochlorotriazine/masked vinylsulfone dyes were both pH- and temperature-dependent. Optimum dye fixation was obtained at pH 8, as a corollary of a high number of nucleophilic $-NH_2$ groups in the fibre, high conversion of the masked form of the dye to the reactive VS variant as well as reaction with OH-containing amino acid residues. The marked, temperature-dependence of dye fixation achieved in the pH range 3 to 9 demonstrated the importance of kinetic factors in dye–fibre reaction. The wash-off method used was very effective in removing unfixed/hydrolysed dye from the silk fabric and, as a result, the dyeings displayed very good fastness to washing at 40 °C.

1. Introduction

The triangular cross-section, smooth surface and fineness of cultivated silk fibre are responsible for its unique and highly prized, drape, handle and lustre. However, these particular physical characteristics result in the fibre's dyeing behaviour resembling that of microfibre synthetic fibre [1] insofar as even moderate depths of shade require the use of large amounts of dye and such dyeings typically posses characteristically low fastness to wet treatments. Although the application of reactive dyes to silk has attracted much attention over the past four or so decades, as no exclusive reactive dye range has been developed for silk, the publications that describe the use of reactive dyes on silk [2–22] concern reactive dyes intended for other fibres, notably cotton and other cellulosics.

This paper describes approaches to achieve dyeings of good wet fastness on cultivated silk. The first two parts of the paper concerned the fastness of, respectively, C.I. Solubilised Sulphur dyes [23] and aftertreated non-metallised and pre-metallised acid dyes [24] to washing at 40 °C, whilst the third part of the paper described the application and wash-off characteristics of three modified vinyl sulfone reactive dyes designed for use on nylon fibres [25]. This part of the paper concerns the application of *Yoracron BF* (Yorkshire) heterobifunctional, aminochlorotriazine/masked vinyl sulfone dyes to silk intended for application to cotton.

Bifunctional reactive dyes, which carry two reactive groups per dye molecule, were first introduced commercially in the late 1960's/early 1970's as a means of increasing dye fixation levels in the exhaust dyeing of cellulosic fibres [26]. Such early bifunctional dyes were *homobifunctional* types in which both reactive groups were identical, as typified by the bis(aminochlorotriazine) dye, C.I. Reactive Red 120 (**1**). The first commercial range of *heterobifunctional* reactive dyes for cellulosic fibres, namely the aminochlorotriazine/masked vinylsulfone *Sumifix Supra* range, exemplified by C.I. Reactive Red 194 (**2**), was launched some ten or so years later by Sumitomo. Characteristically, this particular dye type displays high substantivity towards cotton and other cellulosic fibres, as well as high exhaustion and dye fixation imparted by the triazine group. The presence of the two dissimilar reactive groups (aminochlorotriazine and masked vinylsulfone) offer a wide application temperature range, favouring shade reproducibility and also result in high fastness to acid hydrolysis and good resistance to degradation by peroxide during laundering [26].



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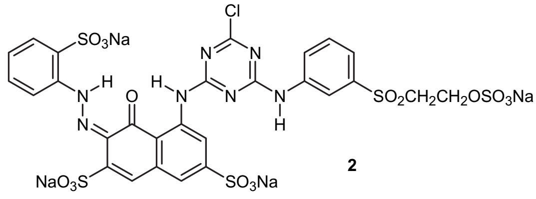

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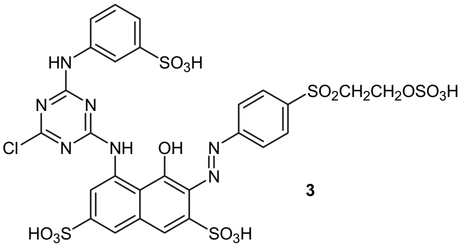
Of the comparatively few publications that concern the application of heterobifunctional dyes to silk, those which concern aminochlorotriazine/masked vinylsulfone dyes mostly relate to the use of one example of this particular dye type namely C.I. Reactive Red 194 (**2**) [8–10,13,14,16,17], although more recent papers have concerned aspects of the application of C.I. Reactive Red 195 (**3**; [27]) [12,18] and C.I. Reactive Blue 194 [17]. Agarwal [8] established optimum conditions for the exhaustion and fixation of the aminochlorotriazine/masked vinylsulfone dye C.I. Reactive Red 194 (**2**) on silk as pH 7 and 90 °C. Whilst these conditions have been subsequently adopted for the application of this particular dye to silk by several workers [9,10,13,14], alkaline pH values were employed in the cases of C.I. Reactive Red 195 (**3s**) [12,18] and C.I. Reactive Blue 194 [17]. However, despite the fact that all dyeings, irrespective of the type of colorant and textile substrate used, are routinely subjected to a wash-off treatment to remove surplus dye, electrolyte, levelling agent, etc. so as to achieve optimum fastness [28], very few of the papers that concern the dyeing of silk with aminochlorotriazine/vinylsulfone dyes describe the use of a wash-off process at the end of dyeing [12,17,18].



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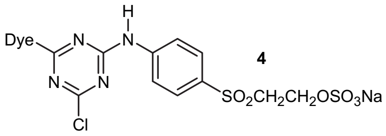
In the context of previous work carried out on heterobifunctional dyes to silk, it was decided to study the effects of both pH and temperature on the extents of dye exhaustion and fixation of members of the *Yoracron BF* range of aminochlorotriazine/masked vinylsulfone dyes on silk, as well as with the fastness of washed-off dyeings. The dyes within this range, which are marketed for use on cellulosic fibres, are of generic structure **4**, being based on 4-aminophenyl-β-sulfatoethylsulfone (**5**), commonly known as 'para-base' rather than 3-aminophenyl-β-sulfatoethylsulfone (**6**) or 'meta-base', which is commonly reported as being employed in aminochlorotriazine/masked vinylsulfone dyes [6,29–32]. As such, the three dyes used in this work are the para-base equivalents [33] of C.I. Reactive Red 194 (**2**; [34] [*Yoracron Red BF-2B*]), C.I. Reactive Yellow 145 (**7**; [35] [*Yoracron Yellow BF-3R*]) and C.I. Reactive Blue 222 (no structure disclosed in the Colour Index [34] [*Yoracron Navy Blue BF-B*]).



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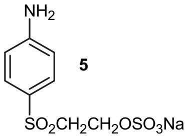

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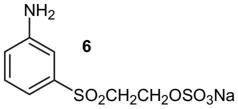

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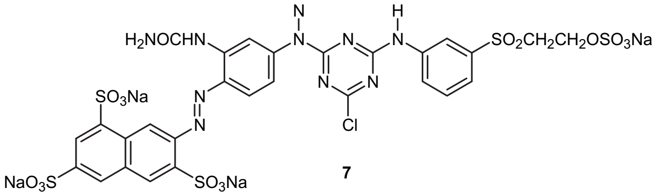

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2. Experimental

2.1. Materials

The, degummed, scoured, *Bombyx mori* silk fabric twill described previously [23] was used. The three dyes used namely, *Yoracron Red BF-2B, Yoracron Yellow BF-3R* and *Yoracron Navy Blue BF-B* were generously provided by Yorkshire. *Lanapex R* (a mixture of modified phosphate esters with polyphosphates [36]; Uniqema) was kindly provided by the respective maker. All other chemicals used were of laboratory grade purity. The McIlvaine buffer solutions [37] previously described [25] were used to control the pH of the dyebaths.

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 and fixation

The extents of dye exhaustion (%*E*), dye fixation (%*F*) and overall fixation efficiency (%*T*) 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) were determined as described previously [25].

2.2.3. 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.

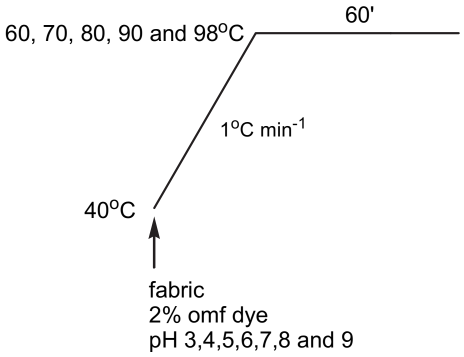

Fig. 1. Dyeing method.

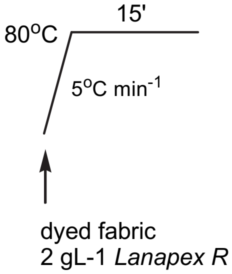

Fig. 2. Wash-off method.

2.2.4. Colour measurement

The equipment and techniques described previously [25] were used.

2.2.5. Effect of wash fastness testing on depth of shade

The dyeings were subjected to the ISO C06/A2C (40 °C) [38] wash test.

3. Results and discussion

3.1. Dye exhaustion and fixation

Fig. 3 shows the extent of dye exhaustion (%*E*) achieved as a function of both dyeing temperature (60, 70, 80, 90 and 98 °C) and pH (3, 4, 5, 6, 7, 8 and 9). In the context of the effect of pH upon dye exhaustion, it is apparent that a difference exists between the trends in dye exhaustion obtained at pH 3 and 4 and those obtained at pH values 5 to 9. For each of the three dyes used, the greater dye exhaustion at pH 3 and 4 can be attributed to the isoelectric point of the silk fibre (pI), which varies between pH 3.6 and 5.2 [39], a value for pI of pH 3.8 having recently been obtained in the case of the dyeing of silk with acid dyes [40]. Silk fibroin possesses four major amino acid components namely glycine, alanine, serine and tyrosine (Table 1 [41–43]). Although silk contains notably fewer acidic and basic side chains than its proteinaceous relative, wool (Table 1), which results in silk displaying much lower acid absorption than wool (silk: 150 mmol kg^{-1}; wool: 840 mmol kg^{-1} [41]), the acidic and, especially the basic amino groups in silk, are considered to be of prime importance in the uptake of anionic dyes onto the substrate [44]. In this context, the adsorption of anionic (commonly sulfonated) dyes, such as acid dyes or direct dyes, onto silk under acidic conditions is generally considered to arise through the operation of, principally electrostatic forces, including ion-ion forces and H-bonding, with van der Waals' forces, hydrophobic interactions as well as $\pi-\pi$ interactions also contributing to dye–fibre substantivity. Consequently, as proposed for the exhaustion trends obtained for modified vinylsulfone dyes on silk [25], the high %*E* results observed for the three *Yoracron BF* dyes at pH 3 and 4 (Fig. 3) can be attributed to mostly electrostatic attraction operating between each of the three sulfonated dye molecules (C.I. Reactive Blue 222 is penta-sulfonated [33]) and protonated amino groups in the substrate, although van der Waals' forces, hydrophobic interactions as well as $\pi-\pi$ interactions are also likely to contribute. In this context, the lower extents of dye exhaustion observed at pH values >5 (Fig. 3) can be attributed to not only a decrease in the extent of such amino group protonation but, as silk also contains OH-containing amino acid residues, to a corresponding increase in electrostatic repulsion operating between the sulfonated dye molecules and ionised OH-containing residues within the fibre. However, the observed trends in %*E* that were obtained at pH 5 to 9 (Fig. 3) are also a consequence of the corresponding extents of dye fixation (%*F*) and overall fixation efficiency (%*T*) achieved, as described below.

In terms of the effect of application temperature (60, 70, 80, 90 and 98 °C) on dye exhaustion, Fig. 3 shows that generally, a difference exists between the trends obtained at pH 3 and 4 compared to those secured at pH 5 to 9. The observed reduction in %*E* that accompanied an increase in dyeing temperature from 60 to 98 °C at pH 3 and 4 can be attributed to the facts that dye uptake under these acidic conditions arose primarily from physical forces of interaction and that little dye fixation occurred (Fig. 4) and, that, in such a case, it is well known that for given conditions of pH, liquor ratio, etc.,

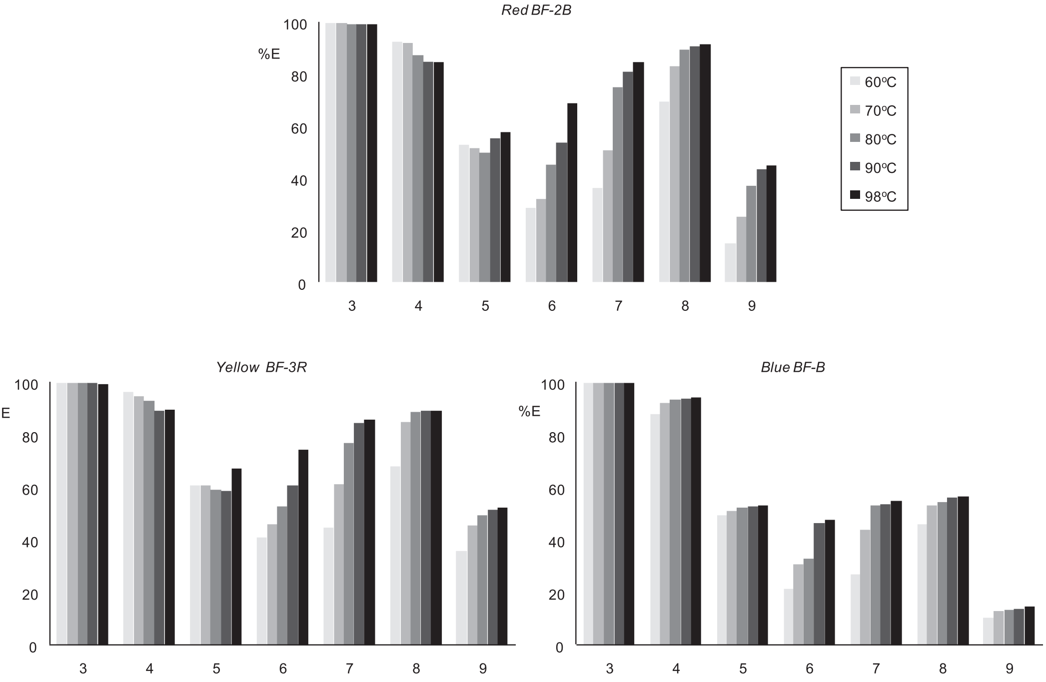

Fig. 3. %*E* as a function of dyeing pH and temperature.

Table 1
Amino acid composition of silk fibroin [41].

Nature of side-chain	Amino acid	mol%	
		wool [42]	silk fibroin [43]
acidic	aspartic acid	6.5	1.3
	glutamic acid	11.9	1.0
basic	histidine	0.9	0.2
	arginine	6.9	0.5
	lysine	2.9	0.3
hydroxyl	serine	10.4	12.1
	threonine	6.4	0.9
	tyrosine	3.8	5.2
non-polar	glycine	8.4	44.5
	alanine	5.4	29.3
	leucine	7.7	0.5
	isoleucine	3.1	0.7
	phenylalanine	2.9	0.6
	valine	5.6	2.2
	proline	6.6	0.3
sulphur	methionine	0.5	0.1
	cystine	10.3	0.2

whilst the rate of dye uptake increases with increasing temperature, the extent of dye exhaustion decreases with increasing temperature. The findings (Fig. 3) that %*E* generally increased with increasing application temperature at pH 5 to 9 are a consequence of the greater role which dye fixation plays in the levels of dye exhaustion obtained, as described below.

From the viewpoint of dye fixation, the nucleophilic groups in silk of relevance include the amino groups in lysine, arginine and histidine, which have been shown to be important for reaction under acidic, neutral and alkaline pH conditions, as well as both alcoholic hydroxyl (serine) and phenolic hydroxyl (tyrosine) groups, which contribute under alkaline conditions [6,11,44]. Each of the three dyes used contain two reactive groups, namely aminochlorotriazine and masked vinylsulfone, as exemplified by C.I. Reactive Red 194 (**2**). Whilst both types of reactive group are able to react with silk fibre [10] and several workers have reported that such bifunctional dyes form crosslinks in silk [8,9,18], the VS group is considered to be the preferred route for fixation [8].

Fig. 4 shows that dye fixation (%*F*) increased with increasing pH over the range pH 3 to 8 and, thereafter, decreased at pH 9; also, for each pH value used, %*F* generally increased with increasing temperature over the range 60–98 °C. Whilst the total fixation (%*T*) results obtained (Fig. 5) followed the same pattern as that of dye fixation (%*F*), the %*T* values reveal that maximum dye fixation occurred at pH 8 and, also, that the marked temperature-dependence of dye fixation was lowest at this particular pH. The %*F* and %*T* results shown in Figs. 4 and 5 agree generally with those secured for the dyeing of silk with a β-sulfatoethylsulfone VS derivative for which an optimum dyeing pH of 7-8 was reported [11], as well as both VS dyes [6] and modified VS dyes [25], in that maximum dye fixation also occurred at pH 7–8 and for which reaction was considered to involve the amino groups of glycine, alanine, serine, histidine and lysine. As such, the pH dependence of both %*F* and %*T* (Figs. 4 and 5) can be explained in terms of the $-NH_2$ groups within the substrate, as discussed previously [25] for the pH dependence observed for the fixation of modified VS dyes on silk. Protonation of the amino groups follows the equilibrium situation depicted in Scheme 1, with the equilibrium moving to the right with decreasing pH. As dye–fibre reaction can only occur at nucleophilic (ie non-protonated) amino groups, then as protonation of the $-NH_2$ groups decreases with increasing dyeing pH, the number of nucleophilic amino groups in the silk which are available for dye–fibre reaction will also increase with increasing pH and, therefore, both %*F* and %*T* will increase with increasing pH, as was indeed found over the pH range 3 to 8. Furthermore, the peak in %*F* and %*T* found at pH 8 may be explained by the related facts that the conversion of the β-sulfatoethylsulfone form to the reactive form of the aminochlorotriazine/masked vinylsulfone dyes used in this work is likely to be very high at pH 7–8 [7] but very low under acidic conditions [7, 8], and, furthermore, that VS dye exhaustion on silk is primarily a function of reaction with the fibre rather than the number of $-NH_3^+$ groups in the fibre [8]. Thus, the variation in %*F* and %*T* as a function of pH (Figs. 4 and 5) obtained for the three masked VS/aminochlorotriazine dyes appears, initially at least, to be described by the reaction of the unmasked VS form of the dye with predominantly amino groups in the substrate.

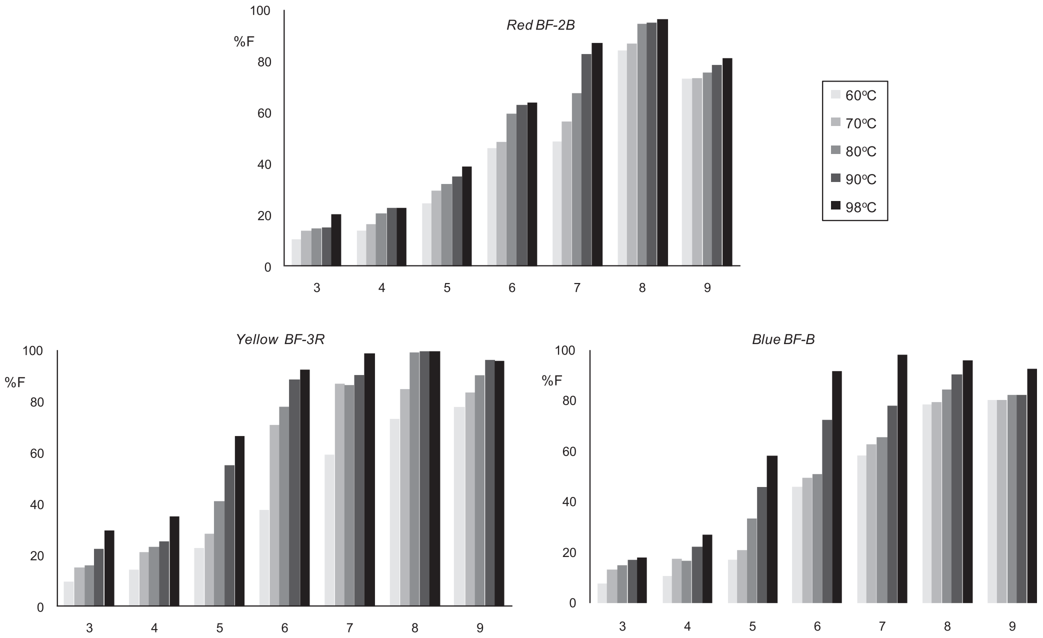

Fig. 4. %*F* as a function of dyeing pH and temperature.

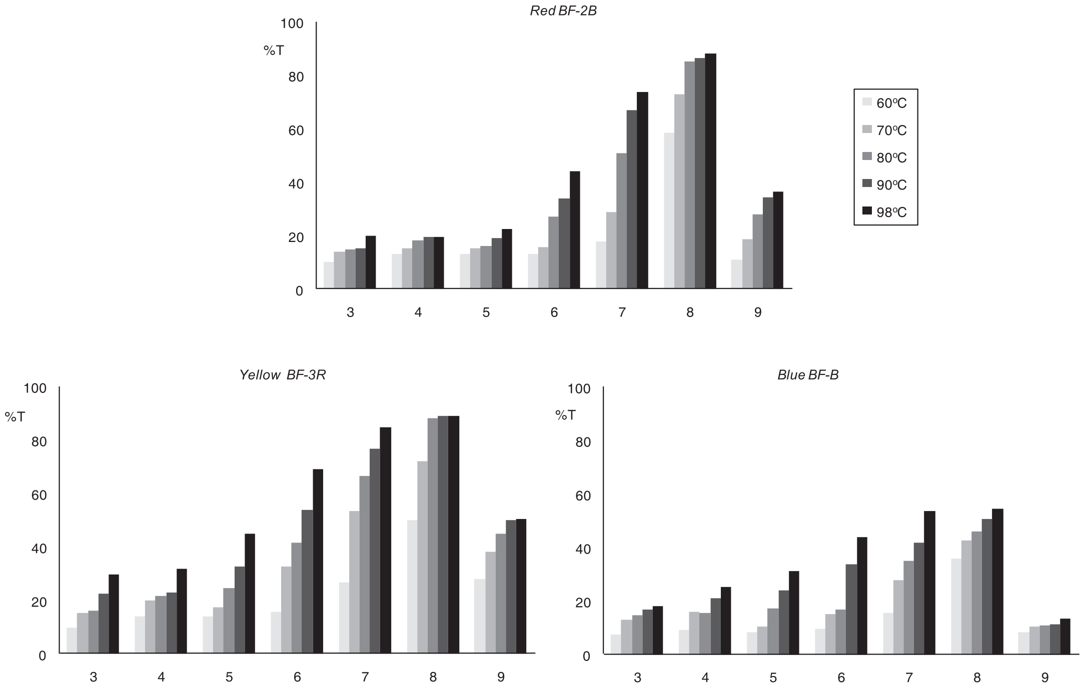

Fig. 5. *%T* as a function of dyeing pH and temperature.

However, Figs. 4 and 5 show that maximum dye fixation was achieved at pH 8, even though pH 7 has been considered by many workers [8–10,13,14] as providing optimum conditions for the application of C.I. Reactive Red 194 (**2**) to silk. The observed peak in dye fixation achieved at pH 8 (Figs. 4 and 5) may be due to the additional reaction of the VS form of the dyes with OH-containing side chains such as serine and tyrosine, as proposed for the reaction of various types of dye with silk [5,11,12]. Interestingly, Fig. 5 clearly shows that dye fixation was markedly lower at pH 9 than at pH 8, which can be considered to be a corollary of low dye exhaustion having occurred because of a paucity of protonated amino groups (Fig. 3), even though, according to Scheme 1, dye fixation at pH 9 should have been high owing to the large number of nucleophilic $-NH_2$ groups likely to be present in the silk; in addition, dye hydrolysis can be expected to be higher at pH 9 than at the other pH values employed.

The finding that for each of the three dyes used, both maximum dye fixation (*%F*) and total dye fixation (*%T*) were obtained at 98 °C over the pH range 3 to 9 (Figs. 4 and 5) demonstrates the importance of kinetic factors in dye–fibre reaction. Since, in the case of reactive dyeing in general, dye fixation promotes dye sorption, which, under conditions of high fixation, results in greater dye exhaustion and, thereby enhanced dye fixation, it follows that at pH 8, which resulted in maximum *%T* (Fig. 5), the effect of temperature on dye fixation should have been less marked than at the other pH values used, as indeed was the case (Fig. 5) for each of the three dyes used.

3.2. Wash-off

As mentioned, although it is common practice that all dyeings, regardless of dye and fibre type, be routinely subjected to a wash-off treatment to remove surplus dye, electrolyte, levelling agent, etc., so as to achieve optimum fastness [28], surprisingly few papers which concern the dyeing of silk with aminochlorotriazine/vinylsulfone dyes describe the use of a wash-off process at the end of dyeing [12,17,18]. In the case of the reactive dyeing of cellulosic, wool and nylon fibres, the typically hot, aqueous wash-off process employed, uses specific auxiliaries (e.g., surfactants) to expedite the removal of both unfixed and hydrolysed dye. In this work, as the *Yoracron BF* range of dyes are not intended for use on silk and, therefore, there is no recommended wash-off process, that used in Fig. 2 was used, which employed the proprietary anionic surfactant, *Lanapex R*, which had been used for the wash-off of modified VS dyes on silk [25]. Fig. 6 shows the colour strength (fk values) achieved for dyeings obtained at pH 8 and 90 °C, which had received a wash-off as well as dyeings which had not received a wash-off, but, instead had been rinsed in water and allowed to dry in the open air; the corresponding colorimetric parameters of the dyeings are displayed in Table 2.

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, which clearly demonstrate that the wash-off method used 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. Also shown in Table 2 and

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

Scheme 1. Protonation of amino groups in silk.

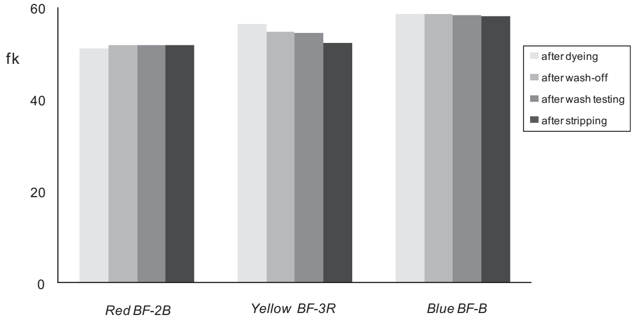

Fig. 6. Colour strength of dyeings obtained at pH 8 and 90 °C.

Table 2
Colorimetric data and shade changes for dyeings obtained at pH 8 and 90 °C.

Dye	Sample	$L*$	$a*$	$b*$	$C*$	$h°$	Shade change
Red BF-2B	after dyeing	51.5	60.7	1.6	60.7	1.5	–
	after wash-off	51.5	60.8	1.3	60.8	1.2	–
	after wash testing	51.4	59.3	2.7	59.4	2.6	4/5
	after stripping	51.3	59.5	1.2	59.5	1.1	–
Yellow BF-3R	after dyeing	41.4	–5.5	–19.9	20.6	254.2	–
	after wash-off	41.9	–5.5	–20.1	20.8	255.0	–
	after wash testing	41.9	–5.5	–19.8	20.5	254.6	5
	after stripping	42.4	–5.5	–19.6	20.4	254.5	–
Blue BF-B	after dyeing	73.1	26.6	73.7	78.4	70.2	–
	after wash-off	72.7	27.4	71.9	77.0	69.2	–
	after wash testing	72.6	27.9	72.2	77.4	68.9	4/5
	after stripping	72.4	27.2	71.3	76.3	69.1	–

Fig. 6 are the colorimetric data and fk values obtained for dyeings which had been subjected to the aq pyridine extraction method that was used to determine the extent of dye fixation. Since 'stripping' removed all unfixed and hydrolysed dye from the dyeings, then an fk value greater than that of the stripped dyeing indicates that surplus, unfixed/hydrolysed dye was still present within the dyed silk. Comparison of the fk values obtained for dyeings after wash-off and those secured for the corresponding dyeings after stripping can, therefore, be considered as a relative measure of the effectiveness of the wash-off method in removing surplus dye from the dyeings. In this context, for each of the three dyes used, Fig. 6 shows that although the wash-off process was less effective than stripping with aq pyridine, nevertheless, substantial amounts of unfixed/hydrolysed dye were removed by wash-off. Support for this finding is provided by the fk values secured for washed-off dyeings which had been subjected to wash testing at 40 °C (Fig. 6). Although wash testing removed additional dye from the washed-off dyeings, it is apparent from the small differences in fk value obtained between dyeings after wash-off and after wash testing, that very small amounts of surplus unreacted/hydrolysed dye were present on the fibre before wash testing. In addition, Table 2 shows that wash testing imparted small changes to the shade of the dyeings, which, again, is indicative that little unfixed/hydrolysed dye was present on the washed-off dyeings. The respective colorimetric data obtained for the dyeings (Table 2) reveal that for each of the three dyes, very small changes in hue and chroma were imparted to the dyeings by both wash-off and wash testing.

These findings therefore show that the wash-off process used (Fig. 2) was quite effective in removing surplus dye from the dyeings.

4. Conclusions

Both the exhaustion and fixation of the three aminochlorotriazine/masked vinylsulfone dyes were pH- and temperature-dependent. Whilst high dye exhaustion but low fixation was achieved at pH 3 and 4 and the use of pH 9 resulted in low fixation and low exhaustion, optimum dye fixation was obtained at pH 8, as a corollary of a high number of nucleophilic $-NH_2$ groups in the fibre, high conversion of the masked form of the dye to the reactive VS variant as well as reaction with OH-containing amino acid residues. The temperature-dependence of both dye exhaustion and fixation in the range pH 5 to 9 was attributed to fixation-determined kinetics, as VS dye exhaustion on silk is a function of reaction with the fibre rather than protonated groups in the fibre. The wash-off method used was very effective in removing unfixed/hydrolysed dye from the silk fabric and, as a result, the dyeings displayed very good fastness to washing at 40 °C.

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