

# Effect of Ammonia on Madder-Dyed Natural Protein Fiber

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**ABSTRACT:** Of all the beautiful reds in nature, the only one vegetable source of good dyes ever discovered by man is madder. In this research natural protein fibers (i.e., wool yarns) were dyed with madder and then treated with different ammonia solutions. A UV–visible spectrophotometer was used to measure the absorbency of the remaining ammonia solution. The absorption curves showed the absorption transfer to the visible region. FTIR spectroscopy studies indicated that the changes in intensity at the peaks occurred when the madder-dyed yarns were treated with ammonia solutions. The results of color measurement in the CIELAB system showed that the darkness of samples increased with

an increase in the ammonia percentage in the solution. The vertical wicking test was also carried out on the madder-dyed yarns and the ammonia-treated samples. The results showed that the ammonia treatment causes a decrease in the wicking rate. A change of color was observed on the dyed samples when wash-fastness tests were carried out. The results of light-fastness tests showed more fading of the madder-dyed yarns after ammonia treatment. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2704–2710, 2004

**Key words:** wool; FTIR; UV–vis spectroscopy; natural dyes; madder; ammonia

## INTRODUCTION

Wool fibers have been used in various human cultures for centuries, and for good reason: wool has specific physical and chemical properties such as high water absorption, good dyeability, high elasticity, bulkiness, comfort, and high resistance against fire. These properties enable the use of wool fibers in various textile products.<sup>1–3</sup> For example, because of high elasticity, wool yarns have steadily been used as carpet pile over the years. The science of dyers for application of the natural dyes has been improved and transferred from one generation to the next.<sup>4,5</sup> Initially these yarns were dyed by natural dyes. However, the consumption of natural dyes has been affected and decreased by the invention and fast-spreading pace of synthetic dyes. Natural dyes were replaced by synthetic dyes because of their ability to easily match a desired color, increased variety, high purity, cheap price, and processing properties.<sup>6</sup> However, through use and production of the synthetic dyes, consumers and producers have observed several ecological and biological problems. Therefore because of environmental regulations, care must be taken in the production and consumption of some of these synthetic dyes. Natural dyes are said to be less harmful on humans and environment, and thus the application of natural dyes should be

considered as a better alternative to synthetic dyes.<sup>7</sup> Nevertheless, use of auxiliaries such as acids and mordants in some cases of natural dyeing are environmentally unfriendly. One of the most important applications of natural dyes is the dyeing of wool yarns for use in handwoven carpets.

A richer, more variegated palette of colors (known as abrash) is offered when natural dyed yarns are used to weave carpets. Additionally, carpets dyed with natural dyes age with a warm, pleasing patina. However, natural dyes are more labor intensive and require a large amount of dyestuff to be consumed. Consequently, natural dyed carpets are more expensive, often by as much as 30–50%. Then again, the choice between applying natural and modern synthetic dyes is a matter of preference and costs.<sup>6</sup>

Sources of natural dyes may be classified in five main classes<sup>6</sup>:

1. Different parts of plants such as roots, leaves, and so forth (e.g., madder and weld)
2. Fruit wastes (e.g., walnut shells, pomegranate, and onion skins)
3. Minerals (e.g., ferrous sulfate)
4. Animals (e.g., cochineal)
5. Lichens

Natural dyes with plant, fruit waste, mineral, and animal sources have been used over many decades to the present. Nowadays, lichen is considered as a new source for producing natural dyes.<sup>6</sup>

Application of ammonia on the natural dyed wool yarns that are used as carpet piles could provide a

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way to achieve better performance on handwoven carpets.<sup>6</sup> When wool fibers are treated with ammonia solutions, preferentially, a swelling of orthocortex will occur. The resulting differential contraction of the cortical components (*ortho* and *para* cortex) in the wool fibers can lead to a bulking effect. Some of the natural dyed wool yarns also have the property of changing color after ammonia treatment. This color change under alkaline conditions is caused by changes in the electron configuration (resonance) of the natural dye molecules.<sup>8-11</sup>

In this research, the effect of 1, 3, and 5% ammonia solutions on the physical and chemical properties of madder-dyed yarns and changes in the molecular structure of these yarns were investigated.

## EXPERIMENTAL

### Materials

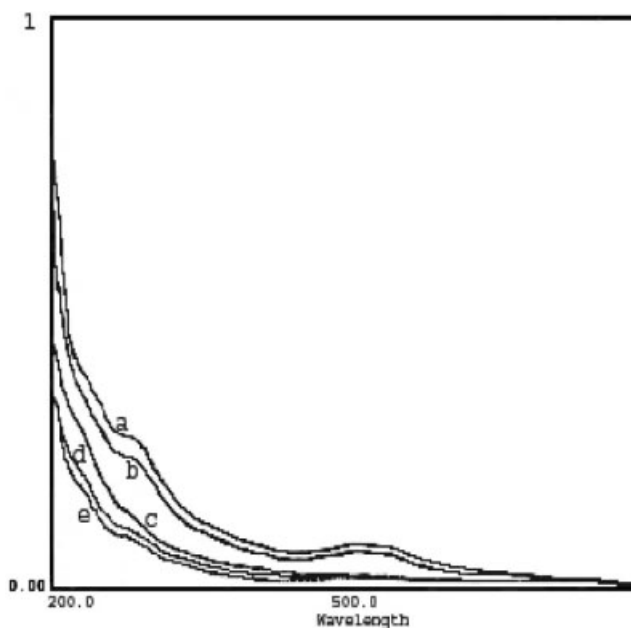
The following materials were used:

- Wool yarns: Iranian wool yarns of 432/2 tex with 144 twist per meter.
- Nonionic detergent (SDL Technologies): for scouring of wool yarns.
- Standard washing soap (SDL Technologies): anionic soap used for wash-fastness test.
- Formic acid (Merck, Darmstadt, Germany): for mordanting and dyeing processes.
- Aluminum potassium sulfate (Merck): for mordanting process.
- Natural dye: powder of Iranian madder roots.

### Procedure

The wool yarns were treated in four steps:

1. *Scouring*. Wool yarns were scoured with 0.5% nonionic detergent. The L : G (liquor to good ratio) of the scouring bath was kept at 40 : 1 for 30 min at 50°C.
2. *Mordanting*. The scoured wool yarns were mordanted with 20% owf (on weight of fiber)  $\text{AlK}(\text{SO}_4)_2$ . The L : G of the mordanting was kept at 40 : 1. Formic acid was used in the mordanting bath for adjusting the pH 5. The mordanting temperature was started at 40°C and then was gradually raised to the boiling point over 20 min. Finally, the mordanting bath was boiled for 1 h.
3. *Dyeing*. Madder powder was poured into water (madder : water = 10 : 1) and left for 24 h. The pH of the dyebath was kept at 5 by adding 5% owf formic acid. The madder concentration was 50% owf and L : G was kept at 40 : 1. The dyeing process started at 40°C and was raised to 85°C



**Figure 1** Absorption curves of remaining ammonia solutions after ammonia treatment on madder-dyed yarns: (a) madder solution (50%); (b) 1% ammonia solution; (c) 3% ammonia solution; (d) 5% ammonia solution; (e) madder solution (150%).

over 20 min. Finally, dyeing was carried out at this temperature for 1 h.

4. *Treatment with ammonia solutions*. The madder-dyed yarns were divided into four parts. One part was kept untreated as a reference sample and the remaining parts were treated with various ammonia solutions (1, 3, and 5%) at 25°C for 10 min. The L : G was kept at 20 : 1.

To investigate the effects of the ammonia solutions on the physical and chemical properties of the scoured and madder-dyed yarns, the following tests were carried out:

- The effect of the ammonia solutions on the color hue changes were examined by using a UV-vis spectrophotometer (UV-2101PC; Shimadzu, Kyoto, Japan).
- The effect of the ammonia solutions on the chemical structure of the madder-dyed yarns were examined by the FTIR spectroscopy [Bomem-MB 100 Series (Hartmann and Broun)rsqb].
- The reflectance spectra of the dyed samples were recorded on an ACS Spectra Sensor II integrated with an IBM-PC. CIELAB color coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$ ,  $h$ ) were calculated from the reflectance data for 10° observer and  $D_{65}$  illuminant.
- Effects of the ammonia solutions on the wicking properties of the madder-dyed yarns were also

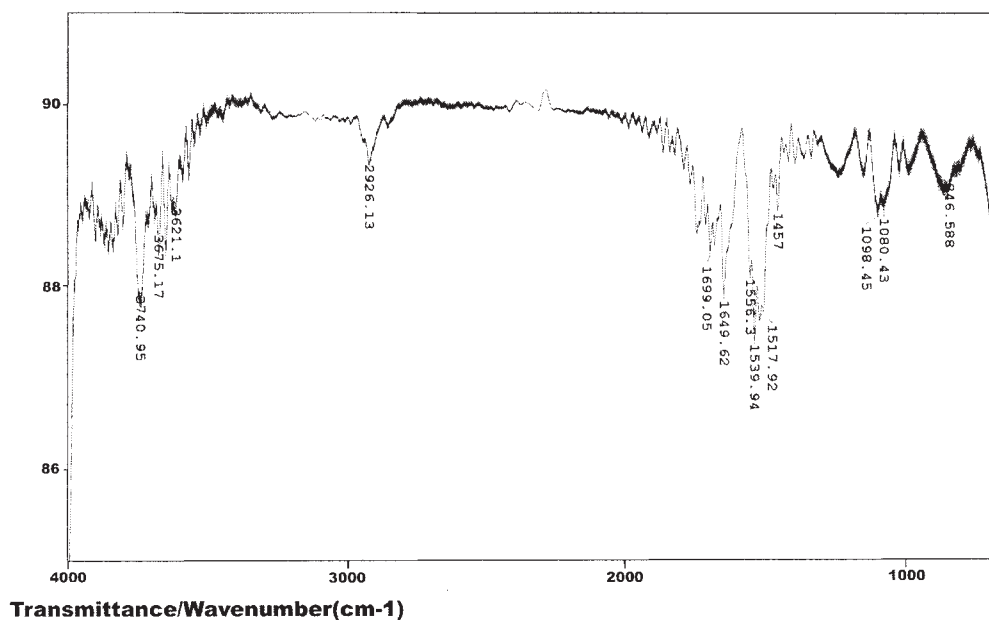


Figure 2 FTIR spectra of raw wool.

examined. For this purpose, samples were hung vertically in such a way that 1 cm of the sample soaked in the water container. After 1 min, the wet height of the samples was measured by means of a ruler. The samples were raw, scoured, scoured and ammonia-treated (1, 3, and 5%), aluminum mordanted, madder-dyed, and ammonia-treated (1, 3, and 5%).

- The wash-fastness properties of the ammonia-treated madder-dyed yarns were measured according to ISO 105-C01. The color hue changes of the yarn and the degree of staining on the adjacent yarns were measured after drying.
- For light-fastness measurements, the yarns were exposed to the daylight for 7 days accord-

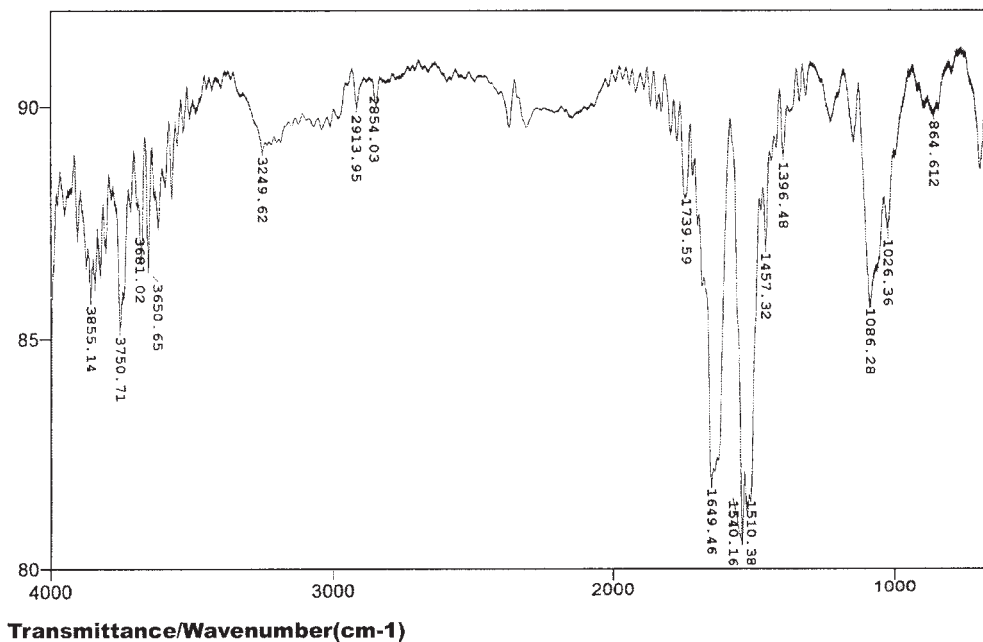


Figure 3 FTIR spectra of mordanted wool with AlK(SO<sub>4</sub>)<sub>2</sub>.

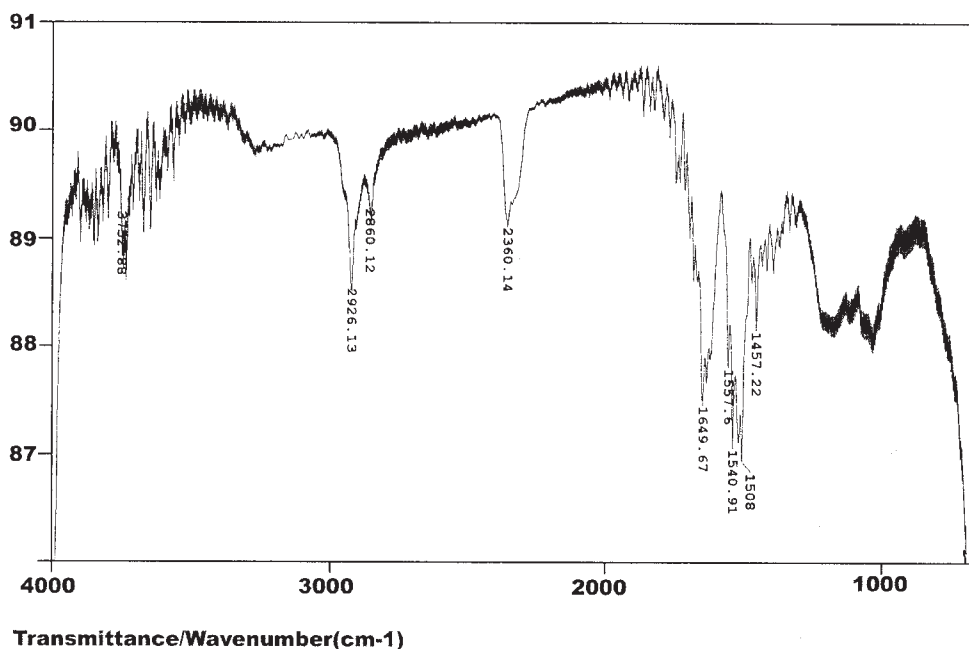


Figure 4 FTIR spectra of madder-dyed wool.

ing to the daylight ISO 105-B01, and the changes in the color (fading) were assessed by the blue scale.

## RESULTS AND DISCUSSION

### Absorption

The color hue of the madder-dyed yarns was changed and a small amount of madder bled from the dyed

yarns because of the ammonia treatment. The change in color hue of madder was also observed in the remaining ammonia solution.

When madder-dyed wool yarn was treated in the ammonia solutions, an increase in the ammonia concentration resulted in an increase in the intensity of the absorption in the visible region (Fig. 1). It was also noted that the absorption curves shifted to a higher level of absorbency. Furthermore, with the increase of

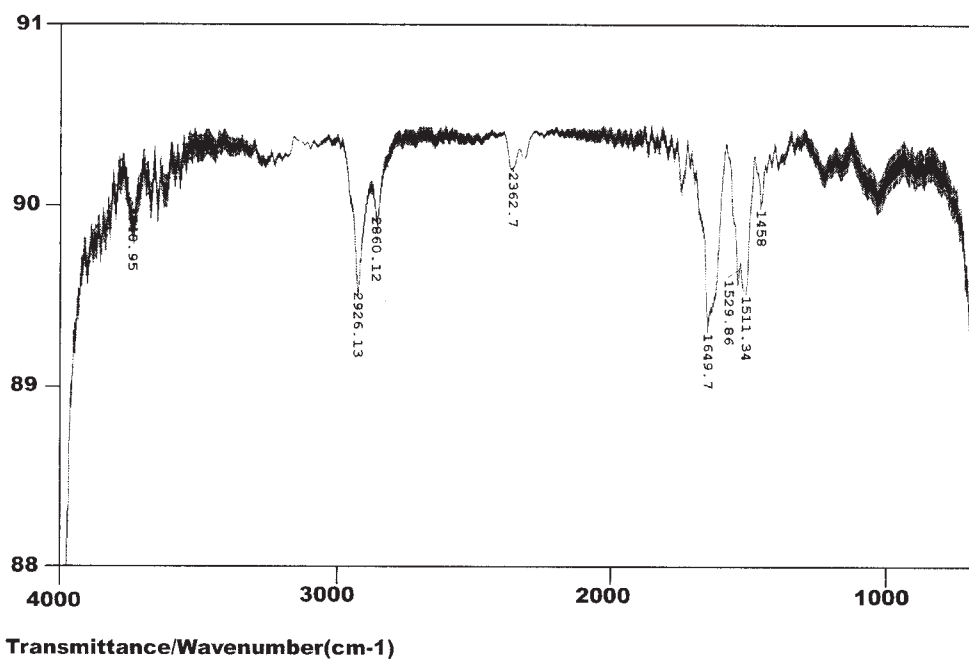
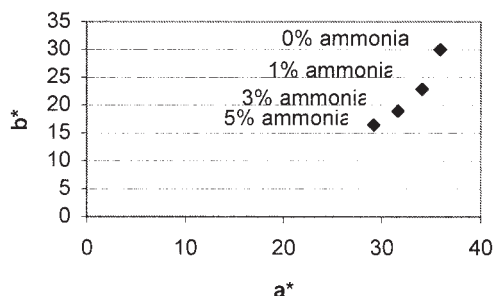


Figure 5 FTIR spectra of ammonia-treated madder-dyed wool.



**Figure 6**  $a^*$  and  $b^*$  values of madder-dyed and madder-dyed/ammonia-treated wool.

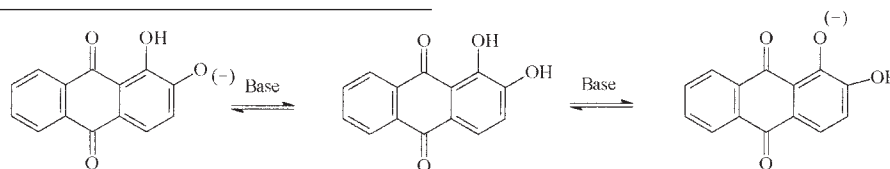
the madder concentration a constant addition in intensity of the absorption was prominent.

From these results, it can be concluded that a transfer toward higher wavelengths occurred after the madder-dyed yarns had been treated with the ammonia solutions. These changes in the absorption curves show a bathochromic shift (or red shift) toward the visible region.

### Structural information

The chemical changes in the raw, mordanted, and the ammonia-treated madder-dyed wool yarns were studied by the means of FTIR spectroscopy.

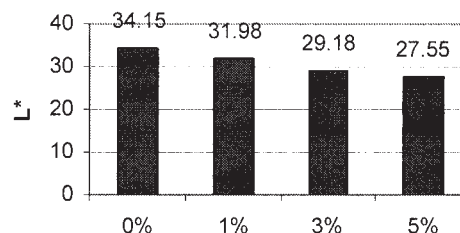
A comparison of the raw and mordanted wool spectra (Figs. 2 and 3) revealed that two new peaks appeared after mordanting. One peak was at  $3249\text{ cm}^{-1}$ , which could be related to NH stretching groups and



### Color measurement

The results of color measurement of ammonia-treated wool yarns dyed with madder are shown in Figures 6 and 7. It can be seen in Figure 6 that the amount of  $a^*$  ( $=35.82$ ),  $b^*$  ( $=30.16$ ), and  $L^*$  ( $=34.15$ ) decreased to 34.14, 23.00, and 31.98, respectively, after the madder-dyed samples were treated with 1% ammonia solution. By increasing the percentage of ammonia in the solution, the amounts of  $a^*$ ,  $b^*$ , and  $L^*$  continue to decrease. It can be seen from Table I that the amount of  $C^*$  decreased from 46.83 to 41.16 by treating madder-dyed wool with 1% ammonia solution. It can also be seen that this decrease continued with an increase in the percentage of ammonia in the solution.

It can be seen in Figure 7 that the amount of  $L^*$  decreases with an increase in the percentage of am-



**Figure 7**  $L^*$  values of madder-dyed and madder-dyed/ammonia-treated wool.

could be attributed to formation of  $\text{NH}_3^+$  groups on the polypeptide chain resulting from the presence of formic acid in the mordanting process. A second, sharp peak was appeared at  $1086\text{ cm}^{-1}$ , which could be attributed to the  $\text{SO}_4^{2-}$  groups of aluminum potassium sulfate.

By comparing the mordanted and madder-dyed wool spectra (Figs. 3 and 4), it can be seen that the intensity band at  $1649.46$  to  $1540.16\text{ cm}^{-1}$  in the mordanted wool has increased compared to the intensity band at  $1649.7$  to  $1529.86\text{ cm}^{-1}$  in madder-dyed wool. This could be as a result of the existence of anthraquinone groups in madder. The intensity band at  $1649.67\text{ cm}^{-1}$  for madder-dyed wool is decreased after treatment of these samples with ammonia solutions (Fig. 5). The reason for this change could be the result of the changes in the chromophoric structure of madder and the extension of the conjugated system of dye molecules. The chromophoric changes in the madder structure can be explained by the following formula:

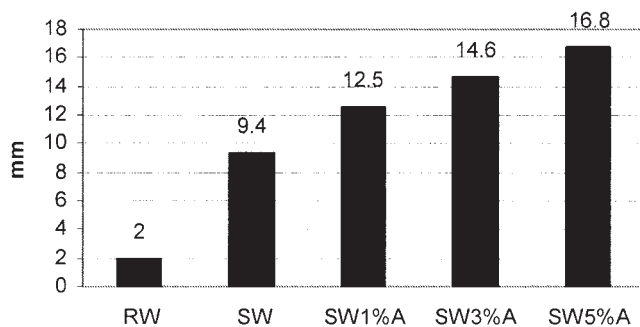
monia in the solution. This shows that the darkness of samples increased with an increase in the ammonia percentage in the solution.

### Vertical wicking test

Results of vertical wicking tests are shown in Figures 8–10. It can be seen in Figure 8 that wicking increased

**TABLE I**  
Amounts of  $a^*$ ,  $b^*$ ,  $C^*$ ,  $h$ , and  $L$  of the Madder-Dyed and Madder/Ammonia-Treated Wool

Ammonia (%)	$a^*$	$b^*$	$C^*$	$h$	$L^*$
0	35.82	30.16	46.83	40.09	34.15
1	34.14	23.00	41.16	33.98	31.98
3	31.58	18.98	36.84	31.01	29.18
5	29.16	16.35	33.43	29.28	27.55



**Figure 8** Vertical wicking height of raw, scoured, and treated wool with 1, 3, and 5% ammonia.

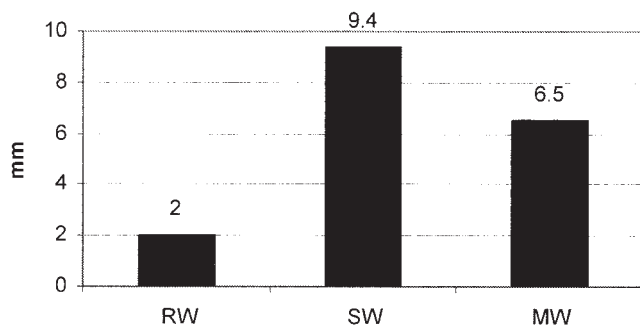
with scouring; this was intensified by the additional treatment of ammonia. Also the wicking rate increases with any increase in the ammonia concentration. This means that the scouring process removes fiber impurities and ammonia treatment then helps to remove the remaining impurities. Removal of any impurities from the fibers could help the water to absorb and wick more easily and quickly.

The result in Figure 9 shows that mordanting the scoured yarns could affect wicking. The mordanting process decreases the wicking.

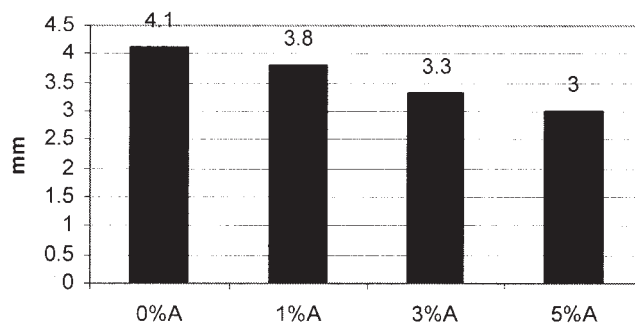
It can be concluded from Figure 10 that the wicking, inside the yarn, was decreased by the ammonia treatment on the madder-dyed yarn. A greater decrease in wicking can be seen by an increase in the ammonia concentration. It seems that the ammonia treatment on the madder-dyed wool can change the hydrophilic groups, such as hydroxyl groups, and decreases the absorbency properties of the yarn.

#### Wash fastness

There is a difference between the results obtained from the wash-fastness test for the untreated and the ammonia-treated dyed yarns (Table II). When the dyed yarns were treated with ammonia, the washing fastness of the samples was improved. This can be



**Figure 9** Vertical wicking height of raw, scoured, and mordanted wool with  $\text{AlK}(\text{SO}_4)_2$ .



**Figure 10** Vertical wicking height of madder-dyed and madder-dyed/ammonia-treated wool with 1, 3, and 5% ammonia.

attributed to the removal of some dyes from the fiber surfaces after ammonia treatment. When the samples were treated with the standard soap in the wash-fastness test, the color hue of the madder-dyed yarns changed toward the visible region. For those samples that were treated with 5% ammonia solution, no further changes were observed on their color hue throughout the wash-fastness tests.

#### Light fastness

After exposing the samples to daylight for 2 days, the color of madder-dyed yarns faded. With an extension of the duration of exposure to the daylight for 7 days, no more fading was observed. This indicates that the color fading of the madder-dyed yarns was limited to a certain period of exposure to daylight.

The results of the light-fastness test show (Table III) that the light-fastness properties of the madder-dyed yarns are low and the ammonia treatment has no positive effect on this property.

## CONCLUSIONS

Madder-dyed wool yarns were treated with 1, 3, and 5% ammonia solutions for 10 min. Results of the UV-vis spectrophotometry analysis on the remaining ammonia solutions showed that there is a transition and a change of peak to higher wavelengths. The absorption intensity of the remaining ammonia solutions

**TABLE II**  
Results of Washing-Fastness Tests of Madder-Dyed and Madder-Dyed/Ammonia-Treated Wool

Wash fastness	Staining on raw wool	Staining on cotton	Ammonia (%)
4	4.5	4	0
4	4.5	4	1
4	5	4	3
4.5	5	4.5	5



**TABLE III**  
**Results of Light Fastness on Madder-Dyed and Madder/Ammonia-Treated Wool**

<i>Light fastness</i>		
after 7 days	after 2 days	Ammonia (%)
5	5	0
3	3	1
3	3	3
2	2	5

increased with an increase in the ammonia concentration. The alteration of peaks after ammonia treatment of madder-dyed wool showed a bathochromic shift, attributed to the extension of the conjugated system of the dye molecule. The color measurement tests confirmed that color alterations occurred with the treatment of ammonia, and also that any increase in the percentage of ammonia in the solution caused a decrease in the amounts of  $a^*$ ,  $b^*$ , and  $L^*$ . The color hue of the madder-dyed wool was changed when the samples were examined for the wash-fastness test. This

created a color hue on the samples in the higher wavelengths. The results of the light-fastness test showed a fading of the madder-dyed yarns.

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