Using nano-pigment for coloration of leather

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Abstract

Mainly leather is dyed using anionic dyestuffs such as acid, direct and metal complex dyes, but the use of pigments is not common for leather dyeing. Dye penetration into the inner layers of the leather is a difficult task due to 3D infrastructure of leather.

In the present study, an attempt has been made to improve the exhaustion of nano-pigment in dyeing leather by using ultrasound. Optimum dyeing conditions including reduced dyeing time is aimed.

Taguchi method was employed for the design of experiments. CIELAB color coordinates reflectance values of dyed leathers were evaluated using a reflectance spectrophotometer. The K/S values of the samples were considered to be proportional to the absorption of nano-pigment into the leather. The optimum level of the effective parameters namely as: wetting time, type of swelling agent, ultrasonic bath time, and amount of pigment were evaluated and confirmed by complementary experiments.

Keywords: Nano pigment; Leather; Taguchi; Coloration; Ultrasonic bath;

1. Introduction

Leather is a material produced from animal hides and skins. It is used for shoes, upholstery, clothing, gloves, hats, books, handbags, cases, prostheses, carpets, tapestries, footballs, and other purposes . Leather is formed from a natural hide and becomes a dry, stable material after tanning, retanning, greasing, and wet dry finishing [1] . These processes prevent putrefaction and rotting under humid conditions. Most leathers are lubricated and contain fat to confer softness, elasticity, and strength. Leather is colored and its surface is often protected by a coating against dust, sweat, water, and scuffing. Different types of hides and skins are used for leather production, including those from the cow, ox, pig, goat, horse, buffalo, kangaroo, ostrich, snake, crocodile, fish, frog, seal, elephant, camel, vicuna, and some other animals. The skins and hides are selected for the specific leather applications according to hide structure, size, thickness, and grain structure [1, 2]. Dyeing leather is a challenging task in order to meet the current market requirement. The need to meet criteria such as: cost-effectiveness, flexibility, fastness standards, levelness and coverage of defects, reproducibility. Efforts have long been made to establish a theory of leather dyeing but the processes that occur during the drum dyeing of leather in an aqueous medium are often obscure. Even with the same processing procedure and chemicals being used, differences in depth and levelness of shade may occur from batch to batch. Practical knowledge of leather dyeing is generally very rudimentary, primarily because wool or polyamide dyeing is seen as the model. This rather empirical approach and the technology developed by Otto in the 1950s still serves as the basis of leather dyeing [2, 3].

1.1. Taguchi Design of Experiments

There is a unique statistical experimental design technique known as Taguchi's Robust Design Method. The design of parameters using Taguchi's method is an offline quality control method. Offline quality control methods are quality and cost control activities conducted at the product and process design stages to improve product manufacturability and reliability and to reduce product development and lifetime costs (Philip, 1988). Parameter design can be used to make a process robust against sources of variation and hence to improve field performance. In Taguchi's concept, the product must be produced at optimal levels with minimal variation in its functional characteristics. Control and noise factors affect the product quality. The former can be easily controlled although noise factors are nuisance variables that are expensive to control [4, 5].

2. Experimental

2.1. Materials

- Chrome tanned leather samples were obtained from local tannery in Varamin, Iran % Cr_2O_3 3.4-3.9, neutralized by 1.5% sodium bicarbonate and sodium formate.
- Reso-Nano Red / C.I. Pigment Red 8 were supplied by Reso Chem. Company (Pakistan)
- The non-ionic detergent was used for the scouring of leather samples obtained from England SDL Company. Swelling agents: Urea, Aniline, Ethylene glycol from Merck chemical company, Acetic acid 85% (Merck) was used for pH adjustment in soaking and dyeing processes.

2.2. Methods

Scouring

The fatty and waxy materials present on the surface of leathers were scoured in 5% non-ionic detergent. The L: G of the scouring bath was kept at 50:1 for 30 minutes at 50^{O}C.

Soaking

The leather samples were soaked in a bath of containing swelling agent and distilled water, the L: G = 70:1, at pH=7 and certain times.

Dyeing

Crust leathers with certain weigh were neutralised to pH about 6.0 using dilute acetic acid and prepared solutions with different concentrations of pigment and swelling agents (L:G = 70:1) then 5 samples dyed without ultrasonic bath and 9 samples dyeing were carried out in a glass beaker with flat bottom, clamped inside the ultrasonic bath (TECHNO-GAZA S.p.A, Parma, Ltd Italy) containing water. A piezo-electric ultrasonic transducer fixed at the centre of the bottom wall of the ultrasonic bath generates ultrasound of 130 W powers at a frequency of 50-60 kHz as quoted by the manufacture. The dyeing procedure used for samples are depicted in Fig.1. Finally, the dyed samples were rinsed thoroughly with cold water and dried in air.

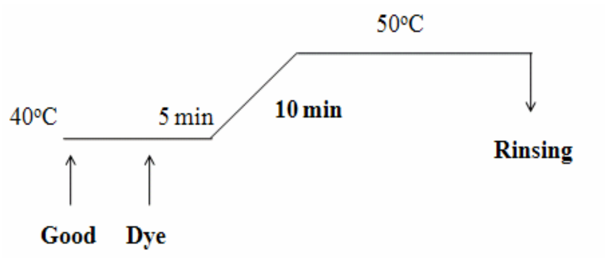


Figure1. Dyeing Diagram used for dyeing of samples with the nano-pigment Red 8

Washing

The dyed leathers were washed in 5% non-ionic detergent. The L: G (liquor to good ratio) of the scouring bath was kept at 50:1 for 10 mins at 50^{O}C.

Reflectance measurement

CIELAB colour coordinated of dyed samples (L*, a* and b*) were measured using a spectrophotometer COLOREYE 7000A from Gretagmacbeth integrated with an IBM computer. Colour co-ordinates were calculated from the reflectance data for 10^{o} observer and illuminant D_{65}.

Light fastness measurement

For Light fastness measurements, the dyed leathers were exposed to daylight for 4 days according to the daylight ISO-B01, and the changes in the colour (fading) were assessed by the blue scale.

Colour Strength

Relative colour Strengths (K/S) were determined using the Kubelka-Mank equation (Eq. 1):

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

Where K, S and R are the absorption coefficient, scatter coefficient and reflectance of the dyed sample, respectively.

Scanning electron microscopy (SEM)

The leather samples were cut into specimens of uniform thickness. A Scanning electron microscope model XL30 manufactured by Netherlands's Philips Company was used for the analysis. The micrographs for the grain surface and cross-section were obtained by operating the SEM at low vacuum with an accelerating voltage 10 kV at different magnification levels.

3. Results and discussion

3.1. Experimental Procedure

The investigation was performed on leather samples. Taguchi design and L_9 (3^4) orthogonal array design was adopted for experimentation for each sample. The nine experiments were conducted by varying all the parameters (conditions adopted in experiments are shown in Table 1) identified to study the influence of these parameters on penetration of dye, colour values levelness defects, and percentage dye exhaustion. The results of the L_9 array in Tables 2
Controllable factors were selected following to:

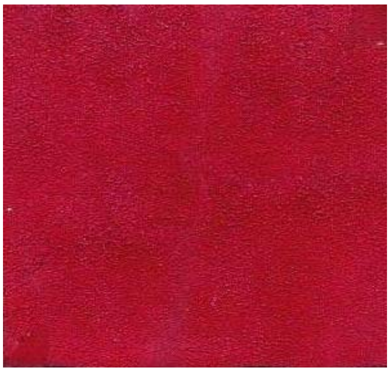
- Factor A**:** is the assigned to the time that sample was treated in ultrasonic bath at three levels (2, 3 and 4 hours)
- Factor B: is the soaking time in dyeing bath that was investigated in three levels (2, 12 and 24 hours)
- Factor C: is the type of swelling agent which affects the dye absorbing value that was investigated in three levels namely as Ethylene glycol, Aniline and Urea with 10% (liquor to good ratio).
- Factor D: is the percentage of dye that was investigated in three levels (5, 10 and 15) %

Table 1: L_9 orthogonal array of leather samples

Exp.No	A	B	C	D	K/S
1	1	1	1	1	12/21
2	1	2	2	2	25/75
3	1	3	3	3	13/94
4	2	1	2	3	12/61
5	2	2	3	1	6/60
6	2	3	1	2	8/83
7	3	1	3	2	15/85
8	3	2	1	3	9/06
9	3	3	2	1	9/48

3.2. Color measurement

Colour coordinates values of dyed samples are summarized in Table 2 . The results clearly show that leathers dyed in the ultrasonic bath have greater colour values compared to those dyed with standard method. Lower L* values for leathers dyed with ultrasonic bath indicate that ultrasound helps in getting brighter shades. Also, higher a* values for leathers dyed with ultrasonic bath indicate that ultrasound helps in getting more redness, the colour of the dye used. Fig. 2 shows a photograph of the grain side of the dyed leather, which indicates more colour intensity for leather dyed in presence of ultrasound compared to that dyed with standard method.



Smaple 2

noraml dyeing sample

Table 2: Colour values of control and dyed leather samples

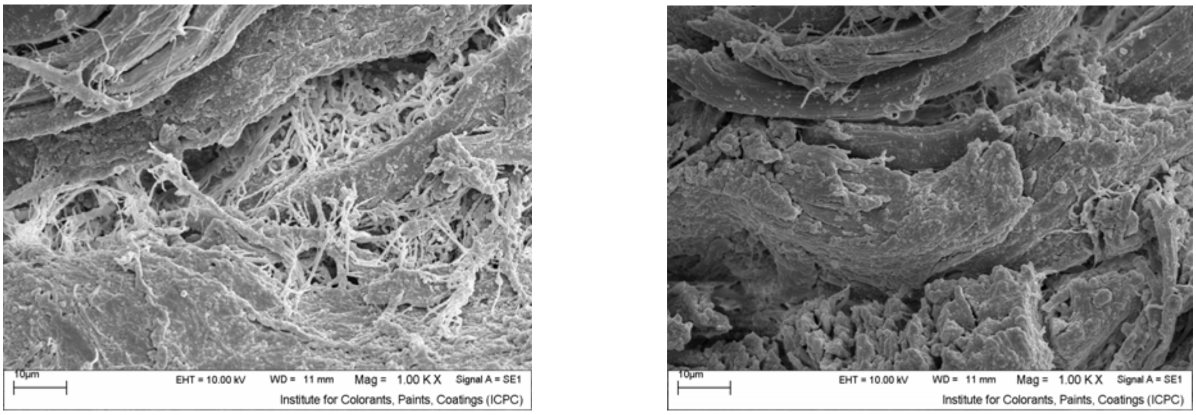
With US*	L*	a*	b*	Without US	L*	a*	b*
L_1	38.885	43.395	16.466	Raw Leather	70.327	-4.397	1.022
L_2	33.632	49.067	3.482	1	47.594	24.690	1.740
L_3	38.428	45.224	10.224	2	56.321	9.882	-0.167
L_4	39.452	44.584	12.102	3	43.172	36.504	4.458
L_5	44.319	36.432	7.72	4	38.501	42.790	9.754
L_6	42.279	47.241	11.216	5	36.950	48.082	16.705
L_7	36.541	46.525	12.700				
L_8	42.808	39.105	27.304				
L_9	42.074	41.377	9.287				

*US = ultrasonic

3.3. Lightness fastness

In the case of light fastness, nine pieces of dyed leathers which formed the blue scale were exposed to the light at the same time as the test was preceded for the specimen. After the exposure, the degree of fading of the test specimen was compared to the standard blue scale. In this test the light fastness values of the samples varied between 5 to 7.

3.4. Scanning electron microscopy (SEM)



(a) (b)

Figure2. SEM micrographs showing the surface structure of (a) dyed leather (b) raw leather

Conclusion

The penetration of dye into the leather, the colour values and fastness properties of dyed leathers were found to be improved due to the use of ultrasonic bath compared to those of dyed control leathers.

The results show that there is a significant improvement in the percentage exhaustion of dye due to the presence of ultrasonic bath when compared to dyeing in absence of ultrasonic bath

The use of nanoparticles can improve the pigment performance in penetration to leather.

SEM And optic microscope micrographs show agglomeration of nano-pigment on surface of leather.

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