Preparation and Storage of Wet-blues in Pigskin Leather Manufacture

Tomoyoshi KUBO and Yasuhiro ISHII

Scleroprotein and Leather Research Institute, Faculty of
Agriculture, Tokyo Noko University, Fuchu-shi 183

(Received September 11, 1981)

Abstract Wet-blue pigskins having various chrome contents and pH values were prepared and stored for 3 months at 20°C or 37°C. Soft-type chrome leathers were prepared from these wet-blue stocks, and the effects of conditions of wet-blue preparation and storage on the quality of finished leathers were evaluated. 1) The chemical composition of wet-blue stocks did not change significantly during storage. 2) Although the differences in chrome content among wet-blue stocks were decreased by the use of chrome tanning agents in their retanning process, they did not disappear completely. 3) The effects of storage conditions of wet-blue stocks on the chemical composition of finished leathers were not clearly demonstrated. 4) The stiffness, elongation at break, and tongue tear strength of finished leathers decreased with increasing chrome content of wet-blue stocks. 5) The stiffness of finished leathers increased with increasing pH values of wet-blue stocks, but did not change with their storage conditions. Thus, the chemical and mechanical properties of finished pigskin leathers were shown to be influenced mainly by conditions of wet-blue preparation rather than their storage conditions.

Jpn. J. Zootech. Sci., 53 (3): 209-216, 1982

Recently the regulation of effluents from factories has become more and more severe from a view point of environmental protection. Therefore, in pigskin leather manufacture, mass production of wet-blue stocks (wet chrome tanned leathers) in a cooperated factory is thought to be a means of solving this serious problem, because highly pollutional beamhouse operations are able to omit in each tannery. When we consider wet-blues as intermediate raw stocks, their storage stability seems to be one of the most important points. Therefore, the past several studies had been carried out on the stability of wet-blue stocks during storage. The effects of conditions of wet-blue preparation (amount of chrome offered and pH values) and their storage (period and temperature of storage) on the mechanical properties^{1,2)}, color changes³⁾, and dyeing characteristics⁴⁾ of the resultant leathers were investigated, and the use of 2-(thiocyanomethylthio) benzothiazole was recommended as a fungicide for wet-blue stocks⁵⁾.

However, in order to practically evaluate the effects of the conditions of wet-blue preparation and their storage, the suitability of wet-blue stocks to the processings that follow, such as retanning, dyeing and fatliquoring, and also the effects on the chemical and physical properties of finished leathers must be evaluated as a whole. Because the stiffness is thought to be one of the most important properties of soft-type pigskin leathers, the effects of conditions of preparation and storage of wet-blue stocks on this property of the resultant pigskin leathers were investigated in this study.

Materials and Methods

Pigskins used

Wet-salted pigskins (4.1 kg/piece) collected in the North-East District of Japan were used in this study, and seven skins were used for each lot.

Preparation of wet-blues and chrome leathers

The method of wet-blue preparation was almost the same as described in the previous paper⁶⁾, but the condition of chrome tanning was slightly modified as follows: 8% of chrome tanning agent, Neochrome (Nippon Chemical Industrial Co., LTD., sulfite-reduced chrome agent, 26% Cr₂O₃, 33% basicity) was used on pelt weight basis, and pH 3.0 was adopted as standard. The conditions of chrome tanning of pigskins were varied according to the experimental design described in next section. Soft-type chrome leathers are produced from these wet-blues under the same conditions as described in the previous paper⁶⁾. Namely the same conditions were adopted for neutralization, retanning with highly basic chrome tanning agent and glutaraldehyde, dyeing, and fatliquoring processes.

Experimental design

Pigskins were processed in a collective lot until pickling, and then these skins were divided into 4 lots, and, according to experimental design shown in Table 1,

Table 1. Design of experiments

No. of experiment	Preparation of wet-blue		Storage	
	chrome agents used in tanning	pH	period	temperature
1	4%(C ₁)	3.0(P ₁)	no storage (S ₀)	
2	4%(C ₁)	3.8(P ₂)		
3	8%(C ₂)	3.0(P ₁)		
4	8%(C ₂)	3.8(P ₂)		
5	4%(C ₁)	3.0(P ₁)	3 months	20°C(S ₁)
6	4%(C ₁)	3.0(P ₁)		37°C(S ₂)
7	4%(C ₁)	3.8(P ₂)		20°C(S ₁)
8	4%(C ₁)	3.8(P ₂)		37°C(S ₂)
9	8%(C ₂)	3.0(P ₁)		20°C(S ₁)
10	8%(C ₂)	3.0(P ₁)		37°C(S ₂)
11	8%(C ₂)	3.8(P ₂)		20°C(S ₁)
12	8%(C ₂)	3.8(P ₂)		37°C(S ₂)

4 kinds of wet blue were prepared with varying amount of chrome offered and pH values. Each lot of wet-blues was then divided into 3 small lots, and they were stored under three different conditions: that is, they were not stored, stored at low temperature (20°C), and at high temperature (37°C) for 3 month. The factors and their levels in this experiment are as follows:

Preparation and Storage of Pigskin Wet-blues

C: Chrome offered

C₁: lower level; 4% chrome agent on pelt weight.

C₂: higher level; 8% chrome agent on pelt weight.

P: pH values

P₁: lower level; after chrome tanning, the wet-blues were rinsed in a new float of water without the addition of sodium bicarbonate.

P₂: higher level; after chrome tanning at pH 3, the pH of the wet-blues was adjusted at pH 3.8 in a new float of water by the addition of sodium bicarbonate.

S: Storage condition

Wet-blues prepared as described above were drummed with 0.1% aqueous solutions of fungicide (Coverside ND, Takeda Chemical Industries LTD.) for 30 min., and then packed in polyethylene bags. These wet-blues were stored under the following condition:

S₀: no storage; after the fungicide treatment, they were immediately put into processings for chrome leathers.

S₁: lower storage level; they were stored for 3 months at 20°C, and then put into subsequent processings for chrome leathers.

S₂: higher storage level; they were stored for 3 months at 37°C, and then put into subsequent processings for chrome leathers.

Chemical analysis of wet-blue stocks

Samples of 5 to 8 cm wide were taken from tail connecting portions of wet-blues before and after storage, and were dehydrated with acetone. These samples were analysed for pH and the contents of moisture, hide substance, fat, ash, and chrome according to the methods of JIS K 6550⁷⁾.

Chemical analysis and physical tests of finished chrome leathers

The chemical analysis of finished pigskin leathers was carried out as described in the previous paper^{6,7)}. Namely, pH and the contents of moisture, hide substance, fat, ash, and chrome were determined by the methods of JIS K 6550⁷⁾. Their tensile strength, elongation at break and tongue tear strength were also measured by the methods of JIS K 6550⁷⁾. The stiffness of these leathers were measured by the Gurley method described in the previous paper^{6,8)} and by the slide method according to JIS L 1079⁸⁾.

Results and Discussion

Chemical composition of wet-blue stocks

The results of chemical analysis of 12 kinds of wet-blue stocks prepared under various conditions are shown in Table 2.

The relationship between the chrome contents and pH values of wet-blues and their preparation condition is shown in Fig. 1. Although the found values of pH were, in general, lower than the levels designed in the experiments, the differences between levels of factor were clear both in respect to chrome content and pH value.

Table 2. Chemical analyses of pigskin wet-blues before and after storage described in Table 1.

No. of experiment	Moisture %	Hide substance* %	Fat* %	Ash* %	Chrome* Cr ₂ O ₃ %	pH
1	18.5	88.9	0.5	3.3	3.1	2.6
2	16.5	88.9	0.4	3.4	3.0	2.9
3	15.2	87.4	0.4	5.8	4.9	2.7
4	19.5	86.4	0.4	6.0	5.2	3.0
5	14.0	88.9	0.2	3.6	3.1	2.6
6	13.2	89.0	0.3	3.6	3.3	2.5
7	15.3	89.1	0.3	3.5	3.0	2.8
8	16.1	88.2	0.2	3.9	3.3	2.8
9	14.7	83.1	0.1	6.1	5.2	2.7
10	14.8	84.6	0.2	6.0	5.1	2.6
11	13.9	84.3	0.1	6.0	5.1	2.9
12	15.6	85.8	0.1	6.1	5.3	3.0

* on the dry weight basis

The preparation conditions are shown in Table 1.

Fig. 1. Relationships between the actual value of chrome content and pH of wet-blue and the designed level of the factors.

There was no difference, however, between the chemical properties of wet-blues subjected to a range of storage conditions, except that the pH values were slightly decreased when wet-blues having lower pH values were stored at higher temperature.

Chemical composition of finished leathers

The chemical compositions of finished chrome leathers prepared from 12 kinds of pigskin wet-blues are shown in Table 3.

The leathers prepared from unstored wet-blues (Exp. No. 1~4) had relatively lower pH values. This seems to be due to the unexpected operational variation in neutralization, because pH values of wet-blues did not change by storage. Since the mechanical properties of the leathers, especially their stiffness are shown to vary with changes of pH values at neutralization⁹⁾, this fact must be taken into consideration

Preparation and Storage of Pigskin Wet-blues

Table 3. Chemical analyses of leathers made from various pigskin wet-blues described in Table 1.

No. of experiment	Moisture %	Hide substance* %	Fat* %	Ash* %	Chrome* Cr ₂ O ₃ %	pH
1	16.6	83.3	3.4	5.2	4.6	3.4
2	16.4	79.2	4.3	5.1	4.4	3.4
3	16.6	70.8	4.6	6.6	5.1	3.3
4	17.6	77.7	3.8	6.5	5.8	3.3
5	13.1	71.1	4.3	5.0	4.6	3.8
6	9.6	69.6	5.1	5.3	4.8	3.8
7	10.8	70.3	3.7	4.9	4.5	3.9
8	12.6	65.9	4.4	5.1	4.6	3.9
9	13.8	69.7	3.9	6.6	6.1	3.7
10	13.6	70.9	3.6	6.4	5.9	3.8
11	14.1	70.4	3.2	6.7	5.9	3.7
12	11.8	69.2	4.2	6.9	6.0	3.7

* on the dry weight basis

when we evaluate the differences in the properties of wet-blues stored under different conditions.

The comparison between chrome contents of wet-blues and finished leathers showed that the chrome content of finished leathers increased by 1.3 to 1.5% from wet-blues of lower chrome level (Exp. No. 1, 2, 5~8), and 0.3 to 0.9% from those of higher chrome level (Exp. No. 3, 4, 9~12). The results indicate that the rate of chrome adsorption in retanning process is higher with wet-blues of lower chrome level than with those of higher chrome level. However, the differences of chrome content at the stage of wet-blues were not able to completely remove by chrome retanning. Therefore, the differences in chrome content of wet-blues may affect the properties of finished leathers, even when the retanning was carried out with a chrome tanning agent.

Mechanical properties of finished leathers

The mechanical properties of finished leathers made from 12 kinds of wet-blues are shown in Table 4.

The stiffness of leathers made from unstored wet-blues (Exp. No. 1~4) showed always higher values than that from wet-blues for 3 months (Exp. No. 5~12). The cause of this result seems to be mainly due to lower pH values in neutralization process for the leathers from unstored wet-blue stocks as previously described. Therefore, statistical analyses were separately carried out for the results on the leathers made from unstored wet-blues (Exp. No. 1~4), and on the leathers from stored wet-blues (Exp. No. 5~12).

The elongation at break and tongue tear strength of the leathers made from unstored wet-blues were lower under the higher level (Exp. No. 3, 4) than under the lower level (Exp. No. 1, 2) of chrome application in wet-blue preparation. The tensile

Table 4. Mechanical properties of leathers made from various pigskin wet-blues described in Table 1.

No. of experiment	Tensile strength kg/mm ²			Elongation at break %	Tongue tear strength kg/mm			Stiffness by slide method						Stiffness by Gurley method 100 mg					
								grain			side-out			grain			side-out		
	$\bar{X}$	SD*		$\bar{X}$	SD*		$\bar{X}$	$\bar{X}$	SD*	$\bar{X}$	SD*	SD*		$\bar{X}$	SD*	$\bar{X}$	SD*	SD*	
1	1.5	0.4		51	9		1.5	17.0	5.3	16.9	5.8	233	51	233	51	233	74		
2	1.5	0.4		49	9		1.7	17.9	5.3	16.2	5.0	264	51	224	51	224	43		
3	1.6	0.4		46	8		1.5	19.0	8.1	15.2	4.9	254	73	214	73	214	37		
4	1.3	0.2		46	8		1.4	18.6	6.1	16.0	4.2	285	62	217	62	217	54		
5	1.5	0.2		48	8		1.8	12.0	4.8	10.4	3.7	194	39	179	39	179	20		
6	1.4	0.3		52	9		1.5	10.7	3.1	11.7	4.1	180	18	188	18	188	17		
7	1.7	0.4		49	8		1.6	12.5	4.2	12.6	3.8	200	39	198	39	198	24		
8	1.6	0.3		50	8		1.7	10.1	3.4	11.4	4.3	189	29	185	29	185	14		
9	1.5	0.4		47	6		1.7	8.6	1.9	9.5	3.2	162	15	170	15	170	10		
10	1.6	0.5		49	5		1.6	8.9	2.2	10.0	2.4	171	9	170	9	170	12		
11	1.5	0.6		46	7		1.6	9.7	3.5	10.2	5.2	187	38	172	38	172	34		
12	1.6	0.2		49	8		1.6	11.7	4.1	11.7	2.7	185	26	186	26	186	11		

* SD; standard deviation.

Preparation and Storage of Pigskin Wet-blues

strength decreased and the stiffness by the Gurley method increased with an increase of pH level in wet-blue preparation. As for the tensile strength of finished leathers, a significant interaction between the factors of the chrome content and pH of wet-blues was found. That is, the effect of pH values of wet-blues on the tensile strength of leathers was depressed in the case of the lower level of chrome offered.

Analysis of the effects of various factors on the mechanical properties of finished leathers from wet-blues stored for 3 months showed the following tendency. The stiffness measured by both method was lower under the higher level (Exp. No. 9~12) than under the lower level (Exp. No. 5~8) of chrome offered in wet-blue preparation. The stiffness measured by the Gurley method was higher at the higher level of pH (Exp. No. 7, 8, 11, 12) than at the lower level (Exp. No. 5, 6, 9, 10) in wet-blue preparation. As to the effect of storage temperature, there was no definite tendency except that the effect of the differences in chrome content of wet-blues decreased at higher temperature level of storage (Exp. No. 6, 8, 10, 12).

The results on the effects of various factors found to be statistically significant are summarised in Table 5.

Table 5. Factorial effects of the preparation and storage condition of wet-blues on the mechanical properties of pigskin leathers

Factors	Tensile strength	Elongation at break	Tongue tear strength	Stiffness by slide method	Stiffness by Gurley method
No storage					
high chrome (C ₂)	decrease	decrease	decrease		increase
high pH (P ₂)	decrease				
low chrome (C ₁)	depress pH effect				
Storage					
high chrome (C ₂)				decrease	decrease
high temperature (S ₂)				depress effect of chrome	
high pH (P ₂)					increase
high pH × high temperature (P ₂) × (S ₂)					depress effect of chrome
low chrome × high temperature (C ₁) × (S ₂)					depress effect of pH

In the case of the leathers made from unstored wet-blues, the elongation at break and tongue tear strength of finished leathers decreased when chrome content of wet-blues was higher. It is suggested that the amount of chrome combined by pigskin in wet-blue preparation has shown to have a greater influence on the mechanical properties of resultant leathers than that combined at the retanning stage. The tensile strength of the leathers decreased and their stiffness increased with increasing pH values of wet-blues. This result indicates that the influence of differences in pH values at the stage of wet-blue preparation can not be removed by the adjustment of conditions in such

processes, as neutralization, retanning, and fatliquoring. This fact must be considered as one of the most important points in the evaluation of quality of wet-blues.

As to the resultant leathers from stored wet-blues, their stiffness decreased when chrome content of wet-blues was higher, and increased when pH of wet-blues was higher. Thus, the effect of chrome content in stored wet-blues was different from that of unstored wet-blues. It is not clear whether these differences resulted from the variation in storage conditions of wet-blues or in pH values of neutralization as previously described. However, the effect of pH of wet-blues showed the same trend in spite of great differences in their storage conditions. In other words it means that the effect of pH values of wet-blues does not disappear by storage, and so the adjustment of pH values of wet-blues is an important point of control for soft-type leather manufacture.

Even when storage temperature of wet-blues was high, the elongation at break and tensile properties, and the chemical compositions of finished leathers did not change although the effect of chrome content of wet-blues on the stiffness of finished leathers was slightly depressed. Thus, the wet-blues prepared seem not to deteriorate during storage.

In conclusion it can be said that the condition of wet-blue preparation has a greater influence on the quality of finished leathers than their storage condition in soft-type pigskin leather manufacture.

References

- 1) RUSSELL, A. E. and D. R. COOPER, J. Soc. Leather Tech. Chem., **59**: 41-48. 1975.
- 2) Rawstock Committee Meeting, J. Am. Leather Chem. Ass. **69**: 462-503. 1974.
- 3) BARLOW, J. R., J. Soc. Leather Tech. Chem., **60**: 156-162. 1976.
- 4) ARNOLDI, H. W., Das Leder, **23**: 191-196. 1972.
- 5) GALLAWAY, A. C. and D. R. COOPER, J. Soc. Leather Tech. Chem., **58**: 67-71. 1974.
- 6) KUBO, T. and Y. ISHII, Jpn. J. Zootech. Sci., **52**: 308-313. 1981.
- 7) Japanese Industrial Standards Committee, Japanese Industrial Standards-Testing methods for leathers-JIS K 6550. Japanese Standards Association. Tokyo. 1974.
- 8) Japanese Industrial Standards Committee, Japanese Industrial Standards-Testing methods for chemical fibre fabric-JIS L 1079. Japanese Standards Association. Tokyo. 1969.
- 9) SHIRAI, K. and H. OKAMURA, HIKAKU-KAGAKU, **18**: 203-215. 1973.

豚革製造におけるウェットブルーの調製と保存

久保 知義・石井 泰博

東京農工大学農学部, 府中市 183

クロム含有量と pH の異なる豚皮ウェットブルーを調製し, これを 20°C および 37°C で 3 カ月間貯蔵後, ソフトクロム革に仕上げ, ウェットブルーの調製条件と貯蔵条件の影響を製品革の性状から検討した. 1) ウェットブルーの化学分析値に対する貯蔵の影響は認められなかった. 2) ウェットブルーのクロム含有量の差異は, 再鞣においてクロム鞣剤を使用することにより縮少するが, 完全には消失しない. 3) 仕上り革の化学分析値に及ぼすウ

ェットブルーの貯蔵の影響は明らかでない. 4) ウェットブルーのクロム量が多いと仕上り革の剛軟度, 伸び, 引裂強さなどが低い. 5) ウェットブルーの pH が高いと仕上り革の剛軟度は上昇し, この傾向はウェットブルーの貯蔵によって影響を受けなかった. これらのことから, ウェットブルーからの製出革の性質は, ウェットブルーの貯蔵よりも調製条件により大きな影響を受けることが示唆された. 日畜会報, **53** (3): 209-216, 1982