FE(III)-CR(III) COMBINATION TANNAGE FOR THE PRODUCTION OF SOFT LEATHERS

by
R. KARTHIKEYAN, R. RAMESH, R. USHA, B. RAMANAIAH AND N.K. CHANDRA BABU*
Tannery Division, Central Leather Research Institute,
ADYAR,CHENNAI 600 020, INDIA

ABSTRACT

There has been a constant search for safer tanning methods for use in leather processing. Due to their similarity in aqueous chemistry, Fe(III) salts are often considered potential alternatives for Cr(III) tanning salts. But Fe(III) tanning methods have certain limitations, which have come in the way of their use in the leather industry. One of the main problems is that iron tanned leathers are less amenable to the production of soft leathers such as garment and gloving leather. In the present study, an attempt has been made to overcome the problems associated with iron tanning for the production of goat suede and sheep nappa garment leathers. A judicious combination with chromium has been attempted and a tanning system that affords good quality leathers at the same time helps in restricting the amount of chromium and iron in the spent liquor to less than 100 mg/L has been standardized. The scanning electron microscopic analysis was carried out on the tanned leathers to study the effect of the new system on the structural characteristics of leathers produced. The strength properties and the color characteristics of the tanned leathers were also analyzed and reported.

RESUMEN

Ha habido una búsqueda constante de métodos de curtición más seguros para su uso en el proceso de cuero. Debido a su semejanza en la química acuosa, las sales de Fe(III) a menudo se consideran como una alternativa potencial a las sales curtientes de Cr(III). Pero los métodos curtientes con Fe(III) tienen ciertas limitaciones, que han venido en la manera que se usa en la industria de cuero. Uno de los problemas principales es que los cueros curtidos con hierro son menos apropiados en la producción de cueros suaves tales como vestimenta y cuero de guantería. En el presente estudio, se ha hecho un intento de superar los problemas asociados al curtido al hierro para la producción de cueros de gamuza de cabra y nappa ovina para vestimenta. Se ha intentado una combinación muy sensata con cromo y se ha estandarizado un sistema curtiente que permite obtener cueros de buena calidad y a la vez restringe la cantidad de cromo y hierro en el licor residual a menos de 100 mg/l. El análisis mediante microscopía electrónica de barrido fue realizado en los cueros curtidos para estudiar el efecto del nuevo sistema en las características estructurales de los cueros producidos. Las propiedades de las resistencias y características de color de los cueros curtidos también fueron analizadas y reportadas.

INTRODUCTION

Chrome tanning occupies an outstanding position in the leather industry[1] and today more than 90% of the tanning processes use chromium tanning salts due to the versatility of the tanning system to produce different types of leather with required properties for different end uses[2]. The ability of Cr(III) to form poly-nuclear complexes of intermediate size and stability[3,4] confers such a unique tanning potential, which results in leather with high degree of stability and shrinkage temperature (T_s). Cationic nature of the tanned leather imparts pronounced capacity for rich dyeing and affinity for fatliquors to produce leather with excellent softness. But this tanning system is coming under increased pressure from the green groups all over the world on account of pollution and toxicological considerations[5-7]. Manganese if present in soil and under specific conditions can lead to oxidation of Cr(III) to Cr(VI), which can affect plant growth and development[8-11]. Though there are several chrome management options advocated to minimize the pollution, development and adoption of alternative tanning system based on safer materials may bring about a permanent solution to the problem[12,13]. Fe(III) is often considered a potential alternative on account of its similar aqueous chemistry. Moreover as iron is one of the most abundantly available minerals, it is expected that majority of flora and fauna may tolerate higher amounts of Fe(III) than Cr(III). However, though the development of iron tanning is as old as chromium, it has not yet gained foothold in the leather industry due to several disadvantages such as instability of its basic solution, deterioration of leather due to high acidity, lower hydro-thermal stability, darker shade, *etc*[14]. Moreover, to produce a satisfactory commercial type of leather, a single iron tanning would not satisfy all the requirements of soft leathers.

* Corresponding Author - email: tanneryclri@yahoo.com
Manuscript received June 20, 2006, accepted for publication April 18, 2007

Earlier, there have been attempts made to standardize combination tanning methods based on Fe(III) and Cr(III). These methods involved the two bath approach in which Fe(II) is used for the reduction of Cr(VI) resulting in fixation of both Cr(III) and Fe(III)[15,16]. In the present study, a combination system using Fe(III) and Cr(III) has been employed for the production of soft leathers. In the initial phase of tanning, the pickled pelts were treated with iron sulphate and the leathers were shaved to avoid chromium in the shaving waste. The shaved iron tanned leathers were treated with optimized amount of basic chromium sulfate so that good quality soft leathers can be produced and at the same time, the chromium discharged in the spent liquor does not exceed 100 mg/L level.

EXPERIMENTAL

Standardization of Iron -Chromium Combination Tannage

Twenty wet salted skins (10 goat skins & 10 sheep skins) were taken and soaked and limed using conventional technique. After fleshing they were cut into two halves and numbered as 1L, 2L---- 10L, and 1R, 2R----10R. Skins 5,6,7,8 were used as such without cutting into two halves. The ferric sulphate used in the tanning process was of laboratory grade. The iron content in the ferric sulphate salt used was determined by a standard spectrophotometric analytical procedure[17]. It contained 18.27% of iron determined as Fe. Goat and sheepskins were separately tanned using sodium tartrate (Fe to tartrate molar ratio of 1: 0.15) and sodium citrate (Fe to citrate molar ratio: 1: 0.22) as chelating masking agents. The process details are given in Appendix 1. The process was repeated four more times using 10 goat and 10 sheep skins each time. After tanning, the iron present in the spent tan liquor (goat skin process) was determined by the standard procedure[17]. Goat skins were then shaved on the grain side to 0.8-0.9 mm thickness and sheepskins were shaved on the flesh side to 0.6-0.7 mm thickness. The shaved leathers (both goat and sheep leather) were treated with 33% basic chromium

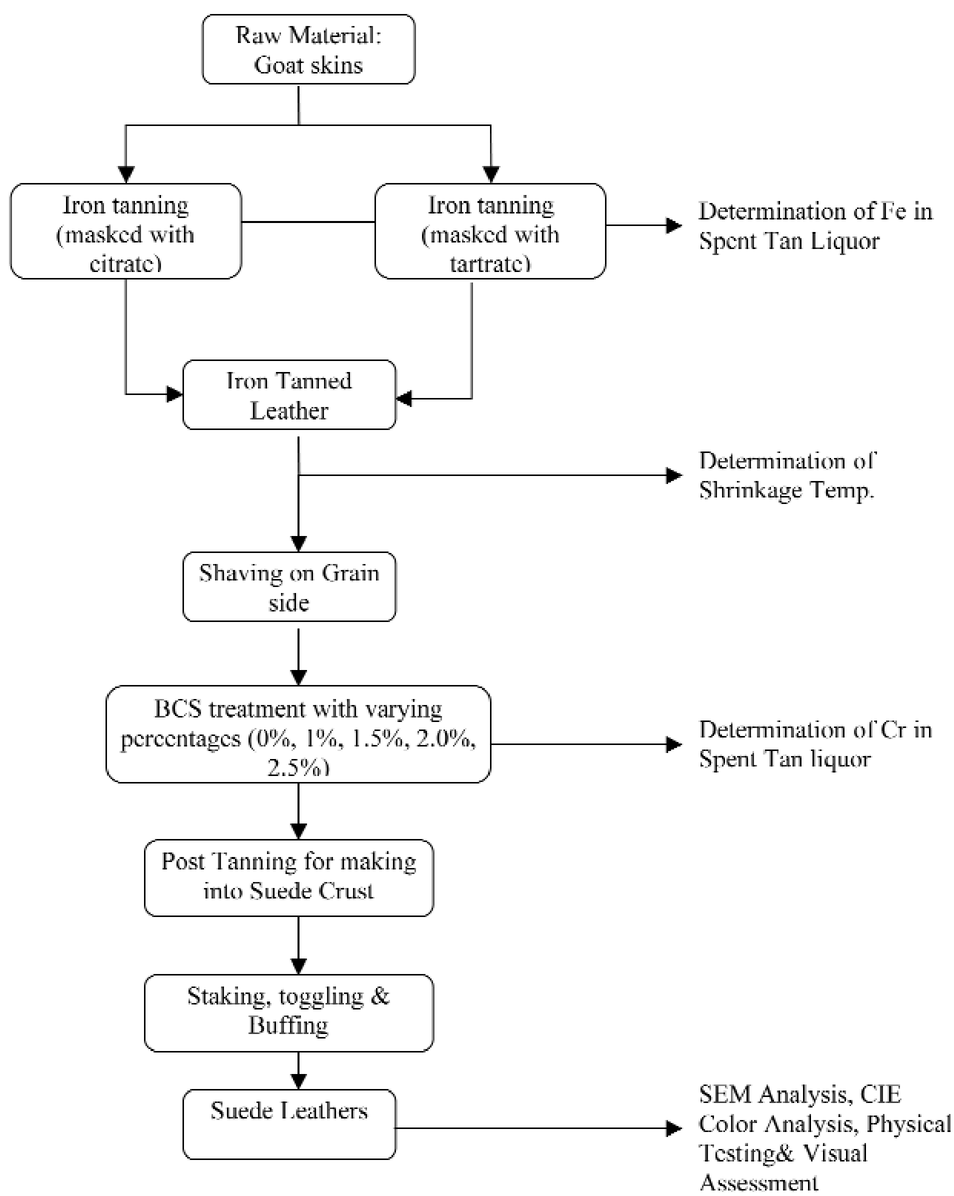

Figure 1: Flow Chart for experiments on goat skins

sulphate (BCS) containing 23% Cr_2O_3 according to the procedure given in Appendix 2. The shrinkage temperature (T_s) of iron tanned goat leathers, before and after treatment of chromium was found using a Theis shrinkage tester[18]. The design of the experiments carried out on the goat and sheep skins is illustrated in Figure 1 and 2 respectively.

Determination of Chromium in Spent Tan Liquors

The chromium content in the spent liquor obtained from the goat skin process in each of the above mentioned tanning experiments was determined by atomic absorption spectrophotometer. From the values, percent exhaustion of chromium has been estimated.

Post Tanning Treatment

After chromium treatment, goat skins were made into suede garment leathers and the sheepskins into grain garment leathers. The post tanning recipes used are given in Appendix 3 and 4 respectively.

Scanning Electron Microscopic (SEM) Analysis

In order to study the effect of the combination tanning on the structural characteristics of the leathers produced, scanning electron microphotographs of iron tanned and iron-chromium combination tanned leathers (both goat and sheep leather masked with citrate and tartrate) were compared. The samples measuring 5mm x 2mm were cut from the official butt portion[19]. The samples were mounted vertically on aluminum stubs using an adhesive. These were then coated with gold using an Edwards E-306 sputter coater. Thickness of coating was adjusted to minimum level required to prevent charging. The stubs were introduced into the specimen chamber of a FEI-Quanta 200 scanning electron microscope. The stubs mounted on the stage could be tilted, rotated and moved to the desired position and orientation. The micrographs for the cross-section were obtained by operating the microscope at higher voltage.

Physical Testing and Visual Assessment

The samples for physical testing were cut from the iron and

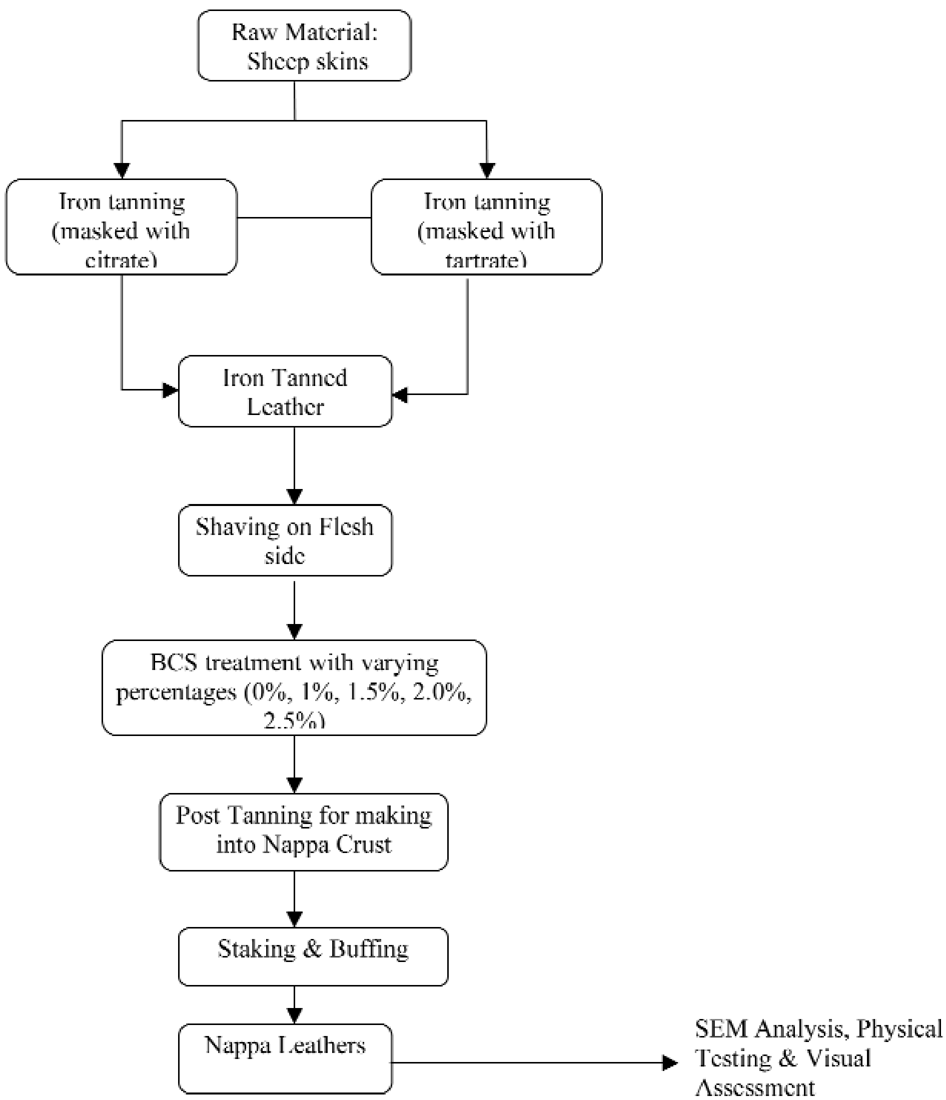

Figure 2: Flow Chart for experiments on sheep skins

TABLE I
Percentage Exhaustion of Fe and T_S for Iron Tanning (Obtained from Goat Skin Process)

Process	% Exhaustion of iron	Iron in spent tan liquor as Fe (mg/L)	Shrinkage temperature °C
Tartrate masked Tanning	98.5 ± 0.5	98 ± 2	90 ± 0.5
Citrate masked Tanning	85 ± 2	890 ± 15	85 ± 1

± refers to standard deviation of the measured values

TABLE II
Results of the Analysis of Spent Chromium Tan Liquor (Goat Skin Process)

% BCS offered for iron tartrate tanned leather	% exhaustion of chromium	Chromium in spent tan liquor as Cr (mg/L)	% BCS offered for iron citrate tanned leather	% exhaustion of chromium	Chromium in spent tan liquor as Cr (mg/L)
1	99 ± 0.2	18.5 ± 1	1	98 ± 0.2	29 ± 1
1.5	98.5 ± 0.3	27 ± 1.5	1.5	97.5 ± 0.4	42 ± 2.5
2	98 ± 0.2	38 ± 2.5	2	96.5 ±0.5	62 ± 4
2.5	97.5 ± 0.5	45 ± 4	2.5	96 ± 0.3	76 ± 3

± refers to standard deviation of the measured values

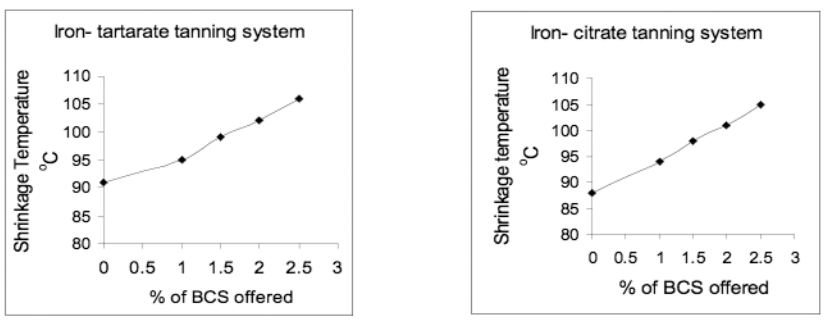

Figure 3: Graphical representation of T_s for iron-chromium tanning system (obtained from goat skin process)

iron-chromium tanned goat and sheep crust leathers (both citrate and tartrate masked) according to the official sampling procedure IUP 2[20]. The samples were conditioned at 80 ± 4°F and 65 ± 4% relative humidity for 48 hr. The tensile and tear strengths were measured as per the IUP 6 and IUP 8 methods respectively[21,22]. Experienced technologists assessed the organoleptic properties such as softness, feel and grain smoothness.

Color Measurement Analysis

The color characteristics of the iron tanned and iron-chromium combination tanned goat suede ready to dye crust leathers (both citrate and tartrate masked) in terms CIE color coordinates L, a and b (additionally saturation C, hue h) were studied using a Gretag- Macbeth Spectrolino instrument interfaced with a computer. 'L' represents the lightness on a scale of 0-100, 'a' represents the green (-a) or red (+a), and 'b' represents yellow (+b) or blue (-b). While the C and h coordinates are computed from a and b coordinates. C is the chroma coordinate, the perpendicular distance from the lightness axis and h is the hue angle expressed in degrees.

Results and Discussion

Standardization of Fe (III)-Cr (III) Combination Tanning System

The present study aims at development of Fe(III)-Cr(III) based combination tanning system for the production of soft leathers, goat suede and sheep nappa garment leathers. In order to understand the tanning performance of the Fe(III), two ligands, citrate and tartrate were chosen and the tanning studies conducted. The percentage exhaustion of iron was estimated from the analysis of the spent liquors (obtained from goat skin process), which were quantitatively collected in each case. The results are presented in Table I. With tartrate, exhaustion was near total with a value of ~99% with only 98 mg/L of Fe in the spent liquor. T_s of the resultant leather was 90°C. In comparison, citrate masked tanning salt exhibited an exhaustion of only 85% with 890 mg/L of Fe in the spent liquor.

The results of the analysis of chromium in the spent liquors when Cr(III) was used in retanning of Fe(III) tanned goat

TABLE III
Strength Characteristics of Iron-Tartrate Tanned Sheep Nappa Leathers

% BCS used	Tensile strength kg/ cm^2	Tear strength kg/cm
0	95.7 ± 4.0	24.4 ± 3.4
1	102.3 ± 3.6	27.7 ± 3.0
1.5	112.7 ± 2.5	30.8 ± 2.6
2	123.8 ± 3.8	33.6 ± 3.0
2.5	130.9 ± 3.2	35.9 ± 2.5

± refers to standard deviation of the measured values

TABLE IV
Strength Characteristics of Iron-Citrate Tanned Sheep Nappa Leathers

% BCS used	Tensile strength kg/ cm^2	Tear strength kg/cm
0	89.8 ± 2.8	22.7 ± 2.6
1	93.5 ± 3.6	25.2 ± 2.9
1.5	106.5 ± 4.2	27.7 ± 3.1
2	119.8 ± 2.8	31.4 ± 3.0
2.5	127.9 ± 3.2	34.1 ± 2.5

± refers to standard deviation of the measured values

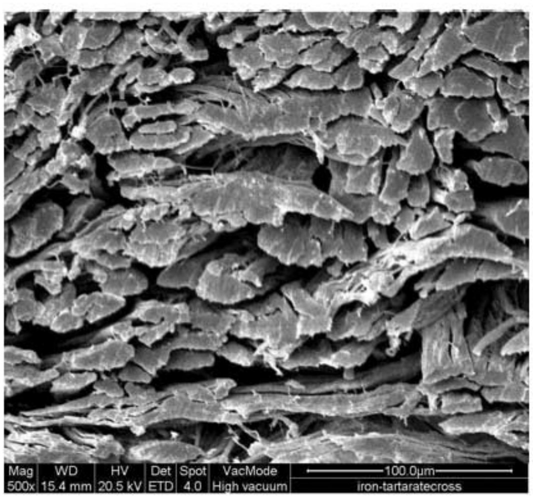

Figure 4: Scanning electron microphotograph of iron- tartrate tanned sheep nappa leather showing the cross section at 500x magnification

leathers are presented in Table II. The exhaustion of chromium was found to be excellent both for iron-tartrate and iron-citrate tanned leathers. The effect of offer of BCS on the percentage exhaustion seems to be negligible, as the exhaustion is more than 95% in all the cases. The concentration of chromium in the spent liquor was also less than 100 mg/L in all the cases.

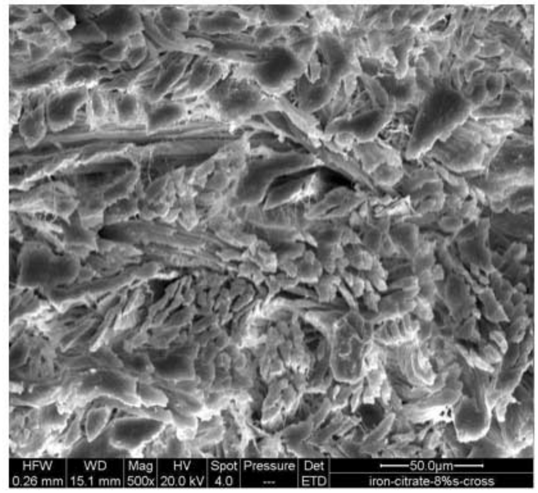

Figure 5: Scanning electron microphotograph of iron- citrate tanned sheep nappa leather showing the cross section at 500x magnification

Effect of Fe(III)-Cr(III) Tannage on Shrinkage Temperature

The effect of chromium retannage on the shrinkage temperature of iron tanned goat leathers produced is presented in the form of a graph in the Figure 3. T_s increases with increasing offer of chromium and with 2% BCS (on shaved weight), T_s goes above 100°C irrespective of the masking system employed in iron tanning.

Effect of Fe(III)-Cr(III) Tannage on Fiber Structure of Leather

The lack of softness in the case of chrome-free leathers in general and iron tanned leathers in particular is due to the lack of sufficient fiber separation. There is an inter-play of tanning, retanning and fatliquoring, which contribute to good fiber separation resulting in softness. Hence, in the present study, an attempt has been made to establish this through SEM studies. Scanning electron microphotographs of iron-tartrate and iron-citrate tanned sheep nappa leathers showing the cross section at a magnification of 500x are given in Figures 4 and 5 respectively. Scanning electron microphotographs of 2.0% BCS retanned iron-tartrate and iron-citrate tanned sheep leathers showing the cross section at a magnification of 500x are given in Figures 6 and 7 respectively. Figures 8 and 9 show the scanning electron microphotographs for iron-tartrate and iron-citrate tanned goat suede leathers. Scanning electron microphotographs of 2.0% BCS retanned iron-tartrate and iron-citrate tanned goat suede leathers showing the cross section at a magnification of 500x are given in Figures 10 and 11 respectively.

From the figures, it is evident that iron tanned leathers have close packing of fiber bundles indicating high degree of fiber cohesion compared to iron-chrome combination tanned leather. The compactness is more in the case of iron-tartrate tanned leather than the iron-citrate tanned leather. This may be due to the fact that iron-tartrate complex is insoluble and hence may have contributed to increased fiber coating and fiber cohesion in the leather matrix. The chrome retanning improves

TABLE V
Strength Characteristics for Iron-Tartrate Tanned Goat Suede Leathers

% BCS used	Tensile strength kg/cm^2	Tear strength kg/cm
0	88.5 ± 4.0	21.5 ± 2.5
1	96.0 ± 3.5	24.8 ± 3.6
1.5	105.4 ± 3.7	28.5 ± 4.2
2	116 ± 4.5	30.2 ± 4.6
2.5	126.7 ± 3.8	33.0 ± 2.5

± refers to standard deviation of the measured values

TABLE VI
Strength Characteristics for Iron-Citrate Tanned Sheep Nappa Leathers

% BCS used	Tensile strength kg/cm^2	Tear strength kg/cm
0	84.6 ± 3.4	20.7 ± 3.6
1	90.5 ± 2.5	23.6 ± 3.2
1.5	101.5 ± 3.2	25.7 ± 4.1
2	115.5 ± 2.5	28.6 ± 3.4
2.5	120 ± 3.0	31.5 ± 2.5

± refers to standard deviation of the measured values

both fiber splitting and softness characteristics of the leather in direct relation to the increase in offer of chromium as seen from the SEM photographs. It is also observed that the mellowness of iron-citrate-BCS tanned goat suede leather is much better compared to that of iron-tartrate-BCS tanned goat suede leather which is evident from the microphotographs.

Physical Testing and Visual Assessment Data

The strength properties of iron tanned sheep nappa and goat suede crust leathers (both tartrate and citrate masked) with varying percentages of BCS are given in Tables III to VI. Both tensile and tearing strength improved with increase in BCS offer in combination tanning. The softness values for sheep nappa and goat suede leather as assessed visually are shown in the Figures 12 and 14. The surface smoothness values for iron tanned nappa leather are given in Figure 13. It is interesting to note that there is an increase in softness and grain smoothness values upon increasing percentages of BCS. It is also observed that the softness and grain smoothness properties are better in the case of iron-citrate-BCS tanned crust leathers compared to that of iron-tartrate-BCS tanned crust leathers.

Color Measurement Data

The CIE color coordinates L, a and b (additionally saturation C, hue h) for iron tartrate and iron citrate tanned goat suede crust leathers are given in the Tables VII and VIII respectively.

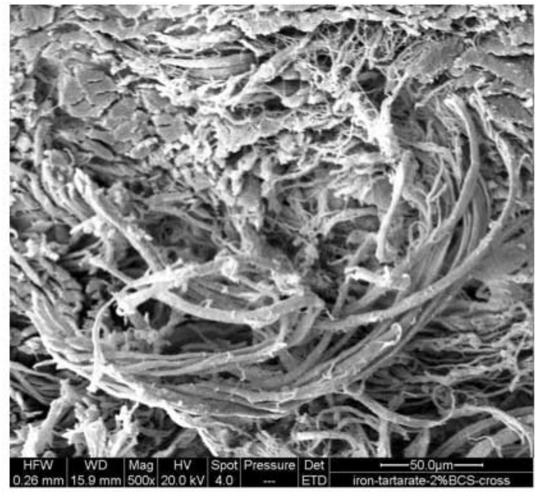

Figure 6: Scanning electron microphotograph of iron-tartrate tanned sheep nappa with 2.0% BCS retanned leather at 500x magnification

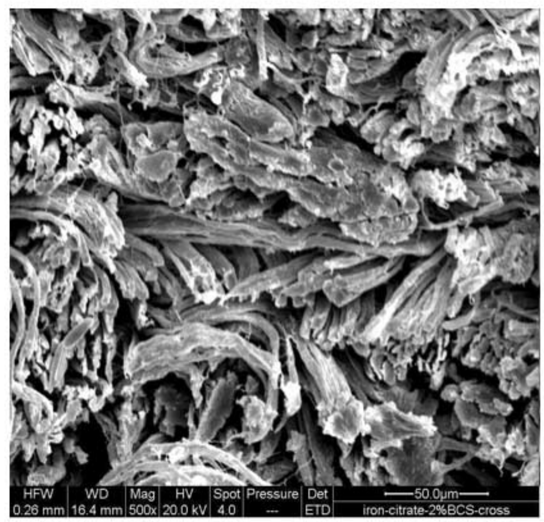

Figure 7: Scanning electron microphotograph of iron-citrate tanned sheep nappa with 2.0% BCS retanned leather at 500x magnification

From the tables, it is observed that upon increasing the BCS percentages in both tanning systems (iron-tartrate and iron-citrate), L value is reduced indicating that depth of shade is increased. For example, the L value for iron tanned leather masked with sodium tartrate is 72.5 (without BCS treatment) which goes to a value of 69.5 when treated with 2.5% BCS. The redness value represented by 'a' is similar for both sodium tartrate and sodium citrate masked iron tanned leather. The b value (yellow) for iron-tartrate tanned leather is 34.5 where as for sodium citrate masking system the value is 32.9. This means that with tartrate masking makes the leather slightly yellow compared to citrate masking.

Conclusion

An iron-chromium combination tanning system has been standardized for the production of soft leathers, goat suede

TABLE VII

CIE Color Values for Iron-Tartrate Tanned Goat Suede Crust

% BCS used	L	a	b	C	h
0	72.478	6.171	34.565	35. 112	79.877
1	70.188	6.394	36.468	37.024	80.055
1.5	71.557	5.047	29.825	30.249	80.396
2	70.777	5.587	32.606	33.082	80.277
2.5	69.471	6.352	34.481	35.061	79.562

TABLE VIII

CIE Color Values for Iron-Citrate Tanned Goat Suede Crust

% BCS used	L	a	b	C	h
0	74.110	6.150	32.941	35.510	79.424
1	71.337	6.273	31.751	32.544	78.045
1.5	71.557	5.047	29.825	30.249	80.396
2.0	70.175	7.217	31.744	32.555	77.191
2.5	68.540	7.557	31.775	32.661	76.622

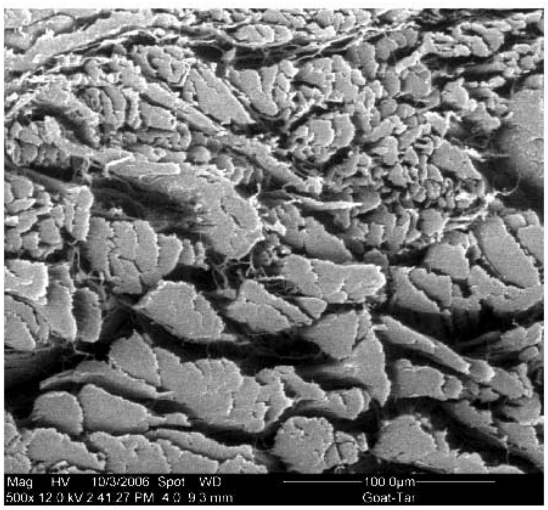

Figure 8: Scanning electron microphotograph of iron- tartrate tanned goat suede leather showing the cross section at 500x magnification

garment leathers and sheep nappa garment leathers. A combination tanning involving 10% ferric sulfate with 2% BCS was found to yield good quality leathers. The tanning trials show that the exhaustion of chromium could be more than 95% in both cases and the iron (with tartrate masking) and chromium content in the spent tan liquors was less than 100 mg/L. Visual assessment data supported by scanning electron microscopic analysis indicate that leathers tanned using iron and chromium combination tanning system exhibited the required degree of softness and surface feel. However, these properties were marginally better in the case of the iron-citrate tanning system compared to iron-tartrate tanning system.

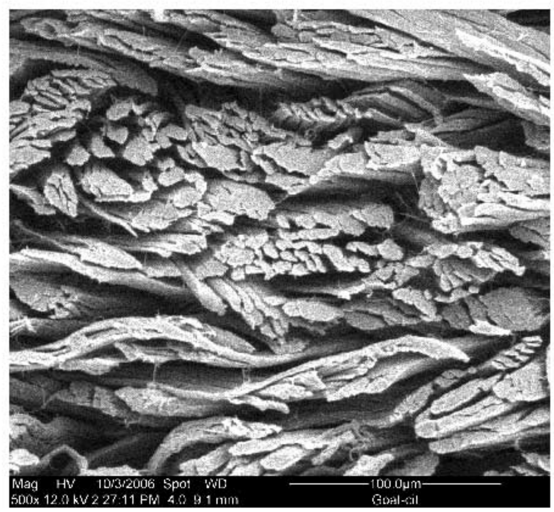

Figure 9: Scanning electron microphotograph of iron- citrate tanned goat suede leather showing the cross section at 500x

References

1. Subbrama Naidu, A. Kotharis desk book on leather, Ed. Sadulla, S; Kothari Publications, Chennai, 35, 1995.
2. Chattapadhyay, B; Datta, S; Chatterjee, A; Mukhopadhayay, K. *JSLTC* **84**, 94, 2000.
3. Swaddle, T.W; Substitution reactions of divalent and trivalent metal ions. *Adv. Inorg. Bioinorg. Mech.* **2**, 95, 1983.
4. Orgel, L.E; Introduction to transition metal chemistry: ligand field theory, Metheun Publishers, London, 1967.
5. Hansen, M.B; Rydin, S; Menne, T; and Johansen, J.D; Quantitative aspects of contact allergy to chromium and exposure to chrome-tanned leather. *Contact Dermatitis* **47**, 127, 2002.

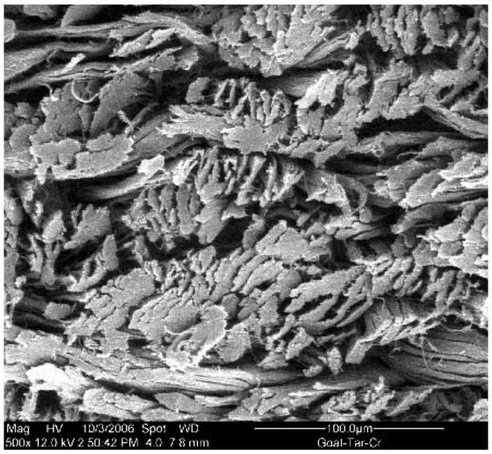

Figure 10: Scanning electron microphotograph of iron-tartrate tanned goat suede with 2.0% BCS retanned leather at 500x magnification

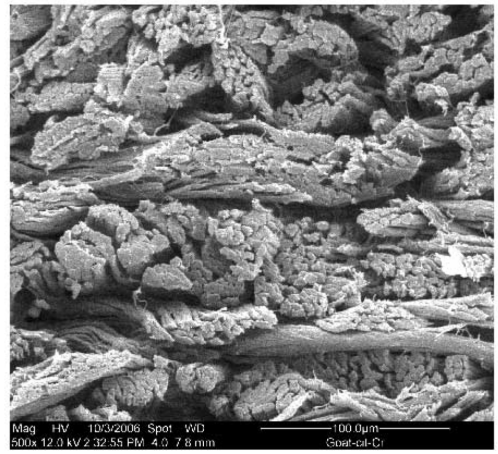

Figure 11: Scanning electron microphotograph of iron-citrate tanned goat suede with 2.0% BCS retanned leather at 500x magnification

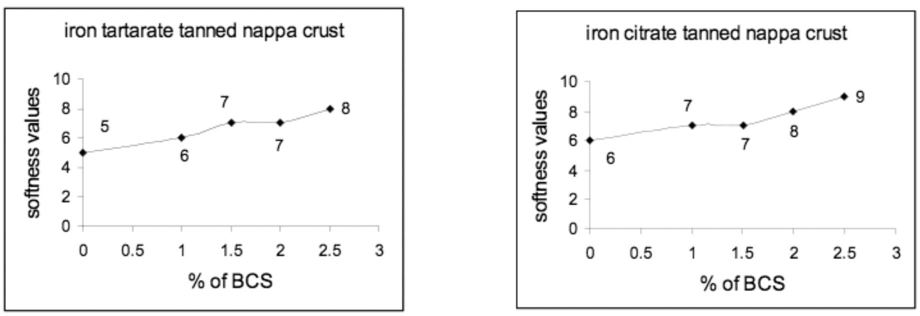

Figure 12: Changes in softness values (visual assessment) for sheep leather with increasing % of BCS

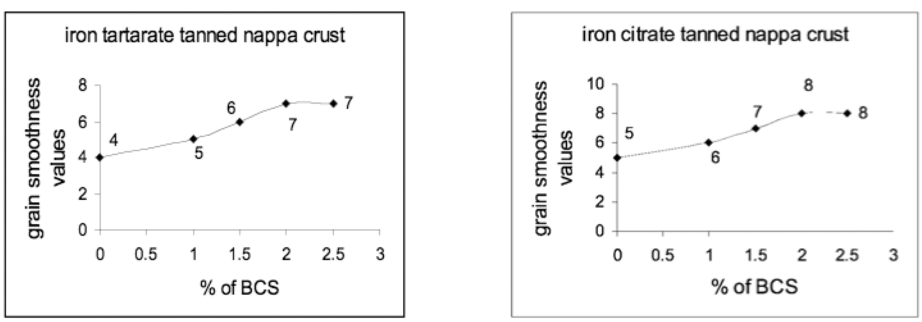

Figure 13: Changes in surface smoothness (visual assessment) for sheep leather with increasing % of BCS

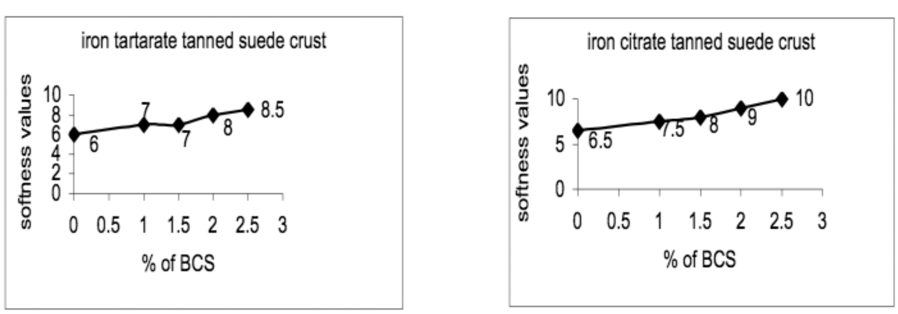

Figure 14: Changes in softness values (visual assessment) for goat leather with increasing % of BCS

6. Hansen, M.B; Johansen, J.D; and Menne, T; Chromium allergy: significance of both Cr(III) and Cr(VI). *Contact Dermatitis* **49**, 206, 2003.
7. Rajaram, R; Nair, B.U; and Ramasami, T; Chromium (III) induced abnormalities in human lymphocyte cell proliferation: Evidence for apoptosis. *Biochem. Biophys. Res. Commun.* **210**, 434, 1995.
8. Sharma, D.C; Sharma, C.P; and Tripathi, R.D; Phytotoxic lesions of chromium in maize, *Chemosphere* **51**, 63, 2003.
9. Rai, D; Eary, L. E; Proceedings of the chromium symposium 1986, Industrial health foundation, Pittsburgh, PA, 331, 1986.
10. Schmid, V. G; and Paucker, W. *Das Leder* **35**, 165, 1984.
11. Barlett, R; and James, J; *J. Environ. Qual.* **8**, 31, 1979.
12. Ciambelli, P., Naviglio, B., Bianchi, L., Sannino, D., and Tomaselli., Aluminosilicates as novel agents in the tanning process, Proceedings of the XXV IULTCS Congress, 153, 1999.
13. Slabbert, N.P., Mimosa-Al tannages-An alternative to chrome tanning, *JALCA* **76**, 230, 1981.
14. Gaidau, C., Palton, F., and Badea, N.,'Investigation into iron tannage', *JSLTC* **82**, 143, 1998.
15. Fleming, R.W; Some studies on iron and combination iron-chrome tannages, *JALCA* **38**, 412, 1943.
16. Ruppenthal, K.F. and Malik, J.P; Investigation of iron and iron chrome tannages, *Shoe and Leather Reporter*, Oct. 17, 1942. Jan. 16, 1943.
17. Jeffery, G.H; Bassett, J; Mendham, J; Denney, R.C; Vogel's textbook of quantitative chemical analysis', ELBS Publication, Longman Scientific & Technical, Longman group UK Ltd; 1994.
18. SLP18 (IUP 16), The Society of Leather Technologists and Chemists, Northampton, 1996.
19. Official methods of analysis, Society of Leather Technol.Chem; Herts, 1965.
20. IUP: 2 Sampling, *JSLTC* **84**, 303, 2000.
21. IUP: 6 Measurement of tensile strength and percentage elongation, *JSLTC* **84**, 317, 2000.
22. IUP: 8 Measurement of tear load -Double edge tear, *JSLTC* **84**, 327, 2000.

Appendix 1

Five sets of trials were carried out. In each set ten wet salted goat skins and ten wet salted sheep skins were taken and marked as 1L 1R, 2L 2R, 3L 3R, 4R 4L, 5,6,7,8, 9L 9R, 10R 10L.

Process Details for Making Pickled Pelts
Raw material: wet salted goat and sheep skins weighing 1 Kg and measuring 5 sq ft per piece.

Soaking: (% on raw weight)
The skins were soaked for 4 hours with 300 % water and then washed with 2 changes of fresh water.
Liming: (% on soaked weight)
Lime 10%
Sodium sulphide 2%

Made into a paste with 20% water and applied on flesh side and left over night. Next day the skins were unhaired.

Reliming:
Lime 10%
Water 150%

Kept in the reliming bath for 3 days. Next day, they were fleshed and pelt weight was noted.

Deliming: (% on pelt weight)
Water 100%
Ammonium Chloride 1%

Run for 45 min, completion of deliming was checked, drained and washed with 200% water.

Pickling:
Water 80%
Salt 8%
Run for 10 min.
Sulphuric Acid 1%
Water 20%

Given in 4 feeds at 10 min. interval and finally run for 60 min. pH of the pelt was kept at 2.8.

Iron-Tartrate Tanning (Goat and Sheep skins were separately tanned)
Material: Pickled pelts numbered as 1L, 2R, 3L, 4R, 5,6,9L, 10R (goat skins) and (1R, 2L, 3R, 4L, 7,8,9R, 10L (sheep skins)

Process
50% pickle water
10% Ferric Sulphate
Fe to tartrate molar ratio of 1: 0.15
2% sodium carbonate
Run for 90 min.
50% water
Run for 30 min
2% sodium formate
2% sodium carbonate

Mixed with 30% water and given in 6 feeds at 10 min. interval and then run for 60 min.

Final pH of the leather was kept at 3.6-3.8.

Iron-Citrate Tanning (Goat and Sheep skins were separately tanned)
Material: Pickled pelts numbered as 1R, 2L, 3R, 4L, 7,8,9R, 10L (goat skins) and 1L, 2R, 3L, 4R, 5,6,9L, 10R (sheep skins)

Process
50% pickle water
10% Ferric Sulphate
Fe to citrate molar ratio of 1: 0.22
2% Soda ash
Run for 90 min.
50% water
Run for 30 min
2% sodium formate
2% sodium carbonate

Mixed with 30% water and given in 6 feeds at 10 min. interval and then run for 60 min.

Final pH of the leather was adjusted to 3.6-3.8.

Appendix 2

Chromium Treatment (% on shaved weight)
Material:
Shaved Iron tanned leathers from 5 sets of trials (both goat and sheep)

Process:
BCS Treatment: Water100%

Five sets of iron tanned (both citrate and tartarate masked) leathers were treated with

BCS as per the details given below.

Trial 1: 0% BCS

Trial 2: 1% BCS

Trial 3: 1.5% BCS

Trial 4: 2% BCS

Trial 5: 2.5% BCS

Run for 60'

The pH of the leather was adjusted to 4.0 using sodium formate and sodium bicarbonate.

APPENDIX 3

Recipe for goat suede crust

Washing

Water 250%
Run for 10 min., drain.

Retanning

Water 100%
Acrylic syntan 2%
Sulphone based retanning syntan 2%
Run for 45 min., drain and wash.

Neutralization

Neutralizing syntan 1.0%
Run for 15 min.
Sodium formate 0.5%
Sodium bicarbonate 0.3%

Given in 2 feeds at 10 minutes interval, finally run for 30 min. and check pH; should be 5.2. Wash twice with 200 % water for 10 min.

Retanning & Fatliquoring

Water 100%
Acrylic syntan 2%
Run for 15 min.
Phenolic syntan 6%
Condensation product based on dicyandiamide 6%
Run for 60 min.
Synthetic fatliquor 5%
Synthetic fatliquor 5%
Synthetic and neutral oils with emulsifiers 2%
Run for 60 min.
Resin syntan 3%
Naphthalene based retanning syntan 3%
Run for 30 min.

Fixing:

Formic acid 2%
Water 20%

Given in 3 feeds at 10 min. interval and finally run for 30 min. Then the leathers were piled overnight. Next day, they were set and hooked for drying. After drying, the leathers were staked, snuffed and buffed using 240, 320 and 400 grit emery papers successively. The grain was completely shaved off and the thickness adjusted to 0.5-0.6 mm thickness. Then buffing was done on the grain side with 320 grit emery paper.

APPENDIX 4

Recipe for sheep nappa crust

Washing

Water 20%
Run for 10 minutes, drain.

Neutralization

Neutralizing syntan 1.0%
Run for 20 min.
Sodium formate 0.5%
Sodium bicarbonate 0.5%

Given in 4 feeds at 10 min. interval, finally run for 30 min., check pH; should be 5.6. Wash twice with 200% water for 10 min.

Retanning & Fatliquoring:

Water100%
Resin syntan 2%
Run for 15 min.
Synthetic fatliquor 4%
Phosphorylated fatliquor 3%
Polymeric fatliquor 6%
Fatliquor based on synthetic and neutral oils 6%
Run for 60 min.
Melamine based syntan 3%
Naphthalene based retanning syntan 3%
Run for 30 min.
Phosphorylated fatliquor 3%
Fatliquor based on sulfochlorinated hydrocarbons 3%
Run for 40 min.

Fixing:

Formic acid 2%
Water 20%

Given in 3 feeds at 10 min. intervals and finally run for 30 min.

Top Fatliquoring

Nonionic fatliquor 0.5%
Cationic fatliquor 0.5%
Run for 20 minutes.

Then the leathers were piled overnight. Next day, they were set and hooked for drying. After drying, the leathers were staked and buffed using 400 grit emery paper.