(REFEREED RESEARCH)

ECOLOGICAL PRINTING OF MADDER OVER VARIOUS NATURAL FIBRES

ÇEŞİTLİ DOĞAL LİFLER ÜZERİNE KÖKBOYANIN EKOLOJİK BASKISI

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ABSTRACT

The applicability of madder by using printing technique over various natural fibers was investigated in the study. The effect of different factors, i.e. dye and urea concentration, type of fixation, fixation temperature and time, effect of mordant type and mordanting methods were studied. Printed fabrics were evaluated by means of color values and fastness properties. The K/S increases rapidly as the concentration of the natural dye powder in the printing paste increases from 15 to 45 g/kg printing paste. The effect of mordant on color was also studied. The results show that the highest K/S value was obtained by using mordant. Application of madder with the printing technique is expected to bring a different and an ecological alternative to new designs.

Keywords: Madder, Printing, Ecology, Natural Fiber, Mordant

ÖZET

Bu çalışmada, çeşitli doğal lifler üzerine kökboyanın baskı tekniği ile uygulanabilirliği incelenmiştir. Boyarmadde ve üre konsantrasyonu, fiksaj tipi, sıcaklığı ve süresi, mordan tipi ve yöntemleri gibi farklı faktörlerin etkisi araştırılmıştır. Basılmış kumaşlar renk verimi ve haslık özellikleri açısından değerlendirilmiştir. Baskı patındaki doğal boya konsantrasyonunun 15'den 45 g/kg'a çıkması ile K/S değeri hızlı bir şekilde artmıştır. Renk üzerine mordan etkisi de incelenmiştir. Sonuçlar, en yüksek K/S değerinin mordan kullanılarak elde edildiğini göstermiştir. Kökboyanın baskı tekniği ile uygulamasının yeni tasarımlara farklı ve ekolojik bir alternatif sunması beklenmektedir.

Anahtar Kelimeler: Kökboya, baskı, ekoloji, doğal lif, mordan.

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1. INTRODUCTION

The nature gave inspiration to people as old as their presence in the world. Man used to color materials by imitating the nature. Dyestuffs based on vegetable, animal or mineral sources in ancient times. Natural dyestuffs have been used widely in order to color textile materials with plants, animals or minerals.

In general, natural dyestuffs can be obtained from almost every kind of plant. It is also possible to get dyestuffs from every part of the plants for example from the flowers, fruits, branches, roots etc. As the result of the extraction of these parts, various colors such as red, yellow, orange, green etc. can be obtained.

After the invention and development of synthetic dyestuffs, the usage of natural dyestuffs decreased gradually. Synthetic dyestuffs are usually produced from petroleum products with simple technologies. Dyers cannot give up using these dyes because of the bright colors, repeatability and good fastness properties. But a trend of using natural dyestuffs is increasing because of their eco-friendly character and negative impacts of synthetic dyestuffs in manner of toxicity and waste water problem of the dyehouses. (1)

In dyeing with natural dyestuffs, madder has an important place with its specific red color. Its agriculture began before 8th century in the East and spread out in Europe in 10th century. It is grown wildly in almost every region of Turkey. (2).

Common madder (*Rubia tinctorum L.*) which produces anthraquinone pigments in its roots, one of them being alizarin (1,2 dihydroxy anthraquinone) and it has been used for dyeing textiles since 2000 B.C. The main components are di- and thrihydroxyanthraquinones, alizarin, and purpurin and their derivatives, ruberythric acid (alizarin–primeveroside), psedopurpurin, and lucidin – primeveroside (3). The red color obtained by madder in the past was named as “Turkish Red” because most of the madder production (approx. two-thirds) was made by Ottoman Empire (4).

Many studies have been carried out on dyeing of natural dyes but there are limited works on natural dye printing technology (5-11).

In this study, madder was chosen as a natural dyestuff. It was applied on cotton, wool and silk fabrics by reactive printing method. The effects of different factors, i.e. dyestuff and urea concentration, type of fixation, fixation temperature and time, effect of mordant were investigated.

2. MATERIALS AND METHODS

2.1. Materials

In this study, mill desized, scoured and bleached 100 % cotton fabric (135g/m^2), mill scoured 100 % pure wool fabric (200 g/m^2) and mill scoured 100 % natural silk fabric (60 g/m^2) were used.

Potassium aluminum sulphate ($KAl[SO_4]_2$), copper sulphate, ferricsulphate and tin chloride were used as mordants. Sodium hydroxide, sodium bicarbonate, m-nitrobenzene sulphonic acid (a weak oxidizing agent from BASF, named Ludigol) and urea were used as chemicals.

High viscosity and low viscosity sodium alginate were used as the thickening agent under the commercial names of Lamalgin G-10 and Alginat STA, respectively.

Madder was chosen as a natural dyestuff in this study because it is grown wildly in almost every region of Turkey. Madder the root of *Rubia tinctorum L.,* is one of the oldest natural dyes, which can generate colors ranging from orange, red to violet. These pigments produce useful colours which have distinctive heat and light resistant properties (12).

It was washed thoroughly with water and dried at room temperature. Powder form of dried madder was obtained by crushing process and used in order to prepare homogeneous printing paste.

2.2. Methods

2.2.1. Mordanting

Two methods of mordanting namely, simultaneous mordanting and pre mordanting were tried to be selected as the best mordanting method. According to the pre mordanting method, fabrics were treated in solutions containing mordants as 10% and fabric to liquor ratio was chosen as 1:50. The treated fabrics were then washed to remove excess chemicals on the surface and dried. In simultaneous mordanting method, mordants were added into the printing paste together with the other chemicals.

2.2.2. Preparation of the printing paste

Printing pastes with using powdered madder were prepared as follows:

Table 1. The recipe of printing paste

	Amount (g)
Natural dyestuff powder	15, 30, 45
Thickening agent	25
Sodium bicarbonate	25
Soda	5
Ludigol (Oxidation agent)	15
Urea	50, 100, 150, 200
Water	X
Total weight of the paste	1000

2.2.3. Printing

Printing pastes were applied to fabrics using the by flat-screen printing technique. Laboratory type of printing was made by Johannes Zimmer MDK printing desk. Printed samples were dried at 100°C for 3 minutes by Rapid Laboratory Type Dryer. Fixation was performed by thermofixation and by steaming at Mathis (Switzerland) steamer for different durations and temperatures.

Printed samples were steamed at 102°C for 15 minutes to fix the dyes immediately after printing. Printed and steamed samples were rinsed in warm, hot, warm and cold water, respectively for 10 minutes and finally all samples were dried at room temperature.

2.2.4 Evaluation of printed sample

The color strength values of the printed fabrics were measured by using a HunterLab ColorQuest II spectrophotometer (D65/10) (HunterLab, USA) over a wavelength range of 390–700 nm.

Washing fastness of the printed samples was tested according to ISO 105-C02 method. Dry and wet rubbing fastness of the samples was tested according to ISO 105-X12 method. Light fastness was tested according to ISO 105-BO2 method.

3. RESULTS AND DISCUSSION

This study was carried out to investigate the suitability of using madder powder as natural dyestuff in printing natural fabrics using the reactive printing technique and different printing pastes were prepared and also effects of different factors were investigated.

Pigment and reactive printing methods were used in pre-trials. However, the best results were obtained with reactive printing method. In pigment printing method, the handle of fabrics was so stiff therefore reactive printing method was chosen in order to prevent natural handle of wool and silk fabrics.

3.1. Effect of urea concentration

Urea is used in the printing pastes to decrease the viscosity of the printing paste film applied to the fabric, so the diffusion of the dye to the fibers is accelerated, urea helps the swelling of fiber pores and the solubility of the dye is increased. During steaming, the temperature of the fabric may continue rising without control after it reaches to the steaming temperature, but the urea in the printing paste may prevent increasing of the temperature because it increases the formation of condensate. By this way, optimum steaming conditions are provided by the regulation of the moisture content. To investigate the effect of urea concentration on the *K/S* values of printing goods, different printing pastes were prepared using different amounts of the urea, 50, 100, 150, 200 g/kg pastes. The printed fabrics were cured by steaming at 102◦C for 10 minutes.

The results obtained are shown in Figure 1.

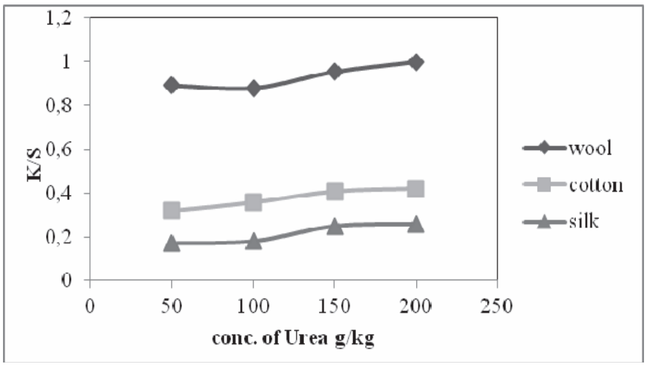


Figure 1. Effect of urea concentration

The K/S values increased rapidly as the concentration of the urea increased from 50 to 200 g/kg in the printing paste. According to color strength values, 150 g/kg was selected as optimum concentration.

3.2. Effect of dyestuff concentration

To investigate the effect of dyestuff concentration on the *K/S* values of printing goods, different printing pastes were prepared using different amounts of the specified natural dyestuff, 15, 30, 45 g/kg pastes. The printed fabrics were cured by steaming at 102°C for 10 minutes.

The results obtained are shown in Figure 2.

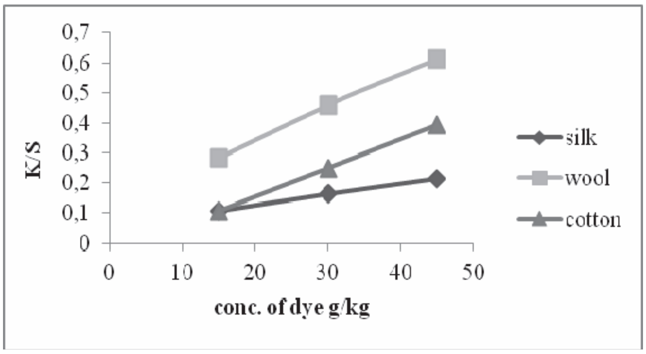


Figure 2. Effect of natural dyestuff concentration

The K/S values increased rapidly as the concentration of the natural dyestuff powder in the printing paste increased from 15 to 45 g/kg printing paste. It seemed that the K/S values would increase as the amount of madder increased, but because of the difficulties of washing dark colors, 45 g/kg was determined as the optimum dyestuff concentration and the higher concentrations were not tried anymore.

3.3. Effect of fixation parameters

Fabrics were printed in optimum urea and dyestuff concentration and then were steamed at 102 ºC for 10 and 30 minutes, at 130 ºC for 5 and 10 minutes and also thermofixation was performed at 150 ºC for 5 minutes to find out the optimum fixation conditions.

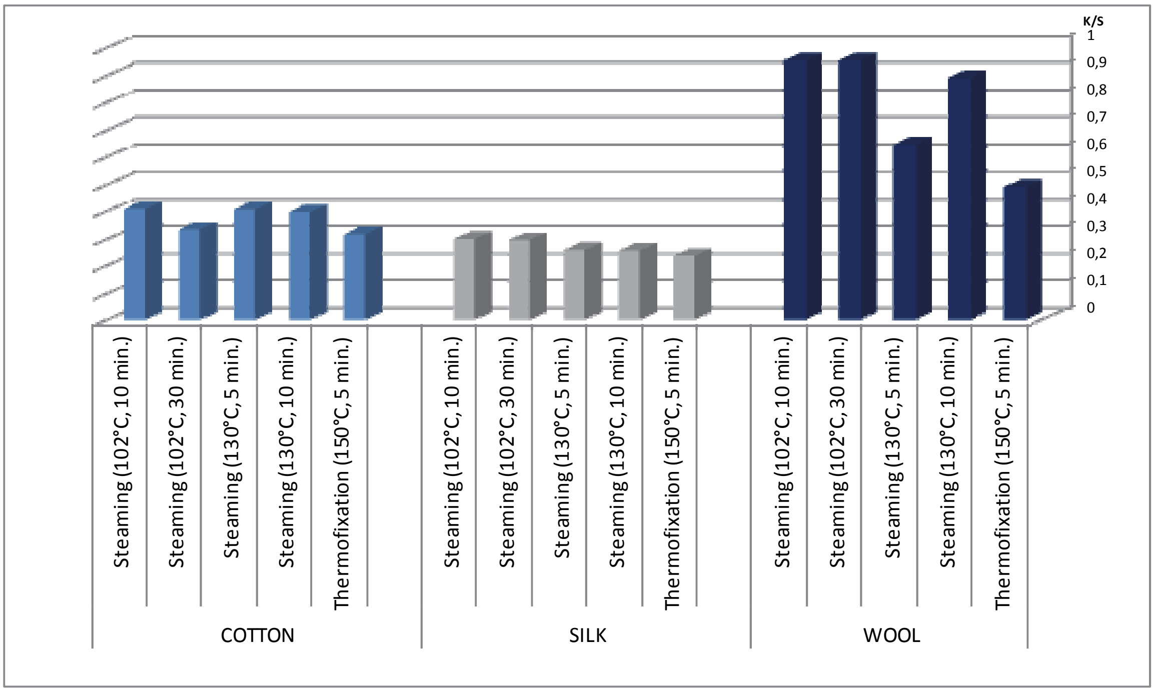


Figure 3. Effect of curing type, temperature and time

Figure 3 shows that both 102 and 130°C temperatures of steaming have similar K/S values. Longer exposures of the fabrics to high degree of steaming also brought the risk of the fabrics' yellowing. Thus, in this study the duration of steaming to give satisfactory results was chosen as 10 minutes at the temperature of 102◦C for all fabrics. Moreover, results show that the printed goods, which were fixed by steaming, have relatively higher color strength than their corresponding samples fixed by thermofixation. The condensed water vapor in steaming method may accelerate the penetration of the dyestuff molecules into the fabrics and hence increases the K/S values of the printed fabrics fixed by steaming than those fixed by using conventional hot air in the thermofixation process (13) .

3.4. Effect of mordant

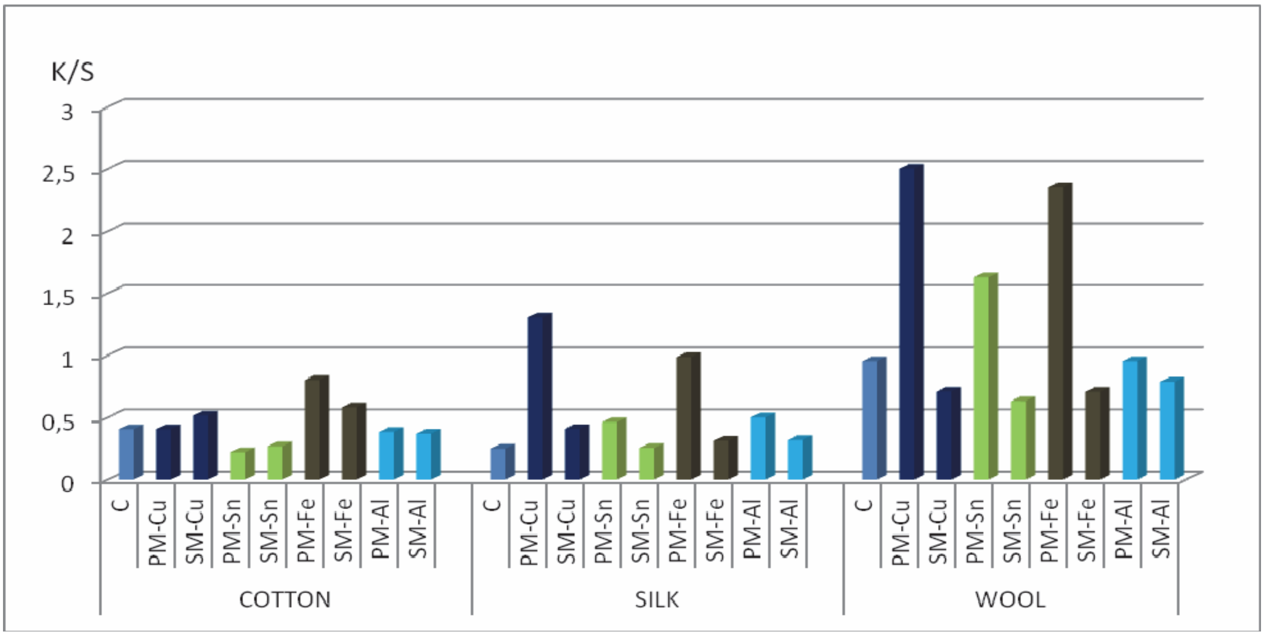
Mordants are often used with natural dyestuffs to fix the dyestuff, keep natural ones from fading and improve their fastness properties. The dyestuff binds better to the fabric by means of a mordant. By using different mordants, a variety of colors may be obtained with natural dyestuffs. In this study, potassium aluminum sulphate ($KAl[SO4]_2$), copper sulphate, ferric sulphate and tin chloride were used as mordants in the printing paste of madder. Two methods of mordanting namely, simultaneous mordanting and pre mordanting were studied. The prepared pastes were then used in printing wool, silk and cotton fabrics. It was observed that the mordants have remarkable effects on the obtained colors where different ranges could be obtained by using different mordants.

Figure 4 shows the effect of mordan type and method on the K/S of cotton, wool and silk fabrics. Cellulosic fibers have weak affinities to the natural dyestuffs compared with the protein fibers. But using mordant can increase its affinity and hence increase the K/S values. Wool fibers have good affinities to the natural dyestuffs; chemical structure of wool enables the fiber to bind chemically with a wide variety of dyestuffs .Wool being a protein fiber, has a high affinity to the natural dyestuffs. Although silk is categorized as a protein fiber, it differs from wool in its weight, absorbance, resilience and reactivity properties (14). The best results were obtained by premordanting method with copper and ferro mordants for wool and silk fabrics.

3.5. Fastness Properties

Washing, rubbing and light fastness of the printed fabrics were tested, the results of simultaneous mordanting and pre mordanting with potassium aluminum sulphate, copper sulphate, ferric sulphate and tin chloride printed fabrics.

As shown in Table 2, staining values in washing fastness results were found as "5" in all fixing conditions. Color change values were "3-4" for in cotton printing for the fixing types of 5 minutes thermofixation at 150°C, 5 minutes steaming at 130°C and 10 minutes steaming at 102°C. For the other fixing and fabric types, color change values were "4".



Without mordant	C
Premordanted with copper sulphate	PM-Cu
Simultaneous mordanted with copper sulphate	SM-Cu
Premordanted with tin (II) chloride	PM_Sn
Simultaneous mordanted with tin (II) chloride	SM-Sn
Premordanted with iron sulphate	PM-Fe
Simultaneous mordanted with iron sulphate	SM-Se
Premordanted with aluminum sulphate	PM-Al
Simultaneous mordanted with aluminum sulphate	SM-Al

Figure 4. Effect of mordant type and method

Table 2. Fastness values of printed samples without mordants and having different fixing conditions

Fabric type	Fixation Type	Washing fastness		Rubbing Fastness		Light Fastness
		Staining	Color Change	Dry	Wet	
Cotton	Steaming (130° C, 5 min.)	5	3-4	4-5	4	2
	Steaming (130° C, 10 min.)	5	4	4-5	4	2
	Steaming (102° C, 10 min.)	5	3-4	4-5	3-4	2
	Steaming (102° C, 30 min.)	5	4	4-5	3-4	2
	Thermofixation (150°C,5 min.)	5	3-4	4-5	3-4	2
Wool	Steaming (130° C, 5 min.)	5	4	5	4	2-3
	Steaming (130° C, 10 min.)	5	4	5	4	2-3
	Steaming (102° C, 10 min.)	5	4	5	4	2
	Steaming (102° C, 30 min.)	5	4	4-5	4	2
	Thermofixation (150° C, 5 min.)	5	4	5	4	2-3
Silk	Steaming (130° C, 5 min.)	5	4	4-5	4-5	2
	Steaming (130° C, 10 min.)	5	4	5	4-5	2-3
	Steaming (102° C, 10 min.)	5	4	5	4-5	2-3
	Steaming (102° C, 30 min.)	5	4	5	4-5	2
	Thermofixation (150° C, 5 min.)	5	4	5	4-5	2

The light fastness values were “2” or “2-3” for all fixing and fabric types, an important difference between them couldn’t be noticed. When all the results and energy saving matters were taken into account, steaming for 10 minutes at 102°C was chosen as the optimum fixing process.

Dry rubbing fastness values were “4-5” or “5” for all fixing and fabric types, it can be concluded that fixing type does not have any effects over dry rubbing fastness value. When wet rubbing fastness of printed cotton fabrics was evaluated, it was “4” for 5 and 10 minutes of steaming at 130°C, “3-4” for 5 minutes of thermofixation at 150°C, 10 and 30 minutes steaming at 102°C. Wet rubbing fastness value for the wool fabrics was “4”, it was “4-5” for silk fabrics. The type of fixing didn’t have any effects over wool and silk fabrics.

Although light fastness values were low for all fixing and fabric types, the lowest values were obtained for the printed cotton fabrics. Printed wool fabrics were a little bit better in this manner, compared to cotton.

Table 3. The fastness values for the fabrics printed with different mordants and mordanting methods.

Fabric type	Fixation Type	Washing fastness		Rubbing Fastness		Light Fastness
		Staining	Color Change	Dry	Wet	
Cotton	Premordanted with aluminum sulphate	5	2	4-5	4	2
	Simultaneous mordanted with aluminum sulphate	5	2	4-5	4-5	2
	Premordanted with coppersulphate	5	3	4-5	4	6
	Simultaneous mordanted with copper sulphate	5	2-3	5	4-5	3
	Premordanted with ferrosulphate	5	2-3	3-4	3-4	2-3
	Simultaneous mordanted with ferrosulphate	5	2	4-5	3-4	2
	Premordanted with tin chloride	5	1-2	4-5	4-5	1-2
	Simultaneous mordanted with tin chloride	5	2	4-5	4-5	2
	Without mordant	5	3-4	4-5	3-4	1-2
Wool	Premordanted with aluminum sulphate	5	3	4-5	4	3-4
	Simultaneous mordanted with aluminum sulphate	5	3	5	4-5	2-3
	Premordanted with copper sulphate	5	3-4	4	4	6
	Simultaneous mordanted with copper sulphate	5	3-4	5	4-5	3
	Premordanted with ferrosulphate	5	2	3	4	3-4
	Simultaneous mordanted with ferrosulphate	5	3-4	4-5	4-5	2
	Premordanted with tin chloride	5	2	4-5	4	2
	Simultaneous mordanted with tin chloride	5	3-4	5	4-5	2
	Without mordant	5	4	5	4	2
Silk	Premordanted with aluminum sulphate	5	3-4	5	4-5	5
	Simultaneous mordanted with aluminum sulphate	5	3-4	5	5	3
	Premordanted with copper sulphate	5	3-4	4-5	4-5	5-6
	Simultaneous mordanted with copper sulphate	5	2	5	5	4
	Premordanted with ferrosulphate	5	3	3-4	4	4
	Simultaneous mordanted with ferrosulphate	5	3	5	5	2-3
	Premordanted with tin chloride	5	3-4	4-5	4-5	3-4
	Simultaneous mordanted with tin chloride	5	3	4-5	4-5	3-4
	Without mordant	5	4	5	4-5	3

When Table 3 was evaluated by means of mordant types, mordanting methods, and fiber types, washing fastness values, it was determined that staining value was “5” in all fabric types, mordants and mordanting methods. Using mordants caused some decreases in values of color change esp. for the printed cotton fabrics.

Dry rubbing fastness values were higher than wet rubbing fastness values and the lowest ones were obtained by premordanting with ferrosulphate. When mordanting methods were compared to each other, better fastness values were obtained by simultaneous mordanting than pre mordanting printing and printing without mordant.

Light fastness values of the printings without any mordants are generally lower than the others and the positive effect of the copper sulphate in pre mordanting method is obvious. The light fastness values increased a little when copper sulphate was used in simultaneous mordanting and ferrosulphate was used in pre mordanting methods. As a result it can be said that the light fastness values increased when pre mordanting method was applied and copper sulphate was chosen as a mordant.

Different colors and fastness values can be obtained by choosing different mordants in printing with madder.

4. CONCLUSION

In this study, madder as a natural dye was used in printing cotton as a cellulosic fiber, wool and silk as protein fibers by using reactive printing method. The parameters of printing were tried and optimum ones were chosen. For this aim, dye and urea concentration, type of fixation, fixation temperature and time, effect of mordant type and mordanting methods were studied.

The K/S increases rapidly as the concentration of the natural dye powder in the printing paste increases from 15 to 45 g/kg and the concentration of the urea increased from 50 to 200 g/kg in printing paste. According to color strength values, 45 g/kg dye and 150 g/kg urea was selected as optimum concentration respectively. The duration of steaming chosen to give satisfactory results was 10 min at temperature of 102°C for all fabrics. Moreover, results show that the printed goods, which were fixed by steaming, had relatively higher color strength than their corresponding samples fixed by steaming. Different color yield and nuances were obtained according to mordant type. The best results were obtained by premordanting method with copper and ferro mordants for wool and silk fabrics. For cotton fabrics, premordanting method with ferric sulphate gave the best K/S values.

When fastness values was take into account, it was determined that staining value was “5” in all fabric types, mordants and mordanting methods. Using mordants caused some decreases in values of color change especially for the printed cotton fabrics. Madder root dyed fabrics showed the most dramatic change in color. The change in color resulting from an alkaline wash could be a result of the loss of colorant due to conversion of the colorant to soluble salts of the dyes and other soluble products (15).

Dry rubbing fastness values were higher than wet rubbing fastness values and the lowest ones were obtained by premordanting with ferrosulphate. In general, mordanting has a positive effect on light fastness values. Light fastness values increased especially pre mordanting method and copper sulphate was used as a mordant.

In the scope of this study, application of madder with the reactive printing technique is expected to bring a different and an ecological alternative to new designs. By using different mordants, different color shades and fastness values are possible. Application of madder with the printing technique is expected to bring a different and an ecological alternative to new designs. The ecological and toxicological problems caused by synthetic dyestuffs can be solved to some extent.

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