doi: 10.1111/j.1478-4408.2012.00389.x

Investigation on colour, fastness properties and HPLC-DAD analysis of silk fibres dyed with *Rubia tinctorium* L. and *Quercus ithaburensis* Decaisne

Coloration Technology

Society of Dyers and Colourists

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Received: 15 December 2010; Accepted: 9 January 2012

Silk fabric samples were dyed according to the various procedures using madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) extracts. The colour coordinates, *K/S*, as well as wash, light, rub and perspiration fastness values were determined. A reversed-phase high-performance liquid chromatography with diode-array detection was utilised for the identification of the components of dyes present in the dyed fabrics and in the plant extracts.

Introduction

The roots of madder have been used for dyeing textile fibres such as wool, silk and cotton in many parts of the world since ancient times [1–7]. The madder (*Rubia tinctorium* L.) plant contains alizarin, pseudopurpurin, munjistin and as many as 15 other anthraquinones as effective dyes [8]. The red anthraquinone dyes present in madder are probably the most widespread than any other red plant dyes since antiquity [2–5]. Madder is a dye found in the roots of various plants of the Rubiaceae family: *Rubia tinctorium, R. peregrina, R. cordifolia, R. munjista, R. davisiana, R. tenifolia* and others. Plants of this family grow in South America and Europe [4]. It has been found in archaeological materials as a colouring material [6]. Many historical red dyes are anthraquinones [9]. Walloon oak (*Quercus ithaburensis* Decaisne) is a tree growing to 15–20 m in open forests in Turkey and Greece. The acorn caps of walloon oak contain 25–35% tannin. The hydrolysable tannin, i.e. ellagic acid, has been found in the bark of walloon oak [10]. The several anthraquinone derivatives used in dyeing fibres exhibit various biological activities, such as anti-oxidant, antimicrobial, anti-fungal, cytotoxic, larvicidal and antiviral, as well as genotoxic activities [11]. Several analytical techniques for the identification of natural dyes present in textiles have been applied, such as high-performance liquid chromatography (HPLC) [12], ultraviolet–visible (UV–vis) spectrophotometry, thin-layer chromatography [8,13], raman spectroscopy [14], microspectrofluorimetry [15] and gas chromatography/mass spectrometry [16]. HPLC has become an important method for identification of natural dyes present in historical textiles, art objects, etc. [17,18]. In this study, the HPLC–diode-array detection (DAD) method was used for the separation and identification of anthraquinone and tannin components present in silk fabrics dyed with madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne). The dyed samples, with or without premordanting (reference sample), were studied colorimetrically and their colour coordinates L^*, a^*, b^*, c^*, h and K/S values are reported. Their fastness properties (wash, light, rub and perspiration), and the effect of the mordant and fibre structure on the colour, dye adsorption and fastness properties were also studied.

Experimental

Materials

In this study, 100% silk, sateen weave S 4/1 (3) fabrics, ready for dyeing, were used. The sateen weave used a 4/1 weaving ratio, floating each weft thread under four warp threads, then over one thread, and the rotation used was 3. The warp density per cm of the fabric was 160 and the weft density per cm was 60. The weight of the fabric was 74 g/m^2. The silk used in this study was obtained from the Armaggan Company (Turkey).

Dye plants and chemicals

All reagents were analytically graded, unless stated otherwise. Madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) were obtained from the Turkish Cultural Foundation, Research and Development Laboratory for Natural Dyes. The following standard dyes have been used as references: alizarin from Carl Roth (Germany); and xanthopurpurin, rubiadin and purpurin, which were synthesised by the University of Jordan. Alum [$KAl(SO_4)_2.12H_2O$], hydrochloric acid and methyl alcohol were obtained from Merck (Germany).

Procedures

Mordanting procedure

For mordanting 116.31 g of silk fabric samples and 40.71 g alum [$KAl(SO_4)_2.12H_2O$] were used. Mordanting was realised with the mordant as a 35% proportion of the quantity of the textile. The alum mordants were dissolved in warm ultra-pure water (silk fabric quantity/water quantity: 1/100). The silk fabrics were then wetted by ultra-pure water and added to the mordant bath at 60 °C. The mordant bath was heated to 90 °C and then kept at 75 °C for 1 h. The silk fabrics were mordanted in the mordant bath for 72 h at room temperature.

Extraction

Dried and ground madder roots (84.5 g) and ground walloon oak acorn cups (34.1 g) were transferred to two separate beakers. Ultra-pure water was then added – 5000 ml to the madder and 2000 ml to the walloon oak. Separately, the extracts of madder roots and walloon oak were heated to 100 °C. During heating, the extracts were mixed with a magnet mixer. The temperature of the extracts was then reduced to 70 °C and the extracts were kept at that temperature for 1 h. The madder and walloon oak extracts were then obtained for the dyeings.

Dyeing procedures

Dyeing with walloon oak (Quercus ithaburensis Decaisne): The fabrics were separately dyed with 50% (80 ml), 40% (65 ml), 30% (50 ml), 20% (30 ml) and 10% (15 ml) of walloon oak extract at 60 °C for 1 h. To reach the total dyebath volume of 325 ml, ultra-pure water was added to the extracts. After dyeing, the dyed silk fabrics were taken out of the dyebaths, washed using ultra-pure water and dried at room temperature.

Dyeing with madder (Rubia tinctorium L.*):* The fabrics were dyed using ultra-pure water (162 ml) with 100% (163 ml) madder (*R. tinctorium* L.) extract at 60 °C for 1 h. The dyed fabrics were then, taken out of the dyebaths, washed with ultra-pure water and dried at room temperature.

Eight different combinations of dyeing procedure with or without walloon oak and madder were investigated for this experimental study:

Procedure I: The mordanted silk fabrics were dyed with different concentrations of the mixture of walloon oak and madder extracts in the same dyebath. The volumes for the dyed silk fabrics with walloon oak and madder in the same baths are given in Table 1.

Procedure II: The mordanted silk fabrics were dyed with 100% madder extract. The dyed and washed fabrics were then dyed again with different concentrations of walloon oak extracts. The volumes for the dyed silk fabrics with the madder and walloon oak dyebaths are given in Table 1.

Procedure III: The mordanted silk fabrics were separately dyed with different concentrations (50–10%) of walloon oak extracts. The dyed fabrics in the walloon oak dyebaths were dyed again with different concentrations of madder extracts (100–20%). The volumes for the dyed silk fabrics with the walloon oak and madder dyebaths are given in Table 1.

Procedure IV: The mordanted silk fabrics were separately dyed with different concentrations of walloon oak extracts. The volumes for the dyed silk fabrics with the walloon oak and madder dyebaths are both summarised in Table 1.

Procedure V: The unmordanted silk fabrics were separately dyed with different concentrations of walloon oak extracts. The dyed fabrics with the walloon oak were then mordanted using a 35% alum [$KAl(SO_4)_2.12H_2O$] mordant solution in 325 ml ultra-pure water. The dyed fabrics were dried at room temperature. The wet mordanted fabrics were dyed with madder extracts. The volumes for the dyed silk fabrics with the walloon oak, mordanted by alum and dyed in the madder dyebaths are given in Table 1.

Procedure VI: The unmordanted silk fabrics were dyed with walloon oak extracts, as explained in procedure III. The dyed fabrics were dyed again using 100% madder extracts. The volumes for the dyed silk fabrics with the walloon oak and madder dyebaths are given in Table 1.

Procedure VII: The wet unmordanted silk fabrics were separetely dyed with walloon oak extracts, as explained in procedure V. The volumes for the dyed unmordanted silk fabrics with walloon oak are given in Table 1.

Procedure VIII: The mordanted silk fabrics were separetely dyed with different concentrations of madder extracts. The volumes for the dyed mordanted silk fabrics with madder are given in Table 1.

Colour measurements

The colour measurements were performed using a Datacolor SF 600 plus spectrophotometer coupled to a PC under D65 illuminant/10° observer with a specular component included. The untreated fabric was taken as standard. The colour differences, according to the CIELab (1976) equation, were obtained from the colour measuring software. The average of the measurements of the samples was recorded as colour yield (*K/S*) and colour difference (ΔE^*).

The Kubelka–Munk equation relates the absorption function of the substrate (*K*), the scattering function of the substrate (*S*) and the reflectance (*R*) in the visible spectrum (400–700 nm), as shown below (Eqn 1) [19]:

$$K/S = \frac{(1-R)^2}{2R} \tag{1}$$

Table 1 Dyeing properties for silk fabrics dyed according to the different procedures

Procedure	Sample no.	Mordant (%)	Walloon oak (%)	Madder (%)	Liquor ratio	Temperature (°C)	Time (min)
I	1	35	50	100	440:1	60	60
	2	35	40	100	440:1	60	60
	3	35	30	100	440:1	60	60
	4	35	20	100	440:1	60	60
	5	35	10	100	440:1	60	60
II	6	35	50	100	440:1	60	60
	7	35	40	100	440:1	60	60
	8	35	30	100	440:1	60	60
	9	35	20	100	440:1	60	60
	10	35	10	100	440:1	60	60
III	11	35	50	100	440:1	60	60
	12	35	40	80	440:1	60	60
	13	35	30	60	440:1	60	60
	14	35	20	40	440:1	60	60
	15	35	10	20	440:1	60	60
IV	16	35	50	–	440:1	60	60
	17	35	40	–	440:1	60	60
	18	35	30	–	440:1	60	60
	19	35	20	–	440:1	60	60
	20	35	10	–	440:1	60	60
V	21	35	50	100	440:1	60	60
	22	35	40	100	440:1	60	60
	23	35	30	100	440:1	60	60
	24	35	20	100	440:1	60	60
	25	35	10	100	440:1	60	60
VI	26	–	50	100	440:1	60	60
	27	–	40	100	440:1	60	60
	28	–	30	100	440:1	60	60
	29	–	20	100	440:1	60	60
	30	–	10	100	440:1	60	60
VII	31	–	50	–	440:1	60	60
	32	–	40	–	440:1	60	60
	33	–	30	–	440:1	60	60
	34	–	20	–	440:1	60	60
	35	–	10	–	440:1	60	60
VIII	36	35	50	100	440:1	60	60
	37	35	40	80	440:1	60	60
	38	35	30	60	440:1	60	60
	39	35	20	40	440:1	60	60
	40	35	10	20	440:1	60	60

The colour difference is expressed as ΔE^* and is calculated by Eqn 2:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (2)$$

where ΔE^* is the CIELab colour difference between batch and standard. Here, ΔL^*, Δa^*, Δb^* and hence ΔE^* are in commensurate units. ΔL^* denotes the difference between lightness (where $L^* = 100$) and darkness (where $L^* = 0$), Δa^* the difference between green ($-a^*$) and red ($+a^*$) and Δb^* the difference between yellow ($+b^*$) and blue ($-b^*$) [19].

Fastness determination

Tests to determine wash, light, rub and perspiration fastness properties were carried out, respectively, in accordance with the methods described in standards ISO 105-C06 (A1S) [20], ISO 105-B02 [21], ISO 105-X12 [22] and ISO 105-E04 [23]. The dyed samples were exposed to the light for 90 h by xenon arch lamp (250 W).

HPLC method

Chromatographic experiments were carried out using an Agilent 1200 series system (Hewlett-Packard, Germany), including a G1329A ALS autosampler and a G1315A diode-array detector. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 255 nm. A G1322A vacuum degasser and a G1316A thermostatted column compartment were used. The data were analysed using an Agilent Chemstation. A Nova-Pak C_{18} analytical column (3.9 × 150 mm, 4 μm, part no. WAT 086344; Waters, Ireland) protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30 °C. The HPLC gradient elution was performed using the methods of Halpine [24] and Karapanagiotis and Chryssoulakis [2]. Chromatographic separations of the hydrolysed samples were performed using a gradient elution programme that utilises two solvents: solvent A, water (H_2O)–0.1% trifluoroacetic acid (TFA); and solvent B, acetonitrile (CH_3CN)–0.1% TFA. The flow rate was 0.5 ml/min and the elution programme was as described earlier [10,25–27].

Extraction procedure for HPLC analysis

The extraction from the dye plants and the dyed silk fabrics was performed by using the previously described method [25–30].

The dyed silk fabrics (4.0–6.7 mg) and the dye plants (11.3 mg for madder and 2.3 mg for walloon oak) were hydrolysed by using water:methanol (MeOH):37% hydrogen chloride (HCl) (1:1:2; v/v/v; 400 μl) in conical glass tubes for precisely 8 min in a water bath at 100 °C to extract the organic dyes. After rapid cooling under running cold water, the solution was evaporated to dryness in a water bath at 50–65 °C under a gentle stream of nitrogen. The dry residues were dissolved in 400 μl of the mixture of methanol:water (2:1; v/v). Supernatant (10 or 35 μl) was injected into the HPLC apparatus.

Results and Discussion

HPLC analysis

The dye compositions were identified based on the literature, the chromatograms and the absorption spectra acquired with the standard reference compounds [10,11,26,29]. One of the metal salts, i.e. the aluminium(III) salt, was used as mordant in the traditional dyeing process with the natural dyes, consisting of tannin and anthraquinones. The sample preparation for the extraction of the dye components from the dyed silk fibres is based on the commonly used hydrolysis procedure with hydrochloric acid. For the extracts, with this treatment it is necessary to isolate the organic dye from its mordant metal. The chromatographic and spectral characteristics of the investigated dyes in this study are given in Table 2.

In the acid-hydrolysed madder (*R. tinctorium* L.), alizarin, rubiadin and purpurin are observed, together with relatively minor amounts of munjistin by HPLC-DAD (monitored at 255 nm). A peak of 30.1 min retention time was determined; however, this could not be identifed and therefore is not discussed.

The gallic acid and ellagic acid identified in the acid-hydrolysed walloon oak (*Q. ithaburensis* Decaisne) acorn cups were identified. A peak of 16.8 min retention time was determined. Probably this unidentifed peak belongs to an ellagic acid derivative.

The natural dyes identified in the silk fabrics dyed according to the different procedures are presented in Table 3. Ellagic acid, alizarin and purpurin are determined in the acid-hydrolysed silk extracts.

Table 2 Chromatographic and spectral characteristics of the investigated reference dyes

Dye(standard)	Retention time in the given protocol (min)	UV–vis data (nm)
Gallic acid	4.4	215, 271
Ellagic acid	17.5	251, 307, 367
Munjistin	28.2	245, 274, 336, 403
Alizarin	28.3	249, 279, 331, 433
Purpurin	30.2	255, 295, 481, 520
Rubiadin	31.6	243, 279, 331, 413

Table 3 The dyes detected in the acid hydrolysed silk extracts

Sample no.	Dyes detected
1	Ellagic acid, alizarin, purpurin
5	Ellagic acid, alizarin, purpurin
6	Ellagic acid, alizarin, purpurin
10	Ellagic acid, alizarin, purpurin
11	Ellagic acid, alizarin, purpurin
15	Ellagic acid, alizarin, purpurin
16	Ellagic acid
20	Ellagic acid
21	Ellagic acid, alizarin, purpurin
25	Ellagic acid, alizarin, purpurin
26	Ellagic acid, alizarin, purpurin
30	Alizarin, purpurin
31	Ellagic acid
35	Ellagic acid
36	Alizarin, purpurin
40	Alizarin, purpurin

Effects of different dyeing procedures on the CIE $L^*a^*b^*$ values

Table 4 shows the maximum *K/S* values of all the dyed silk fabrics by the use of different dyeing processes. The *K/S* value of a dye is related to the concentration of the dye on the textile material; i.e. the importance of the value is a direct measure of the depth of shade of the dye. Therefore, from Table 2, it can be said that, in general, the highest *K/S* values were obtained from groups I, II and III, and the lowest *K/S* value was obtained from group VII. CIE L^*, a^*, b^*, C^* and h values for the untreated and dyed silk fabrics are given in Table 4. The hue angle (h) shows that the fabrics dyed by procedures IV and VII have a yellowish and light colour. Other dyed fabrics have a reddish and dark colour.

Total colour difference (ΔE^*) values are given in Table 4 and are higher in most procedures. These differences have shown that silk fabric samples can be dyed with all procedures by using madder and walloon oak.

Fastness properties

The wash, light, rub and perspiration fastnesses of the dyed samples are given in Table 5. Colour change gradings in general had very poor fastness to wash (grade 1), whereas samples 1, 9, 34 and 35 had quite good colour change gradings (grade 4). The wash fastness results for the staining on nylon and wool showed that dyeing with madder and walloon oak together, in general, decreased wash fastness. The samples dyed with other procedures also gave an improvement in wash fastness.

The unmordanted group VII (samples 31–35) had very poor fastness to light (grade 2), whereas mordanted group IV (samples 16–20) had moderate fastness (grade 3). The light fastness test results of the dyed silk fabric samples, mordanted groups I and II, are much better than the other groups.

Table 4 Effect of different dyeing procedures on the CIE $L^*a^*b^*$ colour coordinates, colour differences and maximum K/S values of dyed silk fabrics with madder and walloon oak

Samples	L^*	a^*	b^*	C^*	h	ΔE^{*a}	K/S (λ_{max} = 400)
Untreated	93.53	0.41	4.03	4.05	84.23	–	0.06
1	57.60	19.72	31.06	39.79	57.59	48.93	9.20
2	57.40	21.05	31.09	37.55	55.90	49.63	8.77
3	57.56	22.16	30.68	37.84	54.15	49.77	8.01
4	57.87	24.63	30.29	39.04	50.88	50.48	6.71
5	56.81	28.26	28.66	40.25	45.40	52.25	5.52
6	56.11	16.11	30.61	34.59	62.25	48.51	9.95
7	55.80	16.28	30.52	34.60	61.92	48.76	9.90
8	56.08	16.84	30.11	34.36	61.22	48.50	8.97
9	56.69	17.90	29.76	34.73	58.97	48.22	7.77
10	57.40	19.79	28.48	34.68	55.20	47.74	6.00
11	58.49	15.08	30.06	33.63	63.35	46.05	9.65
12	59.54	14.49	29.44	32.81	63.79	44.71	8.78
13	62.04	12.15	28.78	31.36	66.60	41.74	7.69
14	64.64	11.31	27.40	29.64	67.58	38.72	6.01
15	69.53	9.06	24.59	26.20	69.78	32.76	3.59
16	67.80	1.13	30.05	30.07	87.86	36.60	9.01
17	68.41	1.04	29.67	29.69	87.99	35.90	8.43
18	69.47	0.80	29.32	29.34	88.43	34.91	7.60
19	71.15	1.05	27.28	27.30	87.80	32.28	5.41
20	73.66	1.31	25.14	25.17	86.99	29.00	3.62
21	58.26	14.21	27.61	31.05	62.76	44.61	6.84
22	57.62	15.81	26.59	30.93	59.26	45.12	6.41
23	56.93	18.34	25.56	31.46	54.35	46.09	5.78
24	56.79	21.85	25.99	33.96	49.95	47.87	5.03
25	58.66	23.79	26.40	35.54	47.98	47.57	3.71
26	63.09	16.28	32.77	36.59	63.58	44.77	4.59
27	63.11	16.92	33.31	37.36	63.08	45.34	4.50
28	63.93	17.41	32.86	37.19	62.09	44.68	3.99
29	64.85	19.50	33.04	38.36	59.45	45.04	3.53
30	67.30	23.09	32.60	39.95	54.86	44.93	2.69
31	69.67	3.69	20.53	20.85	79.80	29.19	3.19
32	69.82	3.75	20.40	20.74	79.59	29.01	3.02
33	71.01	3.52	19.35	19.67	79.69	27.41	2.51
34	75.22	2.81	17.43	17.66	80.83	22.82	1.58
35	81.88	1.83	13.69	13.81	82.38	15.20	0.72
36	56.46	29.27	27.66	40.27	43.38	52.59	3.74
37	59.36	26.90	25.79	37.27	43.80	48.40	2.90
38	61.23	25.27	24.07	34.90	43.61	45.42	2.44
39	64.53	23.40	21.76	31.95	42.92	41.04	1.82
40	69.99	20.75	18.14	27.56	41.17	34.16	1.08

a The untreated fabric was taken as 'standard'

The rub fastness results for the dyed fabrics showed that dyeing silk fabrics with madder or walloon oak in general obtained quite good rub fastness (grades 4–5). The wet rub fastness of group V was only slightly better (grades 3–4).

The perspiration fastness test results of the samples were much better (grade 4) for the mordanted group IV than for the other samples. Groups I, II and VI had very poor (grades 1–2) fastness to perspiration.

Conclusions

In this study, various dyeing procedures using madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne) dye plants were carried out for silk fabrics. Identification of the dyes from the dye plants and the dyed silk fabrics was achieved using reversed-phase high-performance liquid chromatography with diode-array detection. The high-performance liquid chromatography method allowed qualitative determination of the natural dyes in the dyed fabrics and the prepared extracts.

Using the eight different procedures, 100% silk fabric can be dyed with madder (*Rubia tinctorium* L.) and walloon oak (*Quercus ithaburensis* Decaisne). The silk fabrics dyed using procedures IV and VII have a light yellowish colour.

In the overall results, the use of madder and walloon oak together in the same dyebath, in general, appears to improve wash fastness. The light and wet/dry rub fastness test results are quite good. In contrast, perspiration fastness values were, in most cases, except in group IV, slightly decreased.

Finally, it is believed that dyeing protein fibres with natural dyes (madder and walloon oak) can be an important advantage for the environment in the dyeing process.

Acknowledgements

The support of Turkish Cultural Foundation is gratefully acknowledged (http://www.turkishculturalfoundation.org). The authors would like to thank Harry Nikolaides (Lord Byron School, Greece) and Kidane Fanta Gebremariam

Table 5 Fastness results of the dyed silk fabrics

	Wash fastness[a]				Rub fastness		Perspiration fastness[a]			
							Alkaline		Acid	
Samples	CC	SN	SW	Light fastness	Dry	Wet	SN	SW	SN	SW
1	4	3	3	5	4–5	4	1	1	1	1
2	3	3	4	5	4–5	4–5	1	1	1	1
3	2	3	3	5	4–5	4	1	1	1	1
4	1	3	3	6	4–5	4	1	2	1	1
5	1	3	3	7	5	4	1	2	1	1
6	2	3	3	7	5	4	1	1	1	1
7	2	3	3	4	5	4	1	1	1	1
8	3	4	4	5	5	4–5	1	1	1	1
9	4	4	4	5	4–5	4	1	1	1	2
10	1	4	4	7	4–5	4–5	1	2	1	2
11	2	4	4	6	4–5	4	1	2	1	2
12	1	4	4	6	4–5	4	1	2	1	2
13	1	4	4	5	4–5	4	1	2	1	3
14	2	4	4	4	4–5	4–5	1	2	1	3
15	2	4	3	5	4	4	3	4	3	4
16	1	4	4	3	4–5	4–5	3	4	4	4
17	1	4	3–4	3	4	4	3	4	4	4
18	1	4	4	3	4–5	4	4	4	4	4
19	1	4	3	3	4	4	3	4	4	4
20	1	4	4	3	4–5	4	4	4	4	4
21	3	4	4	5	4–5	3–4	1	3	1	2
22	1	4	4	6	4–5	3–4	2	3–4	1	2
23	1	4	4	6	4–5	3–4	3	3–4	1	2
24	1	4	4	5	4–5	4	3	3–4	1	2
25	1	4	2	4	4–5	4	3	3–4	1	1
26	1	3	1	5	5	4	1	1	1	1
27	1	3	1	6	5	4–5	1	1	1	1
28	1	4	3	5	5	4	1	1	1	1
29	1	3–4	2	6	5	5	1	1	1	1
30	3	4	4	2	5	5	1	1	1	1
31	3	4	3–4	2	5	4–5	1	2	4	4
32	2–3	4	4	2	5	4–5	2	2	4	3–4
33	3	4	4	2	5	4–5	2	2	4	3–4
34	4	4	4	3	5	4–5	3	2	4	4
35	4	4	4	4	5	5	2	3	4	4
36	1	4	4	4	4	4	3	3	1	3
37	1	4	4	4	4–5	4	3	3–4	1	3
38	1	4	4	4	4–5	4	3	3–4	1	3
39	2	4	4	3	4–5	4	3	3–4	1	3
40	2	4	4	3	4–5	4	3	3–4	2	3–4

a CC, colour change; SN, staining on nylon; SW, staining on wool

(Norwegian University of Science and Technology) for essential grammar and syntax checking of this manuscript.

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