Cost Effective Fixing Process for Post Tanning Operation

by

N. Nishad Fathima, J. Raghava Rao* and B. U. Nair

Chemical Lab, Central Leather Research Institute, Council of Scientific and Industrial Research,
Adyar, Chennai-20, India

Abstract

Post tanning is an important unit process in leather manufacturing because it imparts bulk properties to leather. Formic acid is used as a fixing agent during the post tanning operation for fixing the post tanning chemicals; namely, dye, fatliquor and retanning agents. However, formic acid, being an organic acid, is expensive in nature. In order to make the fixing operation a cost effective process, replacement of formic acid by other mineral acids has been attempted in this study. Various combinations of organic and mineral acids were attempted to achieve the desired properties. Both sulfuric and hydrochloric acids have been used as fixing agents in the presence of formic acid either as serial addition or as combined addition. It has been observed that both the acids can be used for fixing in admixture with formic acid, with HCl giving slightly better organoleptic properties. Leathers obtained from various studies indicate that both sulfuric and hydrochloric acid in combination with formic acid resulted in properties comparable to that of the control leathers. Estimation of water solubles from experimental leathers indicated that the pH and leaching of dye are similar to that of the control leathers. No significant changes in the organoleptic and strength properties, and fiber structure of leathers were observed. Hence, fixing with a combination of mineral and formic acid is a feasible cost effective alternative for fixing of post tanning chemicals.

Resumen

El recurtido es un importante proceso unitario en la fabricación del cuero, que confiere las propiedades generales al cuero. Ácido fórmico se utiliza como agente fijador de recurtientes en la operación del recurtido; a decir, colorantes, engrases, y agentes recurtientes. No sobra decir que el ácido fórmico, siendo un ácido orgánico, es caro por naturaleza. Para hacer la operación de de fijación un proceso de costo efectivo, sustitución de ácido fórmico por ácidos minerales ha sido tratada de hacerse en este estudio. Varias mezclas de ácidos orgánicos y minerales se ensayaron para obtener las propiedades deseadas. Ambos ácidos sulfúrico e hidroclórico han sido utilizados en presencia de ácido fórmico añadido independientemente o en conjunto. Se ha observado que ambos ácidos [minerales] pueden ser utilizados en combinación con ácido fórmico con HCL resultando en un tacto ligeramente superior. Cueros obtenidos de los varios estudios indican que ambos ácidos tanto sulfúrico como clorhídrico en combinación con ácido fórmico resultaron en propiedades comparables a las de los cueros de control. Estimación de materiales extraíbles por agua de los cueros experimentales indicaron que el valor del pH y el sangrado del colorante fueron similares a los cueros del control. No se detectaron cambios significativos en las propiedades de tacto y resistencias físicas, y estructuras fibrosas observadas. Como tal, la fijación por medio de combinaciones de ácidos minerales y ácido fórmico es una factible y económica opción alternativa para los productos químicos del recurtido.

*Corresponding author email: clrichem@mailcity.com; Fax: +91 44 24911589
Manuscript received August 13, 2009, accepted for publication November 17, 2009

Introduction

Post tanning operation in leather processing involves retanning, dyeing, and fatliquoring. It is a transition process between tanning and finishing. It is an important step in the leather making process as the bulk properties of leathers are added during this process. Isoelectric point of collagen lies in the range of pH 7-7.8, that of chrome tanned collagen pH 6.5, of vegetable tanned collagen pH 4.5 and aldehyde, quinone and oil tanned about pH 4.5.[1] It is essential to choose post tanning chemicals so as to ensure opposite charges on both substances. Vegetable tanned leather is anionic in nature, and basic dyes will have high reactivity with them.[2] However, they fade very badly in sunlight, tend to be soluble in some oils, greases, waxes and solvents and contact color may be transferred to another surface; for these reasons basic dyes are avoided. Hence, preference goes to acid dyes. Generally, we require mild acids for fixing of these dyes in leather. Fixing agent enables to fix the given retanning agent, dyes, and fat liquors. If the dyes, retanning agents and fat liquors are not fixed using suitable fixing agent, then all the given chemicals are ejected and this results not only in wastage of chemicals but also defeats the purpose of carrying out these processes.

Weak acids have been selected over mineral acids since penetration of the dye is more thorough and at a greater depth, thus resulting in greater dye levelness and penetration. Formic acid is one such weak acid and has been a popular choice for the fixing of the post tanning process.[3] Unfortunately, like mineral acids, workers in the tanning industry must handle concentrated formic acid with extreme care since it is a relatively corrosive liquid and exudes noxious vapors. The use of formic acid at greater percent results in higher cost of production. Urea sulfate as a substitute for formic acid was studied. However, various limitations, like treatment of nitrogen emanating from the urea and handling problems are associated with this process.[4] A safe alternative to formic acid in the dyeing process would be highly desired if the alternative demonstrated not only to be an equally efficient but also a cost effective replacement.

The main objective of this work is to find cost effective alternative fixing methodology for post tanning operations due to the following limitations of formic acid: a) expensive, b) unable to provide the same level of fastness and exhaustion for all the dyes, c) exudes noxious vapors. The various selection criteria for fixing of post tanning agents include: a) low cost, b) low free acid generation, c) no adverse effects on quality, d) availability, ease of usage and handling. Addition of mineral acid alone may result in the following challenges: a) pH dip is very high as they are highly concentrated b) affects the strength or quality of leather if used in excess, which results in breakdown of fibers.

Pickling involves a combination of formic and sulfuric acid.[5] This confers advantages like buffering action, avoids sudden dips in pH, prevents acid swelling, enables smooth grain and generates quality leathers. This concept of using combination of mineral with organic acid has been applied in the fixing of post tanning chemicals in this study. In order to make fixing process a cost effective one without altering its physical and organoleptic properties we have tried the combination of mineral acid and formic acid.

Experimental

Materials

Buffalo calf vegetable tanned leather (1.6 to 1.8 mm thickness) was taken as the starting raw material. Sulfuric acid (93% purity), formic acid (85% purity) and hydrochloric acid (34% purity) used in this study were of commercial grade.

Post Tanning Operation

Vegetable tanned leathers were wet back, stripped, soured and taken for retanning with 10-12% retanning agent. The retanned leathers were taken for further processing using formic acid as fixing agent using the recipe given in Table I to make burnish upper leathers. The amount of mineral acids required to lower the pH to same level as formic acid was standardized based on the end pH required. The various combinations of acids used for fixing experimental leathers are given in Table II. The post tanning recipe for experimental is the same as control except for the fixing agent.

Physical Properties and Color Measurement

The samples for physical testing were obtained as per IULTCS methods.[6] Physical properties such as tensile strength, % elongation and tear strength were investigated as per standard procedures.[7,8] Reflectance measurements were made as per standard procedures.[9]

Wet and Dry Rub Fastness and Softness Measurement

Wet and dry rub fastness was measured according to IS 6191-1971 (LF:10)[10] using SATRA Crockmeter and quantitative measurement of softness through compressibility measurements was made as per standard procedure.[11]

pH of Water Solubles and Dye Leaching Measurements

2 g of leather sample was cut into small pieces and weighed again for accuracy. 200 ml of distilled water was added and transferred into the jar of the mechanical shaker. The shaker was run for three hours. The contents were transferred into a conical flask after filtering using Whatmann filter paper. The filtrate was collected and the pH was determined using a pH meter. Absorbance of the filtered solution was measured using a Perkin Elmer Lambda 35 UV-Vis spectrophotometer to identify the extent of dye leaching due to pH of water solubles.

TABLE I

Post Tanning Recipe for Control

Process	Chemicals	Weight	Time (min)	Temp (°C)	End point/Remark
Dyeing	Water	150%		50	
	Dye Leveling agent	0.5%	5'		
	Dye	3%	30'		Penetration
Fixing	Formic acid	3%	30'		pH 3.5 (exhaustion)
	Water	1:10 dilution			
Fat liquoring	Water	150%		60	
	Fatliquor mixer*	10%	85'		
Fixing	Formic acid	1.5%	30'		pH 3.5 (exhaustion) Drain
2nd dyeing	Water	200%		50	
	Dye	1.5%			
Fixing	Formic acid	1.5%	30'		pH 3.5 (exhaustion)
	Water	300ml			
Oiling	TOP OIL	2%	20'	30	Drain

N/D Sammying, Setting, Hook to Dry and Staking
* using a combination of synthetic and semi synthetic fatliquors

TABLE II

Various Combinations of Mineral Acids + Formic Acid Based Fixing

	TRIAL-I	TRIAL-II	TRIAL-III	TRIAL-IV	TRIAL-V
Fixing with different acids	Formic acid (control)	Formic + HCl (mixed)	Formic + HCl (separated)	Formic + Sulfuric (separated)	Formic + Sulfuric (mixed)
Percentage	Formic 3%	Formic 1% HCl 0.5%	Formic 1% HCl 0.5%	Formic 1% Sulfuric 0.25%	Formic 1% Sulfuric 0.25%
Total % used	Formic 6%	Formic 2% HCl 1%	Formic 2% HCl 1%	Formic 2% Sulfuric 0.5%	Formic 2% Sulfuric 0.5%

Scanning Electron Microscopic Studies

Samples from control and experimental leathers were cut from the official sampling position. The specimens were then coated with gold using an Edwards E306 sputter coater. A FEI Quanta 200, Philips make scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

Organoleptic Properties Measurements

Crust leathers were assessed for softness, grain smoothness, grain tightness, fullness and general appearance by tactile evaluation. Experienced tanners rated the leathers in a scale of 0-10 points for each functional property. The values reported are the average of three ratings.

RESULTS AND DISCUSSION

In order to replace formic acid with mineral acids like sulfuric acid and hydrochloric acid, the pH profiling of these acids was carried out. Some experiments to determine the pH equivalence of hydrochloric acid and sulfuric acid in order to find the percentage of acid usage in fixing were carried out. From these experiments, it was found that the dilution of mineral acids to 35% at an offer of 0.5% hydrochloric acid or 0.25% sulfuric acid along with 1% formic acid resulted in the same operational pH range as that of formic acid alone. Based on that, combination trials were run with 1% formic acid and 0.5% of HCl as combination of organic (formic) and mineral acid(HCl). Similarly, 1% of formic acid and 0.25% of sulfuric acid as combination of organic (formic) and mineral acid (H_2SO_4) at 35% dilution of shaved weight both as serial addition as well as combined addition were carried out.

Effect of Various Combinations on Physical Properties

The physical testing values obtained for the leather fixed with a combination of organic and mineral acids are given in the Table III. From the table, it can be seen that tensile, tear strength and elongation strength of leather fixed with a mixture of acids (Formic and HCl, Formic and H_2SO_4) which added in three feeds shows results which are on par with or better than the control. Also, the changes in the color properties seen are not very significant and are not a cause for concern for day to day leather processing. From the results, it can be seen that the physical properties are better for leathers fixed with a combination of acids given in a mixture; rather than given in serial addition as formic followed by HCl or formic followed by H_2SO_4.

Since the study involves the use of mineral acids, which may have adverse effect on strength properties with time, ageing studies were carried out. The effect of ageing on the physical properties of leathers was studied after ageing the leathers for 1 month. Table IV shows that there are no significant changes observed in the strength properties on ageing. Hence, mineral acid based combinations can be used for fixing of post tanning chemicals.

Effect of Various Acid Combinations Fixing Systems on Color Properties

The presence of mineral acids may affect the color of the leathers made. Hence, the effect of these combinations of mineral and formic acid on the various properties of color were studied. The L, a, b, c values for each leather that are fixed with different combination of organic and mineral acids are given in Table V. From the table, it is observed that differences in L,a,b,c values are small and would not normally be cause for concern in normal leather making operations. Visual examination also showed the same results.

Effect of Various Acid Combinations Fixing Systems on pH of Water Solubles and Dye Leaching

In order to determine if the presence of mineral acids affects the pH of water soluble, experiments were carried out. The pH of water solubles for the five trials that were conducted are given in Table VI. As can be seen from the table, the pH values of water soluble for all the combinations are similar to that of the control.

In order to study the effect of various acid combinations fixing systems on dye leaching studies were carried out. It can be seen from the Figure 1 that difference in acid combinations does not have any significant influence on the dye leaching capabilities of leathers.

Effect of Various Acid Combinations Fixing Systems on Softness and Organoleptic Properties

Presence of mineral acids may affect the bulk properties like softness and grain smoothness. In order to study the effect of various acids combinations used on bulk properties, organoleptic assessment and objective measurement of softness of leathers made was carried out. The softness of the control and experimental leathers measured quantitatively is given in Table VII. It should be noted that the higher the value, the better the softness. It can be seen that mixed systems result in softer leathers indicating the fiber structure is not affected.

Figure 2 depicts the visual assessment grade for all the organoleptic properties (general appearance, grain smoothness, color uniformity, softness, grain smoothness, grain tightness, fullness). The minimum grade limit is 0 and the maximum grade is up to 10. It is seen that general appearance of all the trials are almost same. For grain smoothness, mixed acids based leathers (formic and HCl & formic and H_2SO_4) are

TABLE III

Effect of Mineral Acids based Fixing on Physical Properties

Properties	TRIAL-I (Formic acid-control)	TRIAL-II (Formic + HCl mixed)	TRIAL-III (Formic + HCl separated)	TRIAL-IV (Formic + sulfuric separated)	TRIAL-V (Formic + sulfuric mixed)
Tensile strength (N/mm^2)	24±2	28±1	23±2	29±1	29±2
Elongation (%)	33±2	36±3	34±2	32±1	31±1
Tear strength (N)	41±3	55±2	48±1	47±2	49±1
Color fastness Dry 10 rubs Wet 10 rubs	 4/5 3/4	 4/5 3/4	 4/5 4	 4/5 4	 4/5 3/4

TABLE IV

Effect of Mineral Acids Based Fixing on Physical Properties after Ageing for 30 Days

Properties	TRIAL-I (Formic acid-control)	TRIAL-II (Formic + HCl mixed)	TRIAL-III (Formic + HCl separated)	TRIAL-IV (Formic + sulfuric separated)	TRIAL-V (Formic + sulfuric mixed)
Tensile strength (N/mm^2)	21±2	25±2	21±2	29±1	27±1
Elongation (%)	34±1	35±2	32±1	31±1	32±1
Tear strength (N)	39±2	53±2	47±1	49±1	47±1
Color fastness Dry 10 rubs Wet 10 rubs	 4/5 3/4	 4/5 3/4	 4/5 4	 4/5 4	 4/5 3/4

TABLE V

Difference Between L, a, b, c Values of Leathers Fixed with Various Acid Combinations Against Control (formic acid)

Combination	Δa	Δb	Δc	Δh	ΔL
Formic + HCL (mixed)	Less red -1.147	More yellow 0.140	Weaker -0.433	Increase 1.072	5.335
Formic + HCL (separated)	Less red -0.956	Less yellow -1.226	Weaker -1.539	Increase 0.222	1.822
Formic + sulfuric acid (separated)	Less red -1.990	Less yellow -1.557	Weaker -2.327	Increase 0.984	5.560
Formic + sulfuric acid (mixed)	Less red -0.899	Less yellow -1.713	Weaker -1.566	Decrease -0.079	2.490

comparable to control leathers. This indicates that the presence of formic acid enables buffering action; thereby no acid shock is seen on the grain. In case of color uniformity, almost all the trials have nearly the same value. Mixed system of formic and HCl shows better softness property than control, which is in accordance with that obtained through objective assessment of softness. From the organoleptic properties, it can be concluded that mixed acids (formic and HCl & formic and H_2SO_4) based leathers exhibit slightly better bulk properties than serial addition.

Scanning Electron Microscopic Studies

SEM analysis have been conducted to study the distribution of post tanning chemicals and their alignment at the fiber structure and also to view the arrangement of fibers after fixing with different acid combinations. Figure 3 gives the SEM micrographs of grain surface of leathers fixed using various acid combinations. It can be seen that there is no effect of different types of acids on the grain surface. Particularly, no grain damage is seen due to the use of mineral acids. Figure 4 shows the SEM micrographs of the cross-section of the leathers fixed with various acid combinations. The fiber compaction of sulfuric acid mixed system seems to show more compactness than other systems. In general, the distribution of post tanning chemicals does not seem to be affected by various acid combinations.

Costing

The main objective of the present study is to make the fixing operation in post tanning cost effective. Hence, cost analysis was carried out. The cost of processing 1 ton of material for fixing is given in Table VIII. It can be seen that the cost of production for control leathers using formic acid for fixing results in USD 100 whereas for experimental leathers fixed formic acid and HCl/ H_2SO_4 is only USD 34. A reduction of about 66% in cost of fixing agent can be achieved by using

TABLE VI

pH of Water Soluble of Leathers Fixed with Various Acid Combinations

Trials	Acid combination	pH
I	Control (formic acid)	3.40
II	formic + HCl mixed	3.55
III	formic + HCl separated	3.83
IV	formic + sulfuric separated	3.53
V	formic + sulfuric mixed	3.69

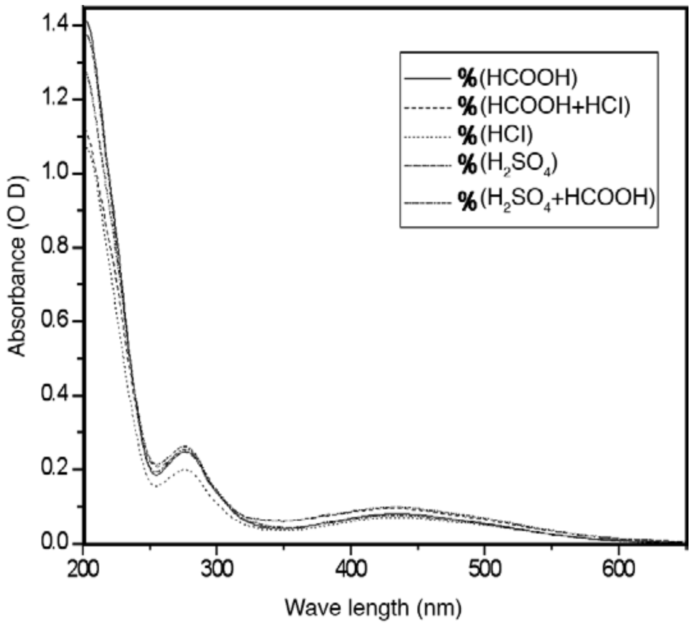

Figure 1. – UV-vis spectra of dye leachates for leathers fixed with various acid combinations.

TABLE VII

Objective Assessment of Softness Values of Leathers Fixed with Various Acid Combinations

Trials	Softness
Formic acid	3.44
Formic + HCl acid (mixed)	4.13
Formic + HCl acid (separated)	3.47
Formic + sulfuric acid (separated)	3.23
Formic + sulfuric acid (mixed)	4.03

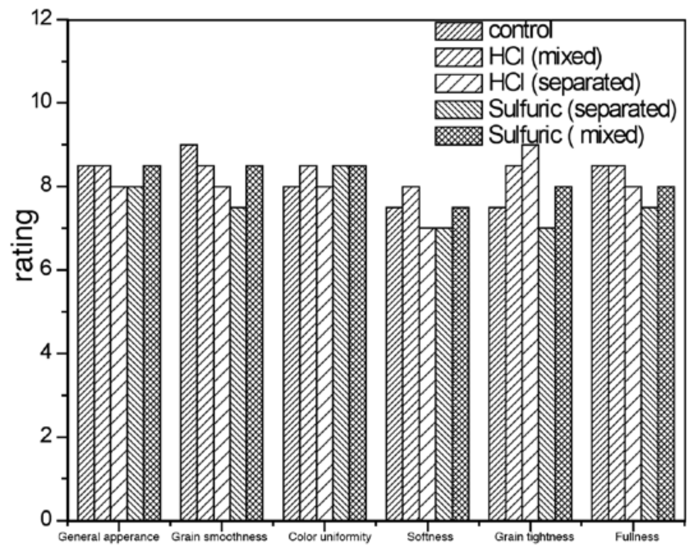

Figure 2. – Organoleptic properties of leathers fixed with various acid combinations.

this combination of acids. Thus, a cost effective method of fixing post tanning chemicals with no adverse affects on various leather properties has been developed.

CONCLUSIONS

Cost effective replacement for fixing post tanning chemicals has been attempted in this study. Mineral acid based fixing as mixed addition and serial addition with formic acid has been studied. 0.5% hydrochloric acid and 0.25% sulfuric acid in combination with 1% formic acid each has been used for fixing. Fixing with mixed acids combination (formic and HCl & formic and H_2SO_4) resulted in leathers with better physical strength and organoleptic properties. The changes observed in the color characteristics of leathers are not a cause for concern in day to day leather processing. pH and dye leachates studies of water solubles did not show any significant change denoting that mineral acids did not alter the pH of the leathers at the offer given. SEM analysis shows that the distribution of post tanning chemicals is not affected by mineral acid based fixing. A reduction in cost of about 66% has been achieved using mineral and formic acid combination without affecting the quality of final leathers made.

ACKNOWLEDGEMENTS

We thank Mr. P. Rajkumar and Mr. J. Mohammed for their help during experiments.

REFERENCES

TABLE VIII

Cost analysis of acid combination fixing systems

	Control	Expt I	Expt II
Fixing with different acids	Formic acid (control)	Formic + HCl (mixed)	Formic + Sulfuric (mixed)
Amount used (%)	Formic-6	Formic-2 HCl-1	Formic-2 Sulfuric-0.5
Cost for 1 ton of material processed	100	34.2	33.8

Formic acid – \$1.67/Kg; HCl – \$0.094/Kg; H_2SO_4 – \$0.1/Kg

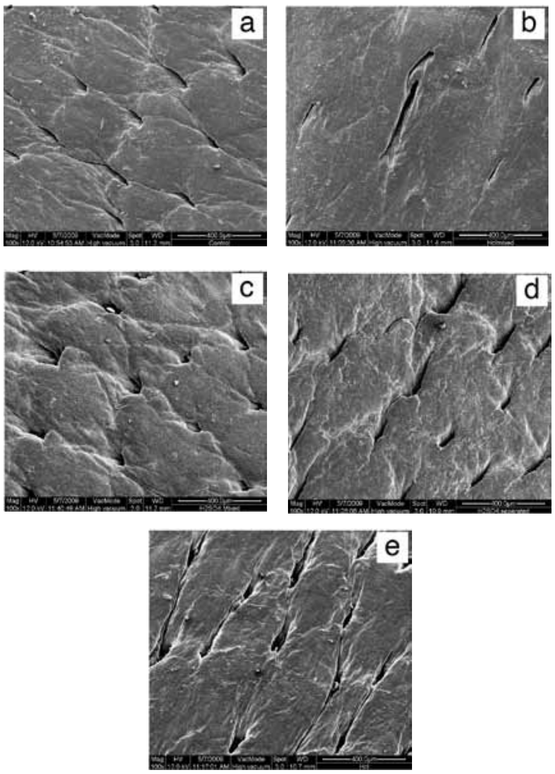

Figure 3. – SEM micrographs showing grain surface of leathers fixed with a) formic acid; b) Formic acid + HCl mixed; c) Formic acid + sulfuric mixed; d) Formic acid + sulfuric separated; e) Formic acid + HCl separated.

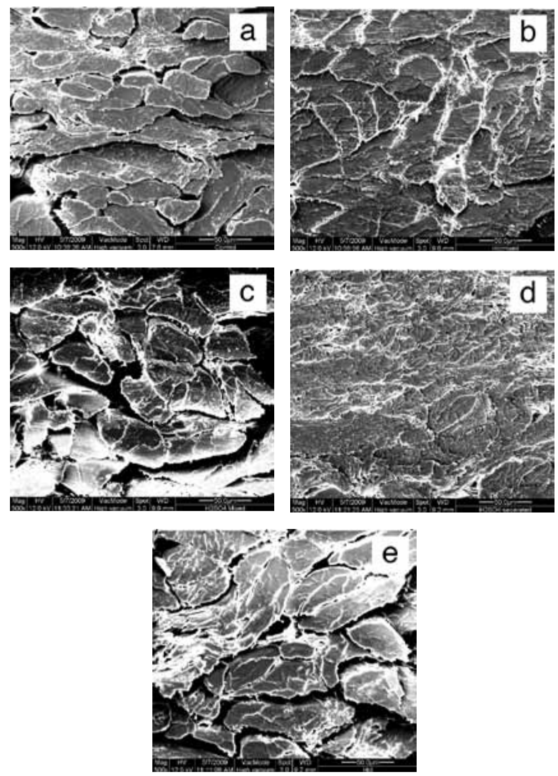

Figure 4. – SEM micrographs showing cross section of leathers fixed with a) formic acid; b) Formic acid + HCl mixed; c) Formic acid + sulfuric mixed; d) Formic acid + sulfuric separated; e) Formic acid + HCl separated.

1. Bienkiewicz, K.; Physical Chemistry of Leather Making. Robert E. Krieger Publishing Co., Malabar, Florida, 1983.
2. Sharphouse, J.H.; Leather Technician's Handbook. Leather producers' association, Northampton, 1983.
3. Rusby, R.W.; Formic acid in dyeing, *JALCA* **2**, 146, 1907. [Ed. says "Wow 1907"]
4. Gehring, A.G., Bailey, D.G., Cardamone, J.M., DiMaio, G.L.; Evaluation of urea sufate as a substitute for formic acid in the retan, color and fatliquor process. *JALCA* **96**, 333-342, 2001.
5. Procter, H.R.; The principles of Leather Manufacture, 2nd Ed. E. & F.N. Spon, Ltd., London, 1922.
6. IUP 2, Sampling. *JSLTC* **84**, 303, 2000.
7. IUP 6, Measurement of tensile strength and percentage elongation. *JSLTC* **84**, 317, 2000.
8. IUP 8, Measurement of tear load-double edge tear. *JSLTC* **84**, 327, 2000.
9. Fathima, N. N., Saravanabhavan, S., Rao, J. R. and Nair,B. U.; An eco-Benign tanning system using aluminium, tannic acid and silica combination. *JALCA* **99**, 73-81, 2004.
10. Determination of color fastness to rubbing (Crocking test), Indian Standards, IS 6191 (LF:10), 1971.
11. Fathima, N. N., Aravindhan, R., Rao, J. R. and Nair, B. U.; Tannic acid-phosphonium combination: a versatile chrome-free organic tanning, *JALCA* **101**, 161-168, 2006.