# Automated Clean Leather Dyeing Assisted by Wringing, Ultrasound and Microwave

*by*

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## Abstract

A "clean" leather dyeing was designed with wringing (8-10kg/cm$^2$), ultrasound (28kHz, 2.4W/cm$^2$) and microwave (2450MHz, 10W/L). Twenty leathers were successively colored with this method in lab scale. The dye exhaustion (%), the color values and the color rub fastnesses were determined respectively. Also, the grain surface and the cross-section of the leathers were analyzed before and after dyeing. As presented, it only needed 5min to color with this method and the dye exhaustion averages 2.3% a leather, which were helpful for the recycle of the dye solution. The color for the first ten leathers just varied within a small range ($\Delta E$<1), when the solution was directly recycled without dye replenishment. The color fastnesses reached up to 4-5 scale (dry rub) and 3 scale (wet rub) after the leathers were coated as a common shoe upper finishing formula. Furthermore, the grain and the collagen fibers were not damaged during the dyeing process, which were proved by Scanning Electron Microscope and X-ray diffraction analysis. In short, this clean and quick dyeing is a potential choice for leather dyeing.

## Resumen

Un teñido "limpio" del cuero ha sido diseñado con escurrido (8-10 kg/cm$^2$) incorporado, así cómo con aplicaciones energéticas de ultrasonido (28 kHz, 2.4 W/cm$^2$) y de microondas (2450 MHz, 10 W/L). Veinte muestras de pieles fueron teñidas sucesivamente con este método en un ensayo a escala de laboratorio. El agotamiento de colorante (%), los valores de color y las solideces del color al frote se determinaron. Además, la superficie de la flor y la sección transversal de los cueros se analizaron antes y después del teñido. Tal como se presenta, sólo se requiere 5 minutos para teñir con este método y agotamientos del teñido en promedio de 2,3%, es útil para el uso por recicle de la solución colorante. El color para el grupo de prueba de los diez cueros varió dentro de un rango pequeño ($\Delta E$ <1) cuando la solución se utilizó directamente sin necesidad de reposición de tinta gastada. Las solideces del color alcanzaron tanto como 4-5 en la escala de frote seco y 3 en la escala de frote húmedo, después de que los cueros fueron recubiertos empleando una fórmula típica de acabado de calzado. Por otra parte, la flor y las fibras de colágeno no fueron dañadas significativamente durante el proceso de tintura, como lo demuestra el análisis por medio del microscopio electrónico de barrido y análisis por difracción de rayos X. En resumen, este teñido limpio y rápido podría considerarse como una opción potencial para el teñido del cuero.

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## INTRODUCTION

Leather production involves a series of chemical reactions and mechanical processes. Amongst these, dyeing is a process imparting colors, in which acid dyes, direct dyes and basic dyes are most commonly used. Up to now, leather is still colored with an aqueous dye solution in a drum, which results in serious pollution, such as high chroma, COD and BOD in the effluent. [1, 2]

The leather is a matrix of pore-size ranging from $3\times10^{-10}$ to $15\times10^{-5}$ m. [3] In the rotating drum, dyes initially penetrate through the pores in the leather and then are fixed by electrostatic attraction and Van der Waal forces.[4, 5] That is, there are two distinct phases, namely 'dye penetration' and 'dye fixation', both of which determine the color properties of the leather and the dye remained in the final liquor. However, the depth of the dye is more influenced by the 'dye penetration', and the color fastness is more affected by the 'dye fixation'. Therefore, a hypothesis was proposed, viz., the two phases may be separately intensified, in turn, which was first confirmed with the process assisted by wringing, ultrasound and microwave.

As shown in Fig. 1, there were three continuous steps in this method. (1) Step I: The crust was prepared by wringing with a pressure of 10 kg/cm$^2$, which lowered the water content to 55%. (2) Step II: The leather was first colored with an aqueous dye solution in the ultrasound field (28kHz, 2.4W/cm$^2$), and then wrung with a pressure of 8 kg/cm$^2$. The water content in the leather decreased to 65% after wringing. (3) Step III: The leather was irradiated using microwave (2450MHz, 10W/L) with the water content reducing to 60% and the temperature rising to 60°C, and then treated with an fixing agent solution in the ultrasound field (28kHz, 2.4W/cm$^2$). Finally, the leather was wrung with a pressure of 8 kg/cm$^2$ to lower the water content to 65%.

In this process, the leather was proposed to be transported with the belts one by one, and the dye solution and the fixing agent solution were to be reclaimed and recycled respectively.

In the present work, twenty leathers were successively colored with this method. The dye penetration was enhanced by both the wringing and the acoustic cavitation. The dye fixation was strengthened with microwave irradiation and aluminum salt. In addition, the dye solution was successfully recycled in lab scale.

## EXPERIMENTAL

### Materials

Wet leathers with thickness about 2.4mm were from a local tannery and prepared as a common bovine shoe upper retanning and fatliquoring procedure. Acid black was a commercial dye (Chroma Chemical Corporation, China) with the same chemical structure as acid black 10B (CI No. 20470), color strength as 100%. Aluminum trichloride and other chemicals used for processing the leathers were commercial available.

### Experimental set-up

The schematic diagram of the ultrasonic set-up is shown in Fig. 2. The ultrasonic cleaner has a capacity of 10L, in which the bath temperature can be maintained within ±2°C. The dye penetration was carried out in one 1.2L glass vessel, while the dye fixation was in the other 1.2L vessel. The leather was placed on the steel mesh grid, about 4cm above the bottom of the ultrasonic cleaner. The ultrasound power intensity at 28kHz was adjusted to 2.4W/cm$^2$.

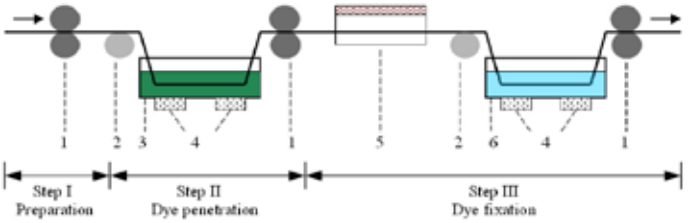



Fig. 1 Schematic diagram of the dyeing process

1– extrusion rolls; 2– tray rollers; 3– staining tank; 4– ultrasonic transducers; 5– microwave chamber; 6– color fixing tank; '→' represents the transport path of the crust.

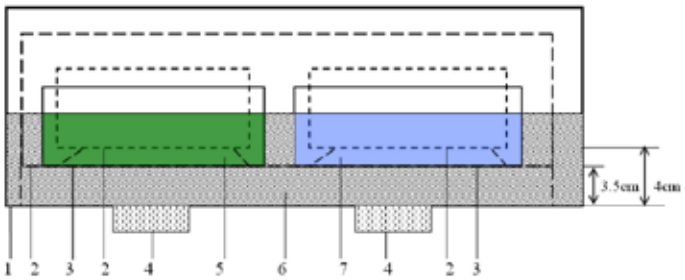



Fig. 2 Schematic diagram of the ultrasonic set-up

1 – ultrasonic cleaner; 2 – steel mesh grid; 3 – glass vessel; 4 – ultrasonic transducers; 5 – dye solution; 6 – bath water; 7 – fixing agent ($AlCl_3$) solution

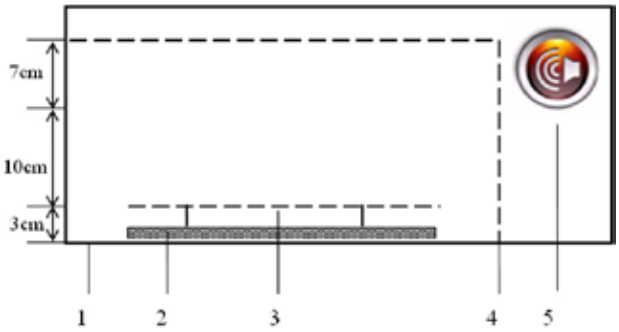



Fig. 3 Schematic diagram of the microwave set-up

1 – microwave oven; 2 – autorotation object stage; 3 – plastic mesh grid; 4 – inside covering; 5 – microwave source

The schematic diagram of the microwave set-up is displayed in Fig. 3. The microwave oven has a capacity of 16L. The leather was placed on the autorotation object stage, about 10 cm below the microwave source. The microwave power intensity at 2450MHz was adjusted to 10W/L.

**Leather dyeing**

Matched twenty leathers (10cm×15cm) were taken from the back area of the retanned, fatliquored hide, and then weighed and colored one by one as the process in Fig. 1. The original acid dye solution in Step II was 500g with dye mass content as 5%, and the initial $AlCl_3$ solution in Step III was 500g with $AlCl_3$ mass content as 1%. The temperature of the two solutions was maintained at 40±2°C. In addition, the duration of the leather was set as consecutive 1 min in the dye solution, the microwave oven, and the $AlCl_3$ solution.

**Analysis methods**

***Analysis of dye exhaustion***

After every five leathers were colored, the dye solution and the $AlCl_3$ solution were weighed and their dye content was analyzed using UV-visible spectrophotometer respectively.[3] The dye exhaustion was calculated as the following formula.

$$\%Exhaustion\ of\ dye = \frac{w_0 \times c_0 - w_1 \times c_1 - w_2 \times c_2}{w_0 \times c_0} \times 100\% \quad (1)$$

Where $w_0$, $w_1$, $w_2$ are the weight of the initial dye solution, the remained dye solution, and the remained $AlCl_3$ solution; $c_0$, $c_1$, $c_2$ are their dye mass content.

**Determination of color difference**

The color of the leather was quantified according to the Commission International de l'Eclairage (CIE) system of color measurement with $10^0$ standard observer data. [6] Color measurements (*L*, *a*, *b* and *C*) were recorded with the Premier 8200 color photometer (USA). The overall color difference ($\Delta E$) and the hue difference ($\Delta H$) were calculated using the following equations.

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

$$\Delta H = \sqrt{\Delta E^2 - \Delta L^2 - \Delta C^2} \quad (3)$$

Where $\Delta E$ = overall color difference; $\Delta L$ = lightness difference; $\Delta a$ and $\Delta b$ = difference in *a* and *b* values, where '*a*' represents the red and green axis and '*b*' represents the yellow and blue axis; $\Delta H$ = hue difference; $\Delta C$ = chromaticity difference.

| | |
|---|---|
| $\Delta L>0$, sample is lighter, | $\Delta L<0$, sample is darker, |
| $\Delta a>0$, sample is redder, | $\Delta a<0$, sample is greener, |
| $\Delta H>0$, sample is yellowier, | $\Delta b<0$, sample is bluer, |
| $\Delta C>0$, sample is brighter/more saturated, | $\Delta C<0$, sample is duller/less saturated. |

***Determination of fastness to wet and dry rub***

Samples of appropriate size (3cm×14cm) were cut from the leather. After conditioning,[7] they were tested for wet and dry rub fastnesses according to QB/T 2537 method using a staining grey scale.[8] The rub fastness was rated in a scale of 1 to 5, in which 1 was the lowest and 5 the best.

***Scanning electron microscopic study (SEM)***

A JSM-5900LV scanning electron microscope (Japan) was used for the analysis. The micrographs for the grain surface and the cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20kV in different magnification levels.

***X-ray diffraction study (XRD)***

An X'Pert Pro X-ray diffractometer (Netherlands) was used to obtain the X-ray diagrams of the grain surface. The testing conditions were as following: generator voltage as 40kV, tube current as 35mA, 2θ as 5° to 60°, step size as 0.03°, time per step as 0.2s.

## RESULTS AND DISCUSSION

**Dye exhaustion**

As shown in Fig. 4, the dye exhaustion (%) was proportional to the number of the leathers. The final exhaustion was determined as 46.0% for the twenty leathers, and the exhaustion averages 2.3%. That is, as for the several successive leathers, there was just slight difference in the dye content of the solution in Step II, which might be helpful for the recycle of the solution.

In this study, the thickness of the leathers was 1.5±0.2mm after drying. All the leathers were colored thoroughly, showing that the dye penetration with this method could meet the demands of the shoe uppers. [9] In addition, the percentage of the dye absorbed was just 2.6%, based on the weight of the leathers.

**Color measurements and fastnesses**

Variation in the color of the leathers was presented in Table I. During the recycle of the dye solution, there was slight difference in the hue ($\Delta H<0.1$), while the darkness and the saturation decreased obviously ($\Delta L>0$, $\Delta C<0$). The overall color difference for the first ten leathers varied within a small range ($\Delta E<1$), while $\Delta E$ rose rapidly for the last ten. These results indicate that the dye might be replenished into the reused solution in time to maintain the least color difference for the leathers; however, the replenishment will be optimized in the later medium-scale trials.

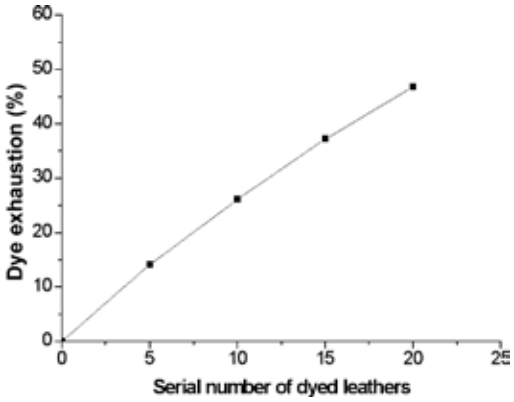



Fig. 4 Dye exhaustion for the twenty leathers

**TABLE I**
**Color difference values for the twenty leathers**

| Serial number | *ΔL* | *Δa* | *Δb* | *ΔC* | *ΔE* | *ΔH* |
|---|---|---|---|---|---|---|
| 1 [a] | 21.33 | 0.23 | 2.20 | 2.21 | | |
| 2 | 0.07 | 0.00 | -0.02 | -0.02 | 0.07 | 0.00 |
| 3 | 0.09 | -0.01 | -0.04 | -0.04 | 0.10 | 0.01 |
| 4 | 0.09 | -0.01 | -0.04 | -0.04 | 0.10 | 0.01 |
| 5 | 0.14 | -0.03 | -0.08 | -0.08 | 0.16 | 0.02 |
| 6 | 0.23 | -0.04 | -0.08 | -0.08 | 0.25 | 0.03 |
| 7 | 0.25 | -0.04 | -0.09 | -0.09 | 0.27 | 0.03 |
| 8 | 0.30 | -0.06 | -0.11 | -0.11 | 0.32 | 0.05 |
| 9 | 0.45 | -0.06 | -0.14 | -0.14 | 0.48 | 0.05 |
| 10 | 0.66 | -0.06 | -0.33 | -0.33 | 0.74 | 0.01 |
| 11 | 0.88 | -0.08 | -0.51 | -0.51 | 1.02 | 0.03 |
| 12 | 0.99 | -0.08 | -0.60 | -0.60 | 1.16 | 0.02 |
| 13 | 1.07 | -0.10 | -0.70 | -0.70 | 1.10 | 0.00 |
| 14 | 1.08 | -0.10 | -0.74 | -0.74 | 1.31 | 0.03 |
| 15 | 1.17 | -0.10 | -0.85 | -0.86 | 1.45 | 0.00 |
| 16 | 1.46 | -0.12 | -0.90 | -0.90 | 1.72 | 0.03 |
| 17 | 1.50 | -0.12 | -1.00 | -1.01 | 1.81 | 0.00 |
| 18 | 1.62 | -0.12 | -1.04 | -1.05 | 1.93 | 0.01 |
| 19 | 1.62 | -0.12 | -1.04 | -1.05 | 1.93 | 0.01 |
| 20 | 1.87 | -0.14 | -1.20 | -1.21 | 2.23 | 0.01 |

[a] The color measurements for the first leather, as the standard.

The color rub fastnesses were rated as 3-4 scale (dry rub) and 2-3 scale (wet rub) for all the dyed leathers, while they reached to 4-5 scale (dry rub) and 3 scale (wet rub) after the leathers were finished as a common shoe upper coating formula. These rub fastnesses could reach the requirements for the shoe uppers.[9]

**SEM analysis**

The scanning electron photomicrographs of the grain surface were displayed in Fig. 5. The photographs showed the clear grain and the hair-follicle holes, which were analogous to the other 19 leathers (SEM images not shown). The results reveal that there was no adverse effect on the grain surface caused by dyeing.

The scanning electron photomicrographs of the cross-section were shown in Fig. 6. The photographs with ×80 magnification indicated the collagen fibers in the grain, corium and flesh layers of the leather. The photographs with ×1000 magnification displayed well separated and opened up fibers in the papillary and reticular layers as well as the particles attached on the surface of the fibers. The patterns for the collagen fibers in the other 19 leathers (SEM images not shown) were also the same as those in the uncolored crust, indicating that the fiber structure was not destroyed distinctly during the dyeing process.

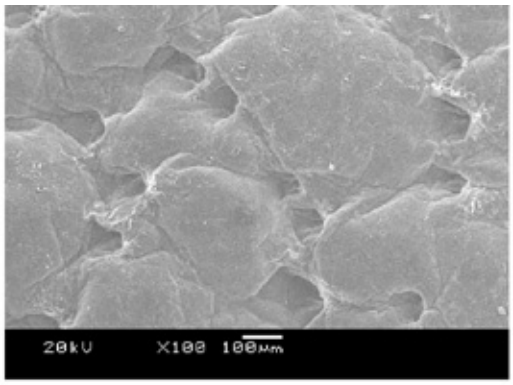
**XRD analysis**

As reported, the two peaks in the X-ray diagram of the collagen fiber in the hide/leather represented the side-chain distance peak (Peak 1) and the backbone reflection peak (Peak 2). [10-12] During the dyeing process, there was a loss of the parallelism of the triple helices, which was proved by the decrease in the intensity of Peak 2 in Fig. 7. However, there was little difference in the crystallinity of the collagen fibers, for Peak 1 just varied slightly.

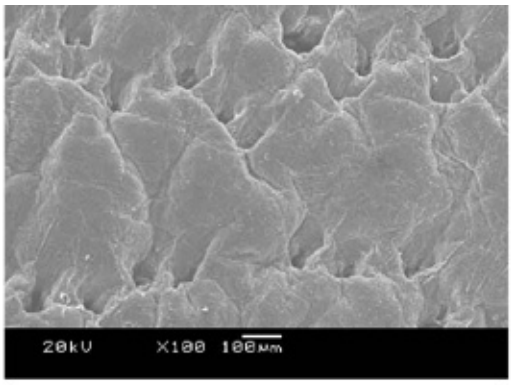
The X-ray patterns for the other 19 leathers (X-ray diagrams not shown) were analogous to the first one, and they all had a moderate decrease (lower than 20counts/s) in Peak 2 in comparison with the uncolored crust. The X-ray shape of the mixture of the dye and the uncolored crust (mass ratio as 2.6%) was the same as the dyed leathers, which demonstrated that the reduction in Peak 2 may be due to the X-ray absorption of the dyes and the collagen structure was not deteriorated as well.

**Discussion**

As for the new method, the leathers were proposed to be successively dyed one by one as shown in Fig. 1. Deep and saturated colors were obtained in 5 min with 2.6% dye based on the weight of the leathers. In addition, the dye solution was successfully recycled in lab scale, for the color difference for the first ten leathers was maintained in a small range($\Delta E$<1).

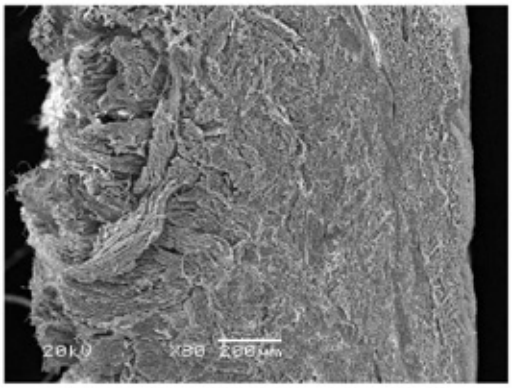



(a) Uncolored crust

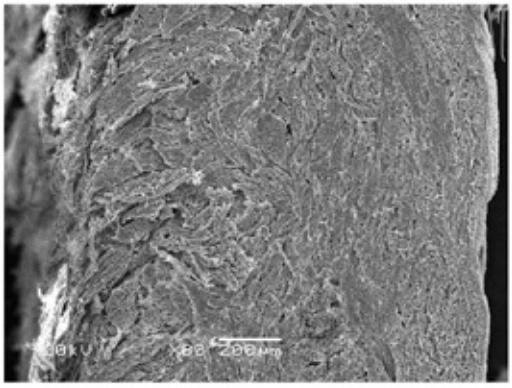



(b) The first dyed leather

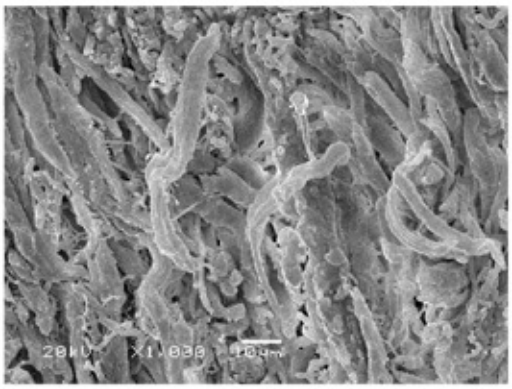
Fig. 5 SEM images of the grain surface of the leathers (×100)



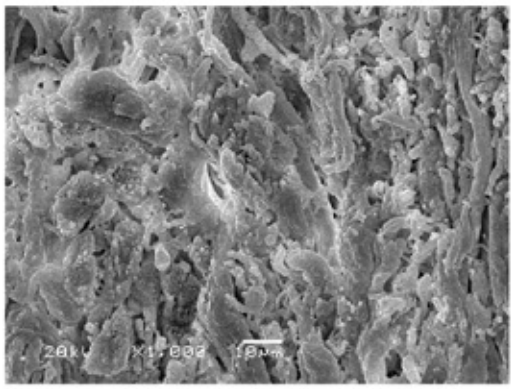
(a) Uncolored crust (×80)



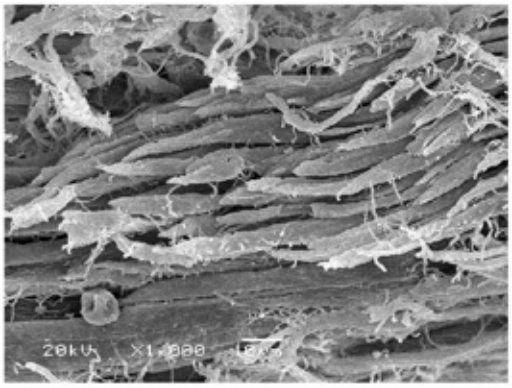
(b) The first dyed leather (×80)



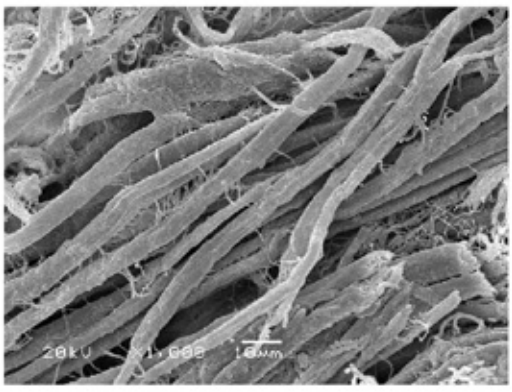
(c) Uncolored crust (papillary layer, ×1000)



(d) The first dyed leather (papillary layer, ×1000)



(e) Uncolored crust (reticular layer, ×1000)



(f) The first dyed leather (reticular layer, ×1000)

Fig. 6 SEM images of the cross-section of the leathers

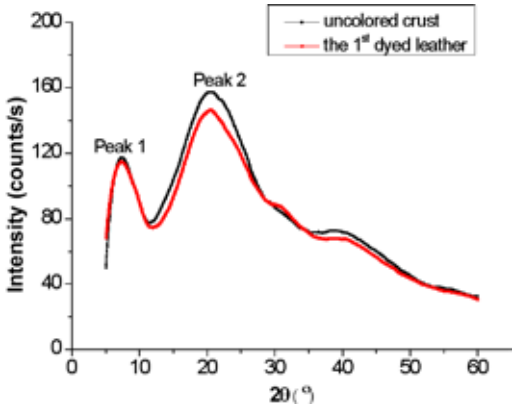


Fig. 7 X-ray diagrams of the leathers

Analogously to the results reported by V. Sivakumar, [3, 13, 14] the acoustic cavitation in Step II was still the primary driving force to the dye penetration. While the acoustic cavitation was accelerated by the low pressure in hollow spaces of the wrung leather from Step I, [15, 16] which further enhanced the dye penetration. Additionally, the dye fixation was strengthened by microwave radiation, similarly to the results published by D.G. Evans. [17]

There were no hazardous materials used in this process, and both the ultrasound and the microwave could be effectively shielded with the commercial available techniques, so this process will not pose harm to the workers. In conclusion, the presented leather dyeing is a potential automated, clean and safe choice.

## Conclusions

A clean leather dyeing was designed with wringing (8-10kg/cm$^2$), ultrasound (28kHz, 2.4W/cm$^2$) and microwave (2450MHz, 10W/L). Twenty leathers were successively colored with this new method. As for the first ten leathers, the overall color difference was lower than 1 unit when the dye solution was directly recycled. The color rub fastnesses could reach to 4-5 scale (dry rub) and 3 scale (wet rub) if the leathers were coated as a common shoe upper finishing formula. In addition, there was not any distinct damage in the fiber structure and the grain. These results confirmed the success of the new dyeing in lab scale.

## Acknowledgements

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