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# The mordant dyeing of wool using tannic acid and $FeSO_4$, Part 1: Initial findings

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ABSTRACT

C.I. Mordant Black 8 produced reddish-brown dyeings on wool of good light fastness, moderate rub fastness but poor fastness to washing at 40 °C. Subsequent afterchroming with $Na_2Cr_2O_7$ provided deep, black dyeings of much improved fastness. The substitution of $Na_2Cr_2O_7$ with $FeSO_4$ also improved the fastness of the unmordanted dyeings but the ensuing brown shades displayed lower, all-round fastness to their afterchromed counterparts. When the dye was applied in combination with tannic acid, subsequent mordanting with ferrous sulfate yielded brown/greyish-brown dyeings of high colour strength and high all-round fastness. Of two methods that were used to produce such dye/tannic acid/$FeSO_4$ 'combination' dyeings, namely, (dye + tannic acid)/$FeSO_4$ and dye/(tannic acid + $FeSO_4$), the latter yielded dyeings of superior fastness.

## 1. Introduction

The pretreatment of textile fibres with a mordant (salts of various metals or tannins) in order to achieve dyeings of improved fastness, depth of shade or different colours, has been practised since time immemorial. Nowadays, the use of *mordant dyes* is mostly confined to wool, on which the dyes, in conjunction with a metallic mordant, provide deep shades of characteristically excellent wet and light fastness. Although, essentially, mordant dyes resemble non-metallised acid dyes, they contain ligands (OH, $NH_2$, COOH) that enable them to form a stable, coordination complex with a metal ion *in situ* within the wool fibre, this being accompanied by a dramatic improvement in both the fastness of the dyeing to light and wet agencies, as well as a marked change in the colour of the dyeing. Whilst, in theory, various transition metals can function as mordants and chromium predominates because of the superior fastness of dyeings obtained using salts of this metal (commonly $Na_2Cr_2O_7$ or $K_2Cr_2O_7$); consequently, the term '*chrome dye*' is often incorrectly used. In the case of wool, for which mordant dyes were first devised, three methods of application can be used namely, *pre-chrome*, *metachrome* and *afterchrome*, depending on whether the mordant is applied before, together with or after the dye; the afterchrome method predominates currently. However, the use of mordant dyes has decreased in recent years, owing to environmental concerns regarding the use of heavy metals, including chromium. In this context, the replacement of chromium with less environmentally challenging Fe(II) and Fe(III) salts wa found to improve the light fastness [1,2] and the wash fastness [2] of various mordant dyes on wool, although the colour of the dyeings obtained using iron salts differed to that achieved using dichromate. It was shown that the use of iron salts resulted in the formation of 1:2 dye:metal complexes within the dyed substrate [1,2].

Vegetable tannin extracts are large $M_r$, water-soluble phenolic compounds that have been used on textiles for several hundreds of years, as exemplified by the dyeing of cotton and silk with natural dyes obtained from 'dyewoods', in which the tannin 'fixed' the metal salt (e.g. $CuSO_4$) that was employed as a mordant for the dye. Natural tannins continue to enjoy textile usage, as represented by the application of tannic acid as an aftertreatment to improve the wet fastness of dyeings on nylon fibres and as a stain resist treatment for nylon carpet [3,4]. The combination of tannins with iron salts has enjoyed varied applications over many centuries, such as the use of tannic acid and iron sulfate in the preparation of iron gall inks and, in the context of the work described herein, the use of *copperas* ($FeSO_4 \cdot 7H_2O$) in conjunction with tannins to produce greyish-brown shades on cotton, silk and wool, which has been practised since medieval times.

This paper concerns the feasibility of obtaining deep, black shades on wool using tannic acid and iron$_{(II)}$ sulfate. This part of the paper concerns initial findings made using C.I. Mordant Black 8 whilst the second part of the paper discusses the nature of the interactions between various mordant dyes, tannic acid and $FeSO_4$.

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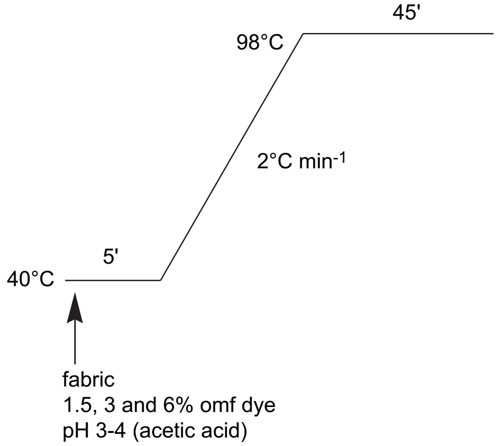

**Fig. 1.** Dyeing method for mordant dyes.

## 2. Experimental

### 2.1. Materials

Wool fabric, obtained from Whaleys (Bradford, UK) was scoured before use by treatment in an aqueous solution of 1 g dm$^{-3}$ *Sandozin NIN* (a non-ionic surfactant supplied by Clariant UK) at 40 °C for 30 min; the scoured fabric was rinsed thoroughly in tap water and allowed to dry in the open air. A commercial sample of C.I Mordant Black 8 was kindly provided by DyStar; the dye was used without purification. Commercial samples of tannic acid, sodium dichromate and ferrous sulfate were obtained from Sigma–Aldrich; all other chemicals were laboratory grade reagents.

### 2.2. Dyeing, mordanting and treatment with tannic acid

The application of the mordant dye, $Na_2Cr_2O_7$, $FeSO_4$ and tannic acid was carried out in 300 cm$^3$ capacity, sealed, stainless steel dyepots housed in a Roaches *Pyrotec S* dyeing machine.

*2.2.1. Dyeing*
Wool fabric was dyed with 1.5%, 3% and 6% omf dye, using the method shown in Fig. 1; the dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

*2.2.2. Afterchrome dyeing*
1.5%, 3% and 6% omf dyeings were treated, respectively, with 0.3%, 0.75% and 1.5% omf $Na_2Cr_2O_7$ or $FeSO_4$ using the method shown in Fig. 2; the mordanted dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

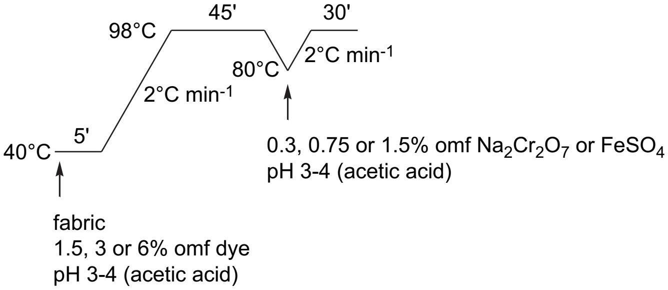

**Fig. 2.** Dyeing and mordanting method.

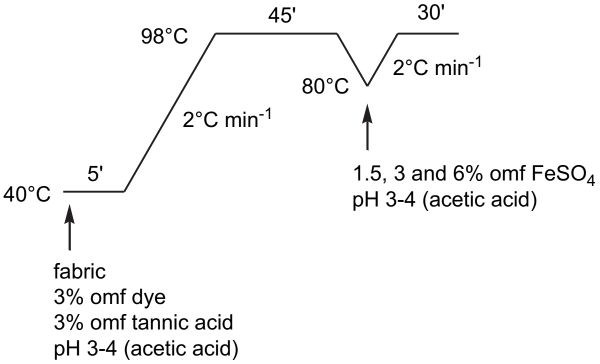

**Fig. 3.** Combination (dye + tannic acid) method.

*2.2.3. Combination mordant dyeing*
Dyeings were produced in which

(a) 3% omf dye and 3% omf tannic acid were applied in admixture to wool and the ensuing dyeings were subsequently mordanted using 1.5%, 3% and 6% omf $FeSO_4$ (Fig. 3);
(b) 3% omf dyeings were mordanted with a combination of 3% tannic acid and 1.5%, 3% and 6% omf $FeSO_4$ (Fig. 4).

In each dyeing method, the mordanted dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

*2.2.4. Treatment with tannic acid*
Wool fabric was treated with 3% omf tannic acid using the method shown in Fig. 5 at the end of which process, the fabric was allowed to dry in the open air.

*2.2.5. Treatment with tannic acid and ferrous sulfate*
Wool fabric which had been treated with 3% omf tannic acid was subsequently mordanted using 1.5% and 3% omf $FeSO_4$ (Fig. 6) at the end of which process, the fabric was allowed to dry in the open air.

### 2.3. Colour measurement

The CIE $L^*$, $a^*$, $b^*$, $C^*$ and $h°$ colour co-ordinates were measured and $K/S$ values calculated from the reflectance values at the appropriate $\lambda_{max}$ for each dyeing, using a *Datacolor Spectroflash 600* spectrophotometer under illuminant $D_{65}$, using a 10° standard observer with UV component included and specular component excluded. The samples were folded so as to realise four thicknesses.

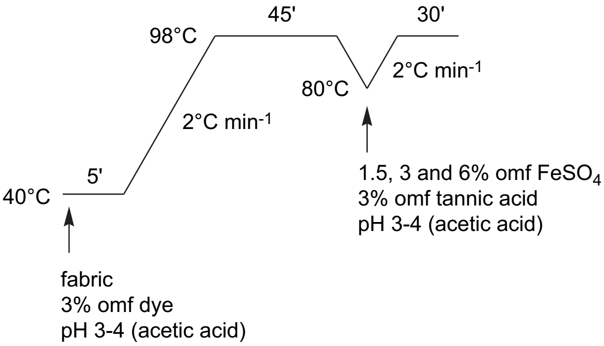

**Fig. 4.** Combination ($FeSO_4$ + tannic acid) method.

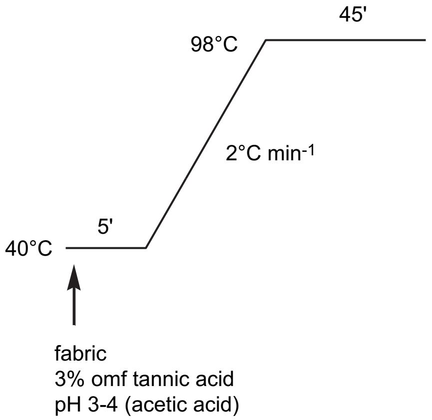

**Fig. 5.** Tannic acid application method.

### 2.4. Fastness testing

The fastness of the samples to washing, light and rubbing (wet and dry) was determined using the ISO CO6/A2S (40_C), ISO BO2 and ISO 105: X12 test methods, respectively [5].

## 3. Results and discussion

Deep, black shades on wool of high, overall, fastness are commonly achieved using afterchromed mordant dyes, as exemplified by C.I. Mordant Black 8, which was selected for use in this work. As mentioned, the role of the chromium mordant is to secure a dramatic improvement in both the fastness of the dyeing to light and wet agencies via the formation of a stable, coordination complex with the metal ion *in situ* within the wool fibre, this being accompanied by a marked change in the colour of the dyeing. Often the colour of the dye on wool in its unmordanted form differs, considerably, to that obtained after mordanting.

**Table 1**
Colorimetric data for mordanted and unmordanted dyeings

| Dyeing/mordanting | No. of washes | $L^*$ | $a^*$ | $b^*$ | $C^*$ | $h^\circ$ | $\lambda_{max}$ |
|---|---|---|---|---|---|---|---|
| 1.5% Dye | 0 | 20.8 | 17.2 | −2.1 | 17.3 | 352.7 | 540 |
| | 1 | 23.9 | 10.5 | −3.1 | 10.7 | 343.9 | 540 |
| 3% Dye | 0 | 17.1 | 14.8 | −0.2 | 14.1 | 359.1 | 540 |
| | 1 | 18.9 | 5.9 | −2.6 | 6.5 | 336.2 | 540 |
| 6% Dye | 0 | 15.4 | 9.3 | −0.2 | 9.5 | 358.8 | 520 |
| | 1 | 13.4 | 2.9 | −0.9 | 3.1 | 342.1 | 520 |
| 1.5% Dye + 0.3% $Na_2Cr_2O_7$ | 0 | 20.7 | 0.1 | −2.8 | 2.8 | 271.6 | 600 |
| | 1 | 20.3 | 1.5 | −2.0 | 2.5 | 306.9 | 580 |
| 3% Dye + 0.75% $Na_2Cr_2O_7$ | 0 | 16.4 | 0.4 | −2.7 | 2.7 | 278.9 | 600 |
| | 1 | 16.4 | 0.5 | −0.5 | 0.7 | 314.5 | 600 |
| 6% Dye + 1.5% $Na_2Cr_2O_7$ | 0 | 13.9 | 0.3 | −1.8 | 1.8 | 280.8 | 580 |
| | 1 | 13.3 | 0.5 | −1.4 | 1.5 | 290.9 | 580 |
| 1.5% Dye + 0.3% $FeSO_4$ | 0 | 24.4 | 5.9 | 9.1 | 10.9 | 57.1 | 480 |
| | 1 | 23.6 | 5.1 | 7.5 | 9.1 | 55.4 | 480 |
| 3% Dye + 0.75% $FeSO_4$ | 0 | 19.1 | 4.7 | 6.1 | 7.6 | 51.7 | 480 |
| | 1 | 23.4 | 2.8 | 2.8 | 3.9 | 44.5 | 480 |
| 6% Dye + 1.5% $FeSO_4$ | 0 | 15.0 | 2.5 | 2.2 | 3.4 | 41.3 | 500 |
| | 1 | 14.1 | 2.4 | 2.2 | 3.3 | 42.4 | 500 |

Table 1 shows the colorimetric data obtained for 1.5%, 3% and 6% omf dyeings of C.I. Mordant Black 8, both before and after wash testing at 40 °C. It is apparent that the dyeings were not black in colour; the bordeaux coloured 1.5% omf dyeing became not only deeper with increasing amount of dye applied but also became browner, with the result that the colour of the 6% omf dyeing was a brownish red. Table 1 also shows that when the dyeings were subjected to wash testing at 40 °C, the colour of the dyeings changed insofar as the dyeings became browner and duller; the extent and nature of this colour change is illustrated by the $a^*$ vs $b^*$ plot depicted in Fig. 7. Table 2 shows that the dyeings displayed poor fastness to washing, as evidenced by the sizeable changes in shade of the dyeings and the marked staining of adjacent nylon, cotton and secondary acetate fibres. The magnitude of the change in the depth of shade that each of the dyeings underwent during wash testing is clearly apparent from the reduction in colour strength data shown in Fig. 8. The findings displayed in Table 2 reveal that the fastness of the dyeings decreased with increasing depth of shade, which can be attributed to an increase in the amount of the dye present in the fibre. Thus, in its unmordanted form, C.I. Mordant Black 8 provided reddish-brown dyeings of poor fastness to washing; this was not surprising, as the mordant dye is intended to be used on wool in conjunction with a chromium mordant and, in its unmordanted form, behaves, in essence, as a low wet fastness, acid dye.

When the dyeings of C.I. Mordant Black 8 were afterchromed using $Na_2Cr_2O_7$, the fastness of the dyeings was improved, considerably (Table 2) with only a small shade change having occurred in the cases of the two higher depth dyeings; significantly, no

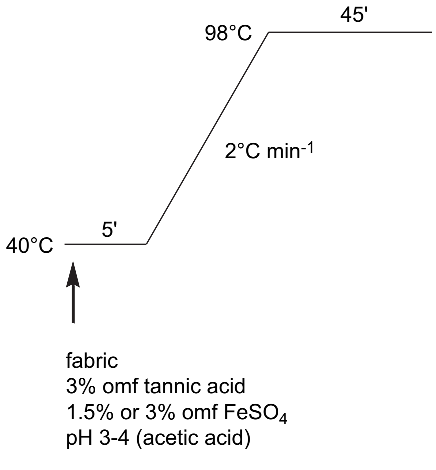

**Fig. 6.** Tannic acid/$FeSO_4$ application method.

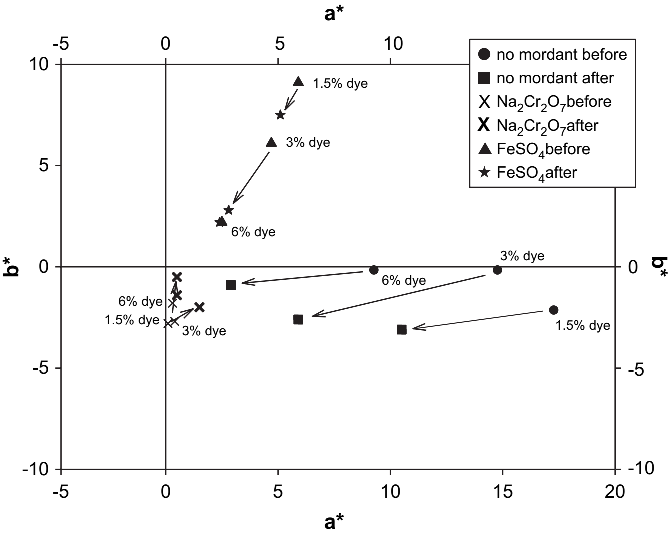

**Fig. 7.** Effects of mordants on the hue of dyeings before and after washing.

**Table 2**
Fastness of dyeings to ISO CO6/A2S (40 °C)

| Dyeing/ mordanting | Change in shade | Staining of adjacent fibres | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wool | Acrylic | Polyester | Nylon 6,6 | Cotton | 2° Acetate |
| 1.5% Dye | 2 | 5 | 5 | 5 | 4 | 2/3 | 4 |
| 3% Dye | 1/2 | 5 | 5 | 5 | 4 | 1/2 | 3 |
| 6% Dye | 2 | 4 | 5 | 5 | 3/4 | 2 | 3 |
| 1.5% Dye + 0.3% $Na_2Cr_2O_7$ | 4 | 5 | 5 | 5 | 5 | 5 | 5 |
| 3% Dye + 0.75% $Na_2Cr_2O_7$ | 3/4 | 5 | 5 | 5 | 5 | 5 | 5 |
| 6% Dye + 1.5% $Na_2Cr_2O_7$ | 4/5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 1.5% dye + 0.3% $FeSO_4$ | 2 | 5 | 5 | 5 | 5 | 3/4 | 5 |
| 3% Dye + 0.75% $FeSO_4$ | 4 | 5 | 5 | 5 | 5 | 4/5 | 5 |
| 6% Dye + 1.5% $FeSO_4$ | 4/5 | 5 | 5 | 5 | 5 | 4 | 5 |

**Table 3**
Colorimetric data for tannic acid treated wool

| Treatment | No. of washes | $L^*$ | $a^*$ | $b^*$ | $C^*$ | $h°$ | $\lambda_{max}$ |
|---|---|---|---|---|---|---|---|
| None | – | 86.7 | 0.2 | 10.7 | 10.7 | 88.8 | 400 |
| 3% Tannic acid | 0 | 74.1 | 2.5 | 19.0 | 19.1 | 82.3 | 400 |
| | 1 | 77.4 | 1.3 | 21.7 | 21.8 | 86.4 | 400 |
| 3% Tannic acid + 1.5% $FeSO_4$ | 0 | 44.3 | 2.6 | 2.6 | 3.6 | 45.0 | 400 |
| | 1 | 48.1 | 6.9 | 9.9 | 12.1 | 55.1 | 400 |
| 3% Tannic acid + 3% $FeSO_4$ | 0 | 34.8 | 1.5 | −2.1 | 2.6 | 306.2 | 560 |
| | 1 | 55.1 | 3.8 | 8.4 | 9.2 | 65.8 | 400 |

staining of adjacent materials was observed. It was, therefore, not surprising that the *K/S* values of the afterchromed dyeings were relatively little changed by wash testing (Fig. 8). The observation that the colour strength of the afterchromed dyeings before washing was lower, for each of the three depths of shade used, than that of the unmordanted dyeings (Fig. 8) can be attributed to dye having been desorbed from the dyeings during the subsequent mordanting stage. Fig. 7 shows that the colour of the mordanted dyeings was little affected by wash testing at 40 °C, this being expected in view of the well-known stability of afterchromed, mordant dyeings. When the corresponding colorimetric data for the afterchromed dyeings are compared with those of the unmordanted dyeings (Table 1) it is evident that treatment with $Na_2Cr_2O_7$ changed the colour of the dyeings insofar as black shades were obtained, at each of the three depths of dye used; this is also apparent from the $a^*$ and $b^*$ data shown in Fig. 7. The marked change in the colour of the dyeings imparted by mordanting with $Na_2Cr_2O_7$ is clearly evident from a comparison of the $\lambda_{max}$ values obtained for the unmordanted and afterchromed dyeings (Table 1). Thus, whilst the unmordanted dye gave red/brown hues on wool, mordanting with $Na_2Cr_2O_7$ produced deep, black shades and also improved the fastness of the dye to washing at 40 °C. These findings were expected and are characteristic of the afterchrome dyeing of wool using mordant dyes.

When the dyeings of C.I. Mordant Black 8 were ‘afterchromed’ using $FeSO_4$ as mordant, brown dyeings were obtained that increased in depth with increasing amount of $FeSO_4$ applied (Table 1; Figs. 7 and 8). The change in the colour of the dyeings imparted by treatment with the iron salt is clearly apparent from a comparison of the $\lambda_{max}$ values obtained for the unmordanted and mordanted dyeings (Table 1). The colour strength of the ferrous sulfate mordanted dyeings prior to wash fastness testing was very similar to that of the corresponding dyeings which had been mordanted with $Na_2Cr_2O_7$ (Fig. 8). The $FeSO_4$ mordanted dyeings displayed higher fastness to washing at 40 °C than the respective unmordanted dyeings (Table 2) with only a small shade change having occurred in the cases of the two higher depth dyeings and little staining of adjacent cotton. However, the fastness of the ferrous sulfate mordanted dyeings was lower than those of the dyeings which had been mordanted using sodium dichromate (Table 2); the reduced colour strength of the washed dyeings (Fig. 8) can be attributed to dye loss that occurred during wash testing. Fig. 7 shows that although the colour of the 1.5% and 3% omf dyeings which had been mordanted using $FeSO_4$ was affected by wash testing at 40 °C, the extent of this colour change was smaller than that secured for the unmordanted dyeings. Fig. 7 also shows quite clearly, that the extent of the colour change recorded for the dyeings which had been mordanted with $FeSO_4$ was, with the exception of the 6% omf dyeing, much greater than that achieved for the dyeings which had been mordanted with $Na_2Cr_2O_7$. This finding, together with the fastness data shown in Table 2, suggests that the stability of the $FeSO_4$ mordanted dyeings may well be lower than that of the dyeings which had been mordanted with $Na_2Cr_2O_7$. Thus, mordanting with iron sulfate not only changed the red/brown hue of the unmordanted dyeings to deep brown but also improved the fastness of C.I. Mordant Black 8 to washing at 40 °C. Indeed, it is of interest to note that not only was the fastness of the $FeSO_4$

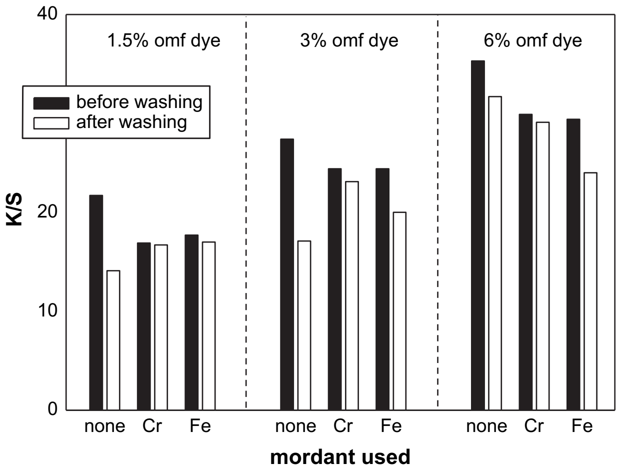

**Fig. 8.** Colour strength of dyeings before and after washing.

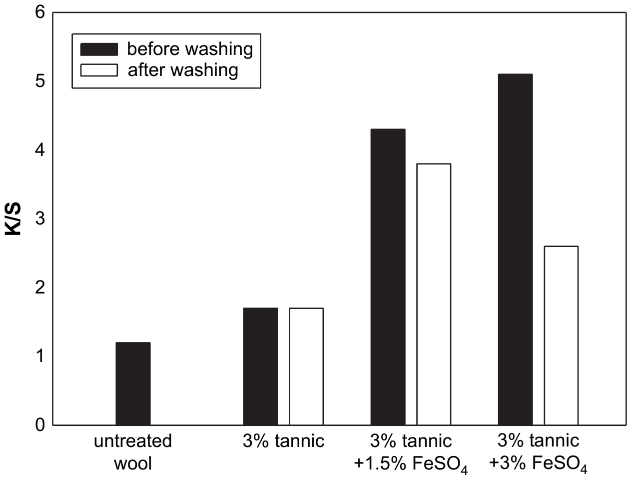

**Fig. 9.** Colour strength before and aftertreatment with tannic acid/mordants.

**Table 4**
Fastness of tannic acid treated wool to ISO CO6/A2S (40 °C)

| Treatment | Change in shade | Staining of adjacent fibres | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wool | Acrylic | Polyester | Nylon 6,6 | Cotton | 2° Acetate |
| 3% Tannic acid | 1/2 | 5 | 5 | 5 | 4/5 | 4 | 5 |
| 3% Tannic acid + 1.5% $FeSO_4$ | 1/2 | 5 | 5 | 5 | 5 | 5 | 5 |
| 3% Tannic acid + 3% $FeSO_4$ | 1 | 4 | 5 | 5 | 5 | 5 | 5 |

**Table 5**
Colorimetric data for combination dye/mordant dyeings

| Dyeing and mordanting method | No. of washes | $L^*$ | $a^*$ | $b^*$ | $C^*$ | $h°$ | $\lambda_{max}$ |
|---|---|---|---|---|---|---|---|
| (3% Dye + 3% tannic acid) + 1.5% $FeSO_4$ | 0 | 14.7 | 3.1 | 1.5 | 3.3 | 27.2 | 500 |
| | 1 | 14.6 | 3.6 | 1.3 | 3.8 | 19.8 | 500 |
| (3% Dye + 3% tannic acid) + 3% $FeSO_4$ | 0 | 14.5 | 1.8 | 1.2 | 2.1 | 33.4 | 500 |
| | 1 | 12.7 | 1.7 | 1.2 | 2.1 | 35.9 | 500 |
| (3% Dye + 3% tannic acid) + 6% $FeSO_4$ | 0 | 15.0 | 2.0 | 1.1 | 2.3 | 25.7 | 500 |
| | 1 | 12.9 | 1.7 | 1.1 | 2.1 | 32.3 | 500 |
| 3% Dye + (3% tannic acid + 1.5% $FeSO_4$) | 0 | 16.3 | 5.2 | 2.7 | 5.9 | 27.6 | 500 |
| | 1 | 15.8 | 4.2 | 2.2 | 4.7 | 27.7 | 500 |
| 3% Dye + (3% tannic acid + 3% $FeSO_4$) | 0 | 15.8 | 3.1 | 3.4 | 4.5 | 48.9 | 480 |
| | 1 | 16.3 | 3.2 | 3.9 | 5.1 | 50.3 | 480 |
| 3% Dye + (3% tannic acid + 6% $FeSO_4$) | 0 | 13.9 | 2.5 | 3.1 | 4.1 | 50.1 | 480 |
| | 1 | 15.2 | 2.6 | 3.2 | 4.1 | 50.1 | 480 |

mordanted dyeings only slightly lower than those of their dichromate mordanted counterparts (Table 2) but the *K*/*S* of the dyeings which had been mordanted with ferrous sulfate was very similar to that of the $Na_2Cr_2O_7$ mordanted dyeings.

As mentioned, tannins have enjoyed widespread use as mordants for various types of dyes on wool and other fibres; the combination of iron salts and tannins to produce greyish-brown shades on cotton, silk and wool has been practised since medieval times. In this context, the treatment of wool with 3% omf tannic acid imparted a yellowish-brown colour to the wool fabric (Table 3), which is a well-known characteristic of the gallotannin [4]. It is also apparent that tannic acid treatment reduced the lightness ($L^*$) of the fabric but did not result in a colouration of high colour strength (Fig. 9). Washing at 40 °C reduced the extent of the discolouration imparted by the gallotannin and reduced the colour strength of the treated wool (Table 3 and Fig. 9). The fastness of the tannic acid was very poor, as shown by the large shade change and staining of adjacent cotton and nylon 6,6 (Table 4). Table 3 shows that subsequent treatment with $FeSO_4$ resulted in a brown shade (1.5% $FeSO_4$) which became greyer with increasing concentration of mordant used (3% $FeSO_4$). The wash fastness of both the 1.5% and 3% mordanted tannic acid samples was poor, in terms of the marked shade change that occurred (Table 4); interestingly, despite the large reduction in shade imparted by washing, none of the adjacent materials were stained during wash testing. Thus, the use of 3% omf tannic acid in conjunction with a 3% omf $FeSO_4$ mordant produced a greyish-brown shade of relatively low colour strength; whilst the mordanted tannic acid sample underwent a large shade during wash fastness testing, adjacent, multifibre strip materials were unstained.

As the use of 6% omf dye in conjunction with both $Na_2Cr_2O_7$ or $FeSO_4$ mordants produced dyeings of high colour strength (Fig. 8) and adequate fastness (Table 2), it was decided to determine whether it would be possible to obtain satisfactory dyeings by replacing a portion of the dye used with tannic acid and mordanting the resulting combination dyeing with ferrous sulfate. In this context, 3% omf dye and 3% omf tannic acid were applied in admixture to wool and the ensuing dyeings were mordanted using 1.5%, 3% and 6% $FeSO_4$. Two methods were used to produce these 'combination' dyeings.

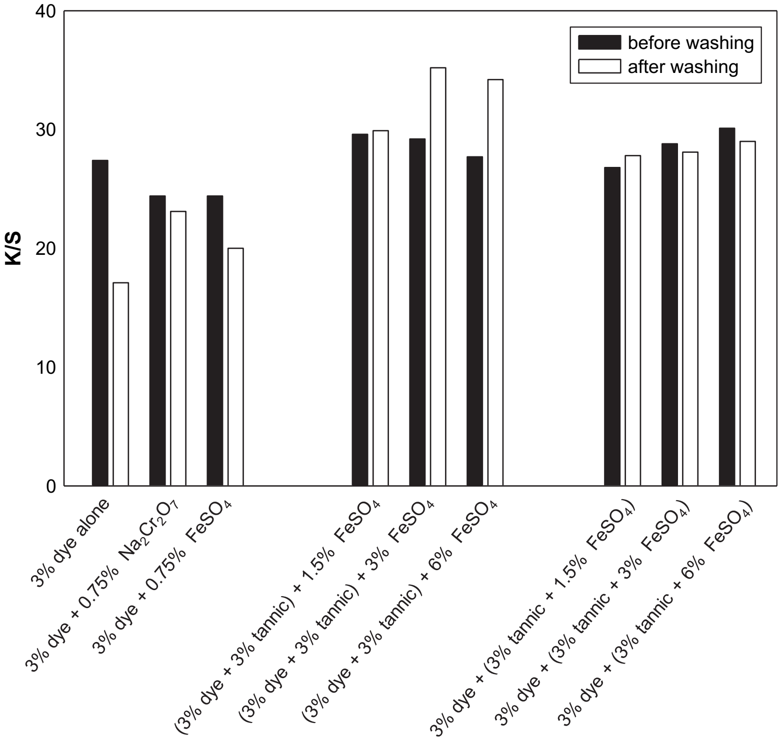

**Fig. 10.** Colour strength of combination dyeings before and after washing.

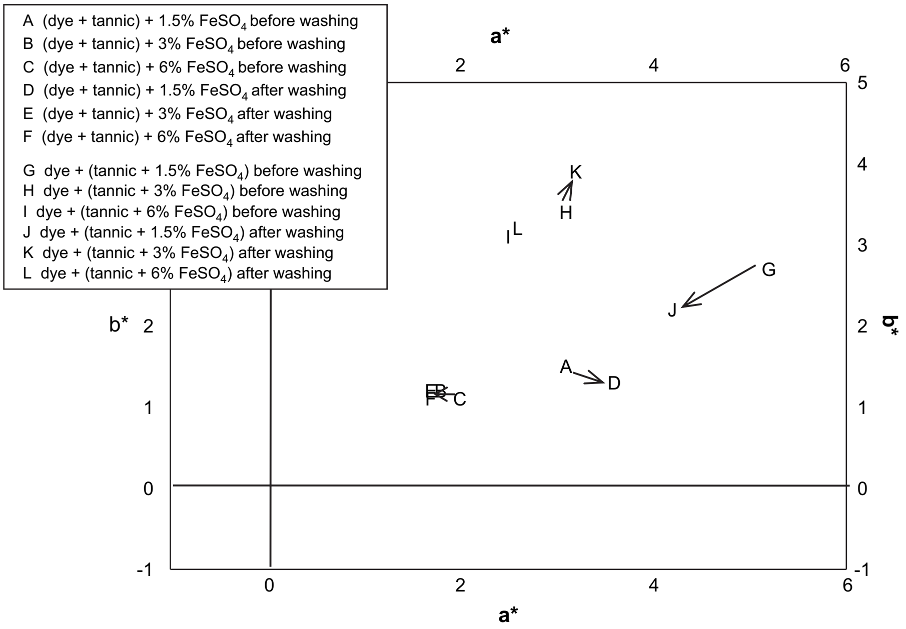

**Fig. 11.** Effects of mordants on the hue of combination dyeings before and after washing.

(a) (Dye + tannic acid)/$FeSO_4$ – 3% omf dye and 3% omf tannic acid were applied in admixture to wool and the ensuing dyeings were subsequently mordanted using 1.5%, 3% or 6% omf $FeSO_4$ (Fig. 3);

(b) Dye/(tannic acid + $FeSO_4$) – 3% omf dyeings were subsequently mordanted using a combination of 3% tannic acid and 1.5%, 3% or 6% omf $FeSO_4$ (Fig. 4).

Table 5 shows that although the colour of the three (3% omf dye + 3% omf tannic acid)/$FeSO_4$ combination dyeings varied from brown (1.5% omf mordant) through to dark brown (6% omf mordant), the combination dyeings were greyer in colour compared to dyeings which had been mordanted using ferrous sulfate in the absence of tannic acid (Table 1), presumably due to the presence of the tannic acid. The colour strength of the three (dye + tannic acid)/$FeSO_4$ combination dyeings (Fig. 10) was higher than that of the 3% omf dyeing and the 3% omf dyeings which had been mordanted using 0.75% omf $FeSO_4$ as well as with 0.75% omf $Na_2Cr_2O_7$ in the absence of tannic acid. Fig. 10 also shows that the colour strength of the (dye + tannic acid)/$FeSO_4$ combination dyeings decreased with increasing amount of ferrous sulfate applied; it is also evident that the colour strength of the dyeings of each of the three (3% omf dye + 3% omf tannic acid)/$FeSO_4$ combination dyeings increased as a result of washing. Although an explanation for these observations is not proposed herein, they form part of an on-going investigation into the nature of the dye/tannic acid/$FeSO_4$ interaction which will be reported in the second part of this paper. The colour of the 3% and 6% mordanted dyeings was little changed by washing (Table 5 and Fig. 11) and each of the three (dye + tannic acid)/$FeSO_4$ combination dyeings displayed moderate fastness to washing at 40 °C, as shown by the shade changes and staining of adjacent cotton and nylon 6,6 (Table 6).

When a 3% omf dyeing was mordanted with a combination of 3% omf tannic acid and 1.5%, 3% and 6% omf $FeSO_4$, deep, brown dyeings were again secured (Table 5) which darkened with increasing amount of $FeSO_4$ used. The colour strength of the combination dyeings (Fig. 10) was higher than that of the 3% omf dyeing and the 3% omf dyeings which had been mordanted using 0.75% omf $FeSO_4$ as well as with 0.75% omf $Na_2Cr_2O_7$ in the absence of tannic acid. Fig. 10 also shows that the colour strength of the dye + (tannic acid/$FeSO_4$) combination dyeings increased with increasing amount of ferrous sulfate used. It is also clear that whilst the *K*/*S* of the (3% omf

**Table 6**
Fastness of combination dyeings to ISO CO6/A2S (40 °C)

| Dyeing and mordanting method | Change in shade | Staining of adjacent fibres | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wool | Acrylic | Polyester | Nylon 6,6 | Cotton | 2° Acetate |
| (3% Dye + 3% tannic acid) + 1.5% $FeSO_4$ | 4/5 | 5 | 5 | 5 | 3/4 | 3 | 5 |
| (3% Dye + 3% tannic acid) + 3% $FeSO_4$ | 4 | 5 | 5 | 5 | 3/4 | 3/4 | 5 |
| (3% Dye + 3% tannic acid) + 6% $FeSO_4$ | 3/4 | 5 | 5 | 5 | 3/4 | 3 | 5 |
| 3% Dye + (3% tannic acid + 1.5% $FeSO_4$) | 4 | 5 | 5 | 5 | 4 | 4/5 | 5 |
| 3% Dye + (3% tannic acid + 3% $FeSO_4$) | 4/5 | 5 | 5 | 5 | 5 | 4/5 | 5 |
| 3% Dye + (3% tannic acid + 6% $FeSO_4$) | 4/5 | 5 | 5 | 5 | 5 | 4/5 | 5 |

**Table 7**
Light fastness of dyeings

| Treatment | |
|---|---|
| 3% Dye | 5 |
| 6% Dye | 5 |
| 3% Dye + 0.75% $Na_2Cr_2O_7$ | 6 |
| 3% Dye + 0.75% $FeSO_4$ | 6 |
| 3% Tannic acid | 5 |
| 3% Tannic acid + 1.5% $FeSO_4$ | 5 |
| | 5 |
| (3% Dye + 3% tannic acid) + 1.5% $FeSO_4$ | |
| | 6 |
| (3% Dye + 3% tannic acid) + 6% $FeSO_4$ | |
| 3% Dye + (3% tannic acid + 1.5% $FeSO_4$) | 5 |
| 3% Dye + (3% tannic acid + 6% $FeSO_4$) | 6 |

**Table 8**
Rub fastness of dyeings

| Treatment | Dry | | Wet | |
|---|---|---|---|---|
| | Change in shade | Staining | Change in shade | Staining |
| 3% Dye | 3/4 | 4 | 3/4 | 3 |
| 6% Dye | 3 | 3/4 | 3 | 3 |
| 3% Dye + 0.75% $Na_2Cr_2O_7$ | 4/5 | 5 | 4/5 | 5 |
| 3% Dye + 0.75% $FeSO_4$ | 4 | 3 | 4 | 3/4 |
| 3% Tannic acid | 2 | 4/5 | 2 | 4/5 |
| 3% Tannic acid + 1.5% $FeSO_4$ | 1 | 3 | 1 | 2 |
| (3% Dye + 3% tannic acid) + 1.5% $FeSO_4$ | 3/4 | 4 | 4 | 3 |
| (3% Dye + 3% tannic acid) + 6% $FeSO_4$ | 4 | 3/4 | 4 | 3/4 |
| 3% Dye + (3% tannic acid + 1.5% $FeSO_4$) | 3/4 | 3/4 | 4 | 3 |
| 3% Dye + (3% tannic acid + 6% $FeSO_4$) | 4/5 | 4/5 | 4/5 | 4/5 |

tannic acid/1.5% FeSO4) dyeing increased slightly as a result of washing, that of both the (3% omf tannic acid/3% FeSO4) and (3% omf tannic acid/6% FeSO4) combination dyeings decreased as a result of washing, which can be attributed to loss of dye. Table 6 shows that the dyeings displayed very good fastness to washing, undergoing little shade change and imparting little staining to adjacent materials; indeed, the wash fastness of the 3% omf dye which had been mordanted using (3% omf tannic acid/3% $FeSO_4$) and (3% omf tannic acid/6% $FeSO_4$) was very similar to that secured for the 3% omf dyeings which had been mordanted with 0.75% omf $Na_2Cr_2O_7$ (Table 2). This finding is all the more interesting bearing in mind the similar colour strengths of the 1.5% omf $Na_2Cr_2O_7$ mordanted dyeing and the 3% omf dye + (3% omf tannic acid/3% $FeSO_4$) and (3% omf tannic acid/6% $FeSO_4$) combination dyeings. The $a^*$ vs $b^*$ plot shown in Fig. 11 reveals that the colour of the 3% omf dye + (3% omf tannic acid/$FeSO_4$) combination dyeings were changed by washing. The extent of this colour change decreased, markedly, as the amount of $FeSO_4$ used increased; indeed, the small shade changes observed for both the (3% omf tannic acid/3% omf $FeSO_4$) and (3% omf tannic acid/6% omf $FeSO_4$) mordanted dyeings were similar to those achieved for the dyeings which had been aftertreated using $Na_2Cr_2O_7$ (Fig. 7). This finding, together with the very good fastness data shown in Table 6, suggests that the stability of the 3% omf dye + (3% omf tannic acid/$FeSO_4$) combination dyeings may well be of a similar level to that of the dyeings which had been mordanted with $Na_2Cr_2O_7$.

Table 7 shows the fastness to light of the dye, both alone and with various mordants from which it is apparent that the fastness of the two types of combination dyeings that employed 3% omf dye was not different to that of the 3% omf dyeings which had been mordanted with either $Na_2Cr_2O_7$ or $FeSO_4$. The rub fastness data displayed in Table 8 show that each of the various mordants used improved both wet and dry rub fastnesses of the dye; the rub fastness of the combination dyeings which employed 6% omf $FeSO_4$ was comparable to that of the dyeing which had been afterchromed using $Na_2Cr_2O_7$. Table 8 reveals that the low rub fastness of tannic acid, both alone and in combination with ferrous sulfate, did not have a deleterious effect upon the rub fastness of the combination dyeings.

In terms of the colour of the combination dyeings obtained, Fig. 12 shows that although both the (dye + tannic acid)/$FeSO_4$ and the dye/(tannic acid + $FeSO_4$) methods yielded dyeings that were brown in colour after wash testing, the use of both 3% omf and 6% omf ferrous sulfate in the dye/(tannic acid + $FeSO_4$) method produced greyer dyeings that were closer in shade to that secured when the dye had been mordanted with sodium dichromate. This can be attributed to the grey shade, which was produced by the interaction of tannic acid with the $FeSO_4$ mordant (Table 3), having moderated the brown hue obtained when the dye had been mordanted with $FeSO_4$.

The results obtained suggest that the co-application of dye and tannic acid, in conjunction with $FeSO_4$ mordant result in the formation of a coloured, dye-gallotannin–mordant complex that is different, in terms of colour and fastness properties, to that secured by the more traditional use of dye and $FeSO_4$ mordant. As mentioned, the nature of the dye/tannic acid/$FeSO_4$ interactions and their contributions to both the colour and fastness properties described in this part of the paper will be reported in the second part of this paper.

## 4. Conclusions

When C.I. Mordant Black 8 was applied to wool in the absence of a mordant, the ensuing, reddish brown coloured, dyeings displayed

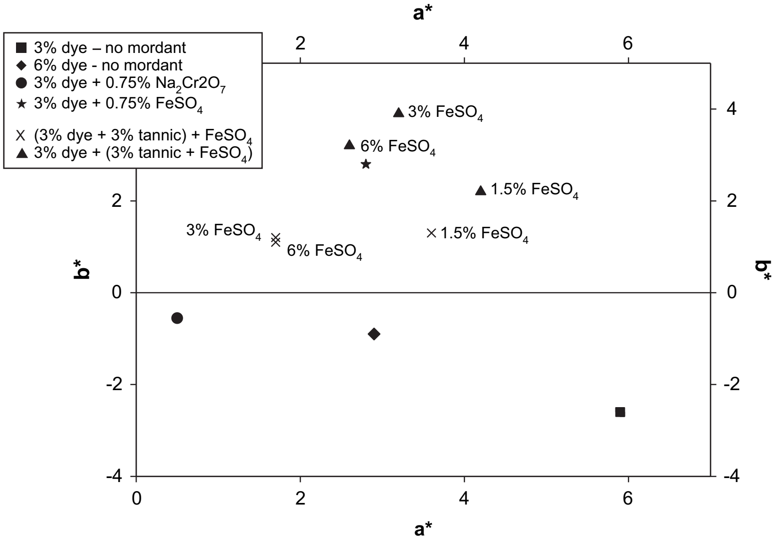

Fig. 12. Hue of combination dyeings after washing.

good light fastness, moderate rub fastness but very poor fastness to washing at 40 °C. When the dyeings were afterchromed using $Na_2Cr_2O_7$, the fastness of the dyeings was improved, considerably, as anticipated and the colour of the dyeings was changed to deep black. The substitution of $Na_2Cr_2O_7$ with $FeSO_4$ also improved the fastness of the unmordanted dyeings but the ensuing brown shades displayed lower, all-round fastness to their afterchromed counterparts. The use of tannic acid in conjunction with $FeSO_4$ as mordant produced greyish-brown shades of relatively low colour strength; whilst the mordanted tannic acid sample underwent a large shade during wash fastness testing, adjacent, multifibre strip materials were unstained. When the dye was applied in combination with tannic acid, subsequent mordanting with ferrous sulfate resulted in brown to greyish-brown shades of high colour strength which displayed very good all-round fastness. Of the two methods that were used to produce the 'combination' dyeings namely, (dye + tannic acid)/$FeSO_4$ and dye/(tannic acid + $FeSO_4$), the latter yielded dyeings of superior fastness.

## References

[1] Czajkowski W, Szymczyk M. Iron complexed afterchrome dyes. Dyes and Pigments 1998;37:197–204.

[2] Bardole HA, Freeman HS, Reife A. Iron salts in the post-metallisation of mordant dyes. Textile Research Journal 1998;68:141–9.

[3] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Blackie; 1990.

[4] Burkinshaw SM, Bahojb-Allafan B. The development of a metal-free, tannic acid-based after-treatment for nylon 6,6 dyed with acid dyes – part 4: tannic acid. Dyes and Pigments 2004;62:159–72.

[5] Standard methods for the determination of the colour fastness of textiles and leather. 5th ed. Society of Dyers and Colourists; 1990.