Rapid and effective rewetting of dried wet blue using a non-ionic oil

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1. Abstract

Rewetting of dried wet blue is usually a difficult work for tanners. In this study, a non-ionic oil (NIO) rewetting agent was prepared by mixing mineral oil and non-ionic surfactants in proper mass ratio. The rewetting effect of NIO for dried bovine wet blue was evaluated by physical and chemical determinations. The results showed that a rapid and effective rewetting of dried wet blue was obtained by using NIO as auxiliary agent, and the optimized conditions were of using 1% NIO and running in 400% water at 40 oC for 2 h. After rewetting, the dried wet blue was fully wetted back in terms of thickness change, moisture content and softness. As a result, the uptakes of the rewetted blue to dyestuffs and fatliquors were comparable with those of undried one.

Keywords: Rewetting, Wet blue, Non-ionic, Surfactant

1. Introduction

Rewetting is usually the first operation of post tanning processes. Its purpose is to make blue leather wet back to achieve proper moisture content and soft handle, so that the leather chemicals used in the following processes are able to smoothly penetrate and fix in leather. Hence, a good rewetting operation is the basis for making satisfactory leather. As we know, wet blue is used as raw material in some tanneries. After samming, transportation and storage for a period, excessive loss of moisture and adhesion of collagen fibres are likely to occur on wet blue. The dehydrated wet blue is very difficult to be fully rewetted in practical leather production, and the ineffective rewetting would result in quality defects of finished leather, such as inflexible handle, uneven distribution of dyestuff and decline of physical strengths.

In order to obtain a well effect of rewetting for dried wet blue, using surfactant, raising temperature and extending time in rewetting process are commonly employed. However, our experiments showed that the rewetting effect was still poor for some fairly dried wet blue even though rewetting at 60 oC for 48 h with a big offer of surfactant. Therefore, we focus on developing a rapid and effective rewetting measure for dried wet blue in this study. A type of non-ionic oil named NIO was prepared. The optimal rewetting conditions were investigated, and the rewetting effect of NIO was evaluated by a series of physical and chemical determinations, as well as the comparison with typical commercial rewetting agents.

2. Material and methods

2.1 Preparation of NIO

The non-ionic oil NIO was prepared as described below. 95 g white oil (10#) was used as oil component. 14 g alcohol ethoxylate (AEO3) and 6 g Span 80, used as lipophilic emulsifiers, were added and stirred at 90 oC for 90 min. Then 17.5 g alcohol ethoxylate (AEO25) and 7.5 g Tween 80, used as hydrophilic emulsifiers, were added and stirred at 90 oC for 90 min. Then 177 g deionized water was added in three times. 59 g deionized water was added each time and stirred at 80 oC for 90 min. After cooled to 45 oC, the product NIO was obtained.

2.2 Materials

Split and shaved bovine wet blues (thickness 1.4~1.5 mm) were used for trails. They were dried at 40 oC for 18 h in order to simulate the dehydrated wet blue. The moisture content of the dried wet blue was controlled to be around 15%. The chemicals used for leather processing were of commercial grade. The chemicals used for analysis were of analytical grade.

2.3 Optimization of rewetting process

using NIO

2.3.1 Optimization of NIO offer

The dried wet blues were rewetted using X% NIO (X=0, 0.5, 1, 1.5, 2, based on blue weight, similarly hereinafter) and 400% water at 30 oC for 3 h. Then the thickness, moisture content and dichloromethane matter soluble in leather were determined.

2.3.2 Optimization of temperature

The dried wet blues were rewetted using 1% NIO and 400% water for 3 h. The operating temperature was 20 oC, 30 oC, 40 oC and 50 oC, respectively. Then the thickness, moisture content and matter soluble in dichloromethane of leather were determined.

2.3.3 Optimization of duration

The dried wet blues were rewetted using 1% NIO and 400% water at 30 oC. The duration was 0.5 h, 1.5 h, 3 h, 5 h and 9 h, respectively. The testing items were the same as above.

2.3.4 Influence of NIO rewetting on softness of crust leather

All the rewetted blues above were processed together according to the post tanning procedures shown in Table 1. Then the softness of the crust leathers was measured.

2.4 Comparison of NIO with commercial auxiliary agents in rewetting

Four pieces of dried wet blues were rewetted using different rewetting agents (as listed in Table 2) in 400% water at 40 oC for 2 h. As control experiment, a piece of undried wet blue was treated in the same conditions without auxiliary agent. The thickness and moisture content of the rewetted wet blues were determined. Then the rewetted wet blues were processed together according to the post tanning procedures as shown in Table 1. Afterwards, the matter soluble in dichloromethane, softness, tensile strength, percentage elongation, tear load and color fastness of the crust leathers were determined. In addition, dyeing performance was evaluated by penetration of dyestuff in crust leather and exhaustion of dyestuff.

Table 1. Post tanning processes

Process	Chemicals	%	Running time	Remarks
Washing	Water	400	10 min	
Retanning	40 °C Water	300		
	Formic acid	0.2	20 min	
	Chrome powder	4	60 min	
	Sodium formate	1	20 min	
	$NaHCO_3$	0.5	60 min, overnight	Run 30 min, washing
Neutralization	35 °C Water	200		
	Sodium formate	1.5	30 min	
	$NaHCO_3$	1.2	100 min	
Washing×2	Water	400	10 min	
Dyeing/Fatliquoring	40 °C Water	150		
	Dyestuff mixture	2	30 min	
	Fatliquoring mixture	15	60 min	
	Formic acid	1.2	40 min	pH 3.6~3.8
Washing×3	Water	400	10 min	
Horsing up, air drying, conditioning and milling.				

Table 2. The rewetting agents used for rewetting

Sample	Chemical	Offer
E1	NIO	1%
E2	Commercial non-ionic surfactant	1%
E3	Commercial anionic sulphated fatty alcohol	1%
E4	Rewetting without auxiliary agent	-

2.5 Determination methods

2.5.1 Determination of basic properties of NIO

The basic properties of NIO were determined by using standard methods[1, 2]. It should be noted that the emulsifying capacity was determined by mixing 8.5 g NIO, 1.5 g fish liver oil and 90 ml deionized water in a 100 ml graduated cylinder with stopper. The change of the emulsion state was observed after standing for 8 h at 25~35 °C.

2.5.2 Determination of moisture content of leather

The moisture content of leather was determined according to standard method[3]. All the leather samples were sammed (pressure 1MPa, speed 3m/s) before measurement. Then they were weighed (W_1) and dried to constant weight (W_2) at 102 °C. The moisture content was calculated as:

moisture content = $(W_1 - W_2)/W_1 \cdot 100\%$ (Eq. 1)

2.5.3 Determination of dichloromethane soluble matter in leather

The dichloromethane soluble matter in leather was determined by using Soxhlet extraction following standard method[4].

2.5.4 Measurement of leather thickness

The thickness of leather was measured by GT313A1 Thickness Tester (Gotech Testing Machines Inc., China). The thickness value was an average of twenty testing positions in a leather sample.

2.5.5 Measurement of softness of leather

The softness of leather was measured by ST-300 Softness Tester (Gotech Testing Machines Inc., China). The softness value was an average of six testing positions in a leather sample.

2.5.6 Measurement of physical strengths of leather

The tensile strength, percentage elongation and tear load of leather were measured by HT-2102 Soc Control Material Testing Machine (Hung Ta Instrument Co., Ltd., China) following standard method[5, 6]. All the values were the average of along and across backbone determinations.

2.5.7 Measurement of color fastness of leather

The color fastness to cycles of to-and-fro rubbing (including dry and wet rubbing) was measured by using standard method[7]. The value was the average of along and across backbone determinations.

3. Results and discussion

3.1 Basic properties of NIO

The basic properties of NIO are shown in Table 3. It can be seen that NIO emulsion is resistant to electrolytes, acid and alkaline. However, the emulsifying capacity of NIO towards water-insoluble oil is relatively weak.

Table 3. The basic properties of NIO

Appearance	milky white emulsion with blue light
Moisture content	58%
pH (10%)	6.5
Emulsion (1: 9) stability	stable
Emulsion (1: 4) stability	stable
Emulsion (1: 2) stability	stable
Vegetable tannin (10%) stability	a little suspended matter
Chrome salt (10%) stability	stable
Acid (1mol/L HCl) stability	stable
Alkaline (1mol/L NH_4OH) stability	stable
Emulsifying capacity	upper oil slick approx. 3ml

3.2 Optimization of rewetting process using NIO

3.2.1 Optimization of NIO offer

The results in Table 4 indicate that the moisture content, thickness and dichloromethane extract of the rewetted wet blue were all remarkably increased when NIO offer was increased from 0 to 1%. Meanwhile, the softness of crust leather was also increased. Then they were nearly unchanged even though NIO offer was further increased. Therefore, the optimal offer of NIO is around 1%. The non-ionic surfactants in NIO would decrease the surface tension of wet blue so that the soakage and penetration of water in wet blue could be accelerated. The white oil in NIO possessed excellent permeability in leather[8], which can be proved by the increase of dichloromethane extracts content in rewetted wet blue. The introduction of mineral oil imparted softness and flexibility to the crust leathers and favored the rewetting. But when a higher offer of NIO was used, the excess mineral oil that penetrated into wet blue may hinder the adequate contact between leather and water, and thus lead to reduced moisture content of rewetted wet blue.

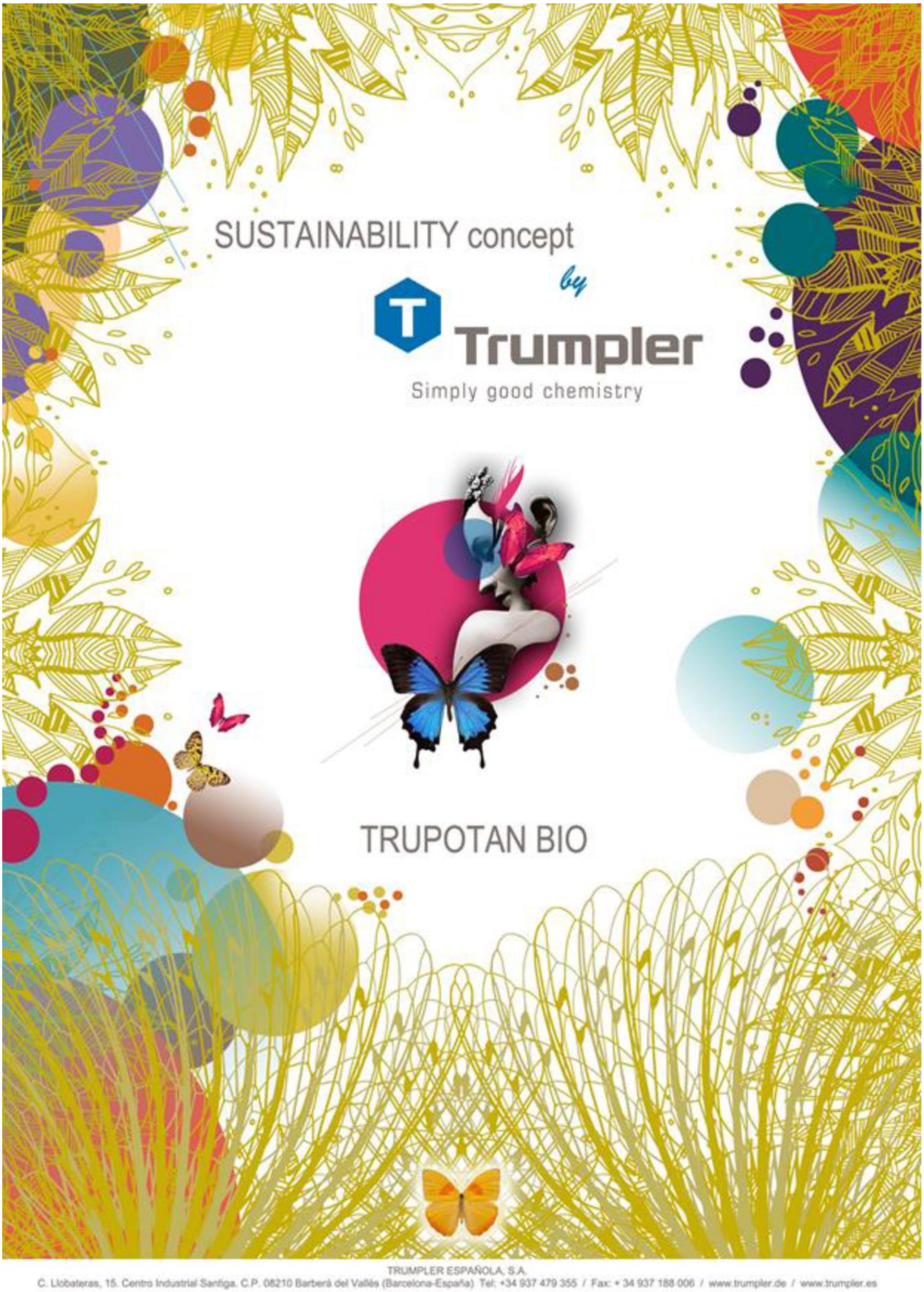
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Table 4. Effect of NIO offer on rewetting

NIO offer/ %	Thickness of rewetted blue/mm	Moisture content/ %	Matter soluble in dichloromethane/%	Softness
0	1.42	32.04	0.51	5.60
0.5	1.53	42.15	0.62	8.54
1	1.61	50.27	0.69	8.60
1.5	1.62	47.98	0.69	8.14
2	1.61	48.06	0.61	8.15

3.2.2 Optimization of temperature

Table 5 shows the effect of temperature on rewetting when 1% NIO was used. The thickness, moisture content and dichloromethane soluble matter of rewetted wet blue were all changed with the change of temperature. Obviously, the optimal temperature to achieve effective rewetting is around 40 °C.

Table 5. Effect of temperature on rewetting

Temperature/°C	Thickness of rewetted blue/mm	Moisture content/ %	Matter soluble in dichloromethane/ %	Softness
20	1.54	42.11	0.62	9.15
30	1.55	47.42	0.65	8.67
40	1.60	51.00	0.70	8.54
50	1.57	46.52	0.61	8.04

3.2.3 Optimization of duration

Table 6 shows the effect of duration on rewetting when 1% NIO was used. As rewetting time extended, water and oil could penetrate into fiber network of wet blue more fully, so as to make crust leather softer and more flexible. However, a long time of mechanical action by drumming may reduce the strength of leather.

Therefore, the duration of rewetting is suggested to be 2~3 h in consideration of the results in Table 6. We can see that the rewetting process of dried blue is remarkably accelerated by using NIO compared with conventional method (usually over 10 h).

Table 6. Effect of duration on rewetting

Duration/h	Thickness of rewetted blue/mm	Moisture content/ %	Matter soluble in dichloromethane/ %	Softness
0.5	1.44	38.42	0.59	8.32
1.5	1.56	46.21	0.62	8.81
3	1.60	50.82	0.62	8.76
5	1.58	51.04	0.61	8.61
9	1.60	50.86	0.63	8.68

3.3 Application of NIO on rewetting

Different rewetting agents were applied in rewetting of dried wet blue. The results are shown in Table 7. By using NIO as rewetting agent, the thickness and moisture content of rewetted blue, as well as the softness of crust leather, were similar to those of undried wet blue (control). This means that dried wet blue could be easily wetted back by NIO-assisted rewetting. On the contrary, the rewetting effect of non-ionic surfactant (E2) or sulfated fatty alcohol (E3) was obviously weaker than that of NIO, although they both resulted in improved rewetting effect compared with E4 (rewetted without auxiliary). It is said that rewetting extent of wet blue will influence the uptake of subsequent chemicals, especially dyestuffs and fatliquors. Table 8 convincingly demonstrates that the well rewetted blues (E1 and Control) performed much better than others (E2, E3 and E4) in dyestuff penetration and absorption. Meanwhile, the contents of dichloromethane soluble matter in crust leathers (shown in Table 7) indicated that the uptake of fatliquors for E1 surpassed all the other samples. This was attributed to the high efficiency of rewetting by NIO. In terms of physical strengths of leathers, as shown in Table 9, E1 was comparable with control. The other samples exhibited higher tensile strength but lower percentage elongation and tear load than those of E1 and control. These may be explained by the fact that the collagen fibers of the well rewetted and fatliquored leathers were well dispersed and more flexible.

The mechanism of rewetting by NIO is suggested in Figure 1. There may be three reasons about how it works. At first, the main components of NIO are stable against electrolytes since they are non-ionic substances. Therefore, they are able to quickly penetrate into leather fiber network. Secondly, the non-ionic surfactants in NIO can reduce the surface tension of leather and improve soakage of leather in water. The last reason is that the mineral oil included in NIO exhibits good permeability in leather. It is absorbed on the surface of leather fibers and lubricates the fiber networks. So the leather is easier to be softened and rewetted during drumming. In summary, NIO is a type of multifunctional auxiliary agent for rewetting of dried wet blue and it works more effective compared with other single component agents.

Table 7. Evaluation of rewetting by using different agents

Sample	Thickness of rewetted blue/mm	Moisture content/ %	Matter soluble in dichloro methane/ %	Softness
E1	1.61	51.21	4.34	8.89
E2	1.49	35.15	2.85	6.14
E3	1.55	39.42	3.28	7.12
E4	1.40	30.24	1.24	4.50
Control*	1.60	49.87	3.89	8.85

* Undried blue

Table 8. Dyeing performance of leathers rewetted by different methods

Sample	Appearance of dyeing spent liquor	Extent of dyestuff penetration/ %	Color fastness	
			Dry rubbing	Wet rubbing
E1	Clear, light red	Complete	3.5	3
E2	Turbid, black	1/4	3.5	3
E3	Little turbid, grey	2/3	3.5	3
E4	Turbid, black	1/8	3.5	2.5
Control*	Clear, light red	Complete	3.5	3

* Undried blue

Table 9. Physical strengths of crust leathers

Sample	Tensile strength/(N/mm)	% elongation at 10 N/%	Tear load/N
E1	13.98	30.55	41.51
E2	24.61	18.40	28.72
E3	20.00	24.54	35.04
E4	26.78	10.48	15.87
Control*	14.05	26.38	37.80

* Undried blue

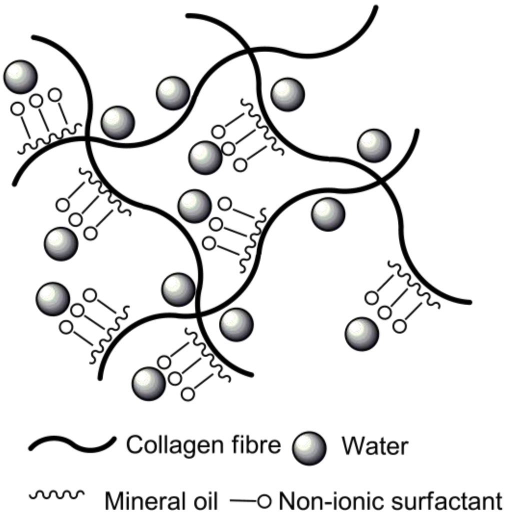

Figure 1. Rewetting process using NIO

4. Conclusions

An effective and rapid rewetting method has been established by using a non-ionic oil (NIO) as auxiliary agent. NIO possesses not only the surface activity contributed by non-ionic surfactants, but also the lubricity contributed by mineral oil. Moreover, it has excellent permeability in leather. These properties of NIO achieve satisfactory rewetting rate for dried blue. The good state of rewetted blue favors the uptake of following chemicals.

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