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An approach towards redefining water quality parameters for leather industry Part 1. Effect of hardness and chlorides in water

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ABSTRACT

The growth of the leather industry in last few decades has been spectacular. The industry is however highly water intensive. Water is the medium currently employed by the leather industry for the conversion of raw hides and skins to leathers. There are tolerance limits for hardness and chlorides in water for use in various operations of leather processing. These limits were designed keeping in view the auxiliaries and chemicals that were available at a particular period of time. Significant changes have taken place in the auxiliaries and chemicals front resulting in enhanced stability and fastness characteristics for various process conditions. Hence it is necessary to assess and review the quality requirements of water for leather making at present. An attempt has been made to study the various water quality parameters that would influence the chemical uptake and properties of the leather. Water quality parameters particularly hardness and chlorides level were examined individually and effect of hardness and chlorides on soaking liming and chrome tanning were studied in this investigation. Some interesting results have emerged based on the studies carried out. The influence of water quality on the physicochemical characteristics of the leather in pretanning and tanning is reported in this paper. The influence of hardness on soaking, liming and chrome tanning were studied individually. Various levels of hardness water from 500 to 20,000 ppm is used in the unit process of leather manufacture to study the effect and the impact of degree of harness. It is believed the study would form basis for revision of standards on water quality requirements for leather making and there by minimizing competition with domestic sector for fresh water. In other words change in water quality requirements would help sustainable growth of the industry, as alternate sources can be used for leather processing.

Keywords: Tannery; Saline water; Hardness; Leather; Water

1. Introduction

Water is one of the most important chemical used in leather processing. The leather industry turnover has surpassed that of meat industry, the base which supplies raw materials for leather industry. The industry is also proven employment generator. Leather making involves a large number of process steps that utilize water as medium. Nearly 30–35 L of water per kilo of raw hide or skin is being used by the tanneries for processing finished leather. The Indian production capacity is estimated to be 10% of global leather making. With the annual raw hide/skin processing in the range of 690,000 tones per annum in India the total water requirement for this industry will be approximately 30 billion liters [1]. Such a huge volume of water used

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Table 1
General tolerances for water used by the tanning industry

Characteristics	Soaking	Liming	Deliming	Chrome tanning	Vegetable tanning	Dyeing
Total hardness $CaCO_3$ (mg/l)	–	–	–	300	30	30
Carbonate hardness $CaCO_3$ (mg/l)	–	50	50	–	–	–
Chlorides (as Cl, mg/l)	–	–	–	–	500	500

for processing pose problems like availability of water in required quantity and quality. The demand for the fresh water is growing for both domestic requirements as well as industrial purposes. Naturally this creates problem in the quality and quantity of water available for industrial uses. Water demand for human consumption is expected to rise further resulting in a sharp decline in water availability for industrial. Evidently the leather industry will be forced to look for other sources for its water requirement [2-4]. However, water from most of the other resources is saline in nature. The ground water in the tannery cluster is perceived to be not suitable for processing based on existing standards as referred in Table 1. Ground water in tannery clusters contains hardness and chlorides of about 20,000–35,000 ppm. Thus the industry often transports water by trucks from the distant places, where the surface and well water is of acceptable quality. Tanners are apprehensive of using the available water in their areas which contains high degree of hardness and chlorides. In the present work leather processing has been carried out using synthetically prepared hard water of varying degrees to assess their influence on leather quality. Therefore a study was undertaken to examine the feasibility of using hard and saline water in leather processing. Leather making involves three stages of processing namely pretanning, tanning and post tanning [6,7]. The flow diagram for pretanning and chrome tanning process is given in Figure 1.

2. Materials and methods

2.1. Experiment

For the present study calcium chloride, magnesium chloride, calcium carbonate, hydrochloric acid used in the preparation of hard water and the chemicals used for the analysis are of laboratory grade (Assay 99%) was obtained from S.D. fine chem. Limited. The conventional process is adopted for pretanning and tanning of leather processing. Fresh goat skins of Indian origin were used for the experiments. The chemicals used in the leather processing were lime, sodium sulphide, ammonium chloride, alkaline proteases, basic chromium sulphate (BCS) of 33% basicity, sodium formate and sodium bicarbonate all of commercial grade was obtained from Golden chemicals Ltd. The process adopted for the experiment is given in Table 2.

2.2. Preparation of standard hard water

1.0 g of pure, dry calcium carbonate is dissolved in minimum quantity of dilute HCl. The concentration of HCl is 2.5 N. To expel excess of acid and CO_2 the contents were boiled. The residue is dissolved in distilled water to make 1 L solution. The hardness of this

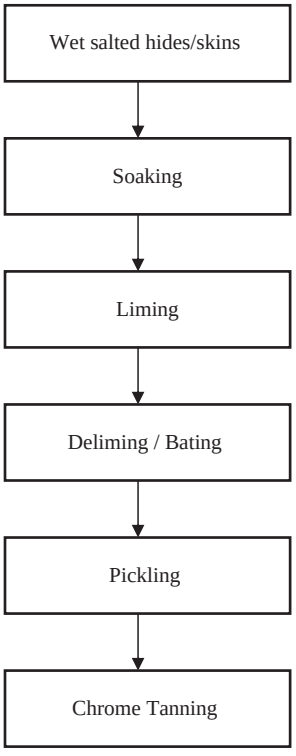

Fig. 1. Flow diagram of chrome tanning in Leather processing.

Table 2

Process	Chemicals	%	Comments
Soaking I	Water*	300	1 h
Soaking II	Water	300	3 h
Soaking III	Water	300	30 min
Liming	Water	25	
	Lime	10	
	Sodium sulphide	2.5	Paint prepared applied on flesh and left overnight Next day the hair was removed over the beam
Reliming	Water	400	
	Lime	10	Left 2–3 days The limed pelts were fleshed and taken for washing
Washing	Water	300	20 min
Deliming	Water	100	
	Ammonium chloride	1	60 min Checked with phenolphthalein indicator
Bating	Microbate AB	1	60 min
Washing	Water	200	20 min
Picking	Water	100	
	Sodium chloride	10	20 min
	Sulphuric acid	1	
	Water	10	4 × 15 min pH 3.0 50% pickle bath was drained
Chrome tanning	Basic chromium sulphate	4	45 min
	Basic chromium sulphate	4	45 min
	Water	50	
	Sodium formate	1	20 min
	Sodium bicarbonate	1	3 × 15 min pH 4.0 Pile O/N

Water* used in the process referred to – 500, 1000, 3000, 6000, 12,000, 20,000 ppm total hardness and chloride hardness.

solution would be 1 g/L or 1,000 ppm or 1 mg/mL. Each mL of this solution thus contains 1 mg of $CaCO_3$ equivalent hardness [8]. For experimental trials 500, 1000, 3000, 6000, 12,000, 20,000 ppm hardness water is prepared as per standard procedure. Chloride hardness water, which is due to calcium chloride and magnesium chloride, was prepared by dissolving required quantities of calcium and magnesium chloride in distilled water, for the study 500, 1000, 3000, 6000, 12,000 20,000 ppm chloride hardness water is prepared [5]. Control trials carried out with distilled water.

2.3. Chemical testing

The analyses were carried out according to SLC methods of chemical analysis [9]. UV-Visible spectrophotometer was used to determine the chromium content in wet blue leathers and spent chrome liquors.

2.4. Scanning electron microscopy analysis

Grain surface and cross section of experimental and control leathers were examined for the changes in fibre structure through a Quanta 200 series Scanning Electron Microscope (SEM). Leather samples were gold coated with Edwards E306 Sputter coater device before SEM analysis. SEM analysis were carried out at two magnifications (×75, ×500).

3. Results and discussion

3.1. Effect of hardness and chlorides in water on pretanning

The effect of hardness and chlorides on pretanning was studied by using water of differential levels of hardness and chlorides. Pretanning process in leather includes soaking, dehairing, liming, deliming, bating

Table 3
Chromium content of wet blue leathers processed with various levels of total hardness water on soaking, liming and chrome tanning

Process	E1	E2	E3	E4	E5	E6	C % Cr_2O_3
Soaking	3.8	3.8	3.7	3.4	3.3	3.2	3.8
Liming	3.1	3.0	3.2	3.5	3.4	3.4	3.6
Chrome tanning	4.1	4.3	4.0	3.0	2.6	2.7	4.4

E1-500 ppm, E2-1000 ppm, E3-3000 ppm, E4-6000 ppm, E5-12,000 ppm, E6-20,000 ppm C-distilled water.

and pickling. Once the hides/skins are flayed from the animals they should be preserved from degradation. The preservation of hides and skins is termed as curing. The most common preservation technique practiced is wet salting method. This is done by applying common salt (sodium chloride) on the flesh side. The principle behind soaking is rehydration of hides and skins. During soaking operation salt, dung, blood and some interfibrillary proteins are removed. The soaking operation was carried out in three steps soak I, soak II and soak III with various levels of hard water and water containing differential level of chlorides. Water with hardness and chlorides variations of 500, 1000, 3000, 6000, 12,000, 20,000 ppm were used for soaking. The skins were visually assessed after rehydration. No major difference was observed between the skins soaked with various levels of hardness, chlorides water and distilled water. The skins were further processed into wet blue leathers as per process shown in Table 2. The various levels of hardness and chlorides in water provided similar results in the soaking operation. The chromium content ($Cr_2O_{3)}$ of the leathers processed with hardness water were found comparable with leathers processed with distilled water in the soaking operation and the values are given in Table 3.

Liming is one of the important operations in leather making. Opening up of the fibre bundles takes place during the liming operation, which decides ultimate feel and softness of leather. The opening up of the fiber bundles enhances the diffusion of chemicals and auxiliaries to the collagen matrix. Various level of hardness water was used in liming operation. Opening up of the fibers was found not affected on using water containing hardness up to the level of 20,000 ppm. The opening up of fiber was viewed through SEM presented in Figures 2 and 3. The control and experimental pelt shows the similar characteristics. This indicates that hardness water up to 20,000 ppm can be used for liming. The lime used in the process probably had a conditioning effect on the hardness of the process water, which in turn perhaps enabled the process to achieve the unaffected fiber opening. When the water containing various levels of chlorides was used in the liming operation, the impairment was not marked. This could probably be due to lyotropic action of chlorides on the skins, which had offset the effect of hardness. If the charges are due to charged ions such as calcium, aluminum or iodide, thiocyanide, then the increase of volume by water separating the charges is termed as lyotropic swelling. The limed pelts were further processed into chrome tanned leathers. The chromium content of leathers processed with various levels of hardness and chlorides were found comparable with control leathers.

3.2. Effect of hardness and chlorides in water on chrome tanning

Tanning is stabilization of collagen against microbial degradation and imparting thermal stability to leather for further processing. Tanning was carried out with basic chromium sulfate. Chrome tanning is the predominant tanning practiced all over the world. The chrome tanning process was carried out with various levels of hardness and chlorides water. The spent chrome liquor was collected and analyzed for chromium content. The chromium content of the leathers are given in Table 3. Variation is seen in the chromium content of the leathers processed with 12,000 and 20,000 ppm of hardness water when compared with the control leathers. The results presented in Table 3 indicate that lower degree of hardness does not have any noticeable effect on chrome tanning. However, higher amount of salt in process water decreases the swelling of the pelt in the chrome bath and produces flatter and tinny leathers. The astringency of the chrome liquor also decreases due to the addition of salt resulting in low uptake of chromium by skin. Similar observation was made when water with hardness to the level of 20,000 ppm was used in chrome tanning process. No major difference is seen in the chromium content of the leathers processed with various levels of chlorides and the values are given in Table 4. The

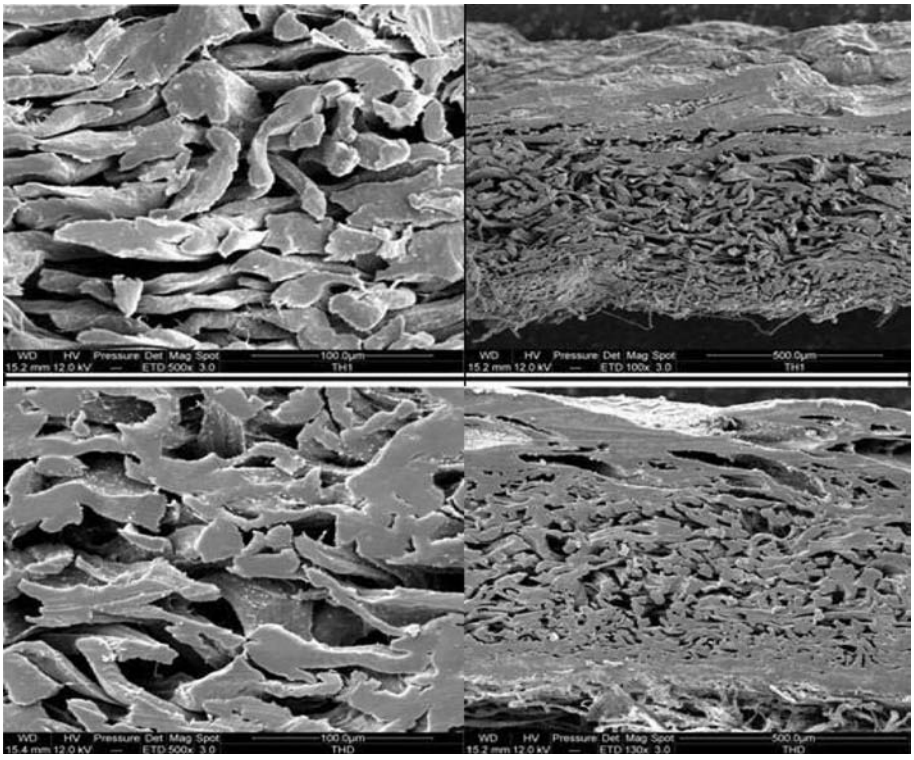

Fig. 2. Scanning electron Micro graphs of control and experimental pelts after fibre opening showing the cross section (×500 and ×75 magnification). Top: Liming (fibre opening) – 20,000 ppm Total Hardness water. Bottom: Liming – Distilled Water (control).

spent chrome liquor was collected from various trials with the water containing hardness and chlorides and analyzed for chromium content. The results are given in Fig 4. The wet blue leathers were visually assessed for properties like grain smoothness, fullness, color, and general appearance and found comparable with the control leathers.

3.3. SEM analysis

The SEM pictures are viewed at 500× and 75× magnifications. Fig. 2 shows the SEM pictures showing the cross sectional view of the experimental and control pelts in the liming operation. The control pelt was processed with distilled water whereas experiment was

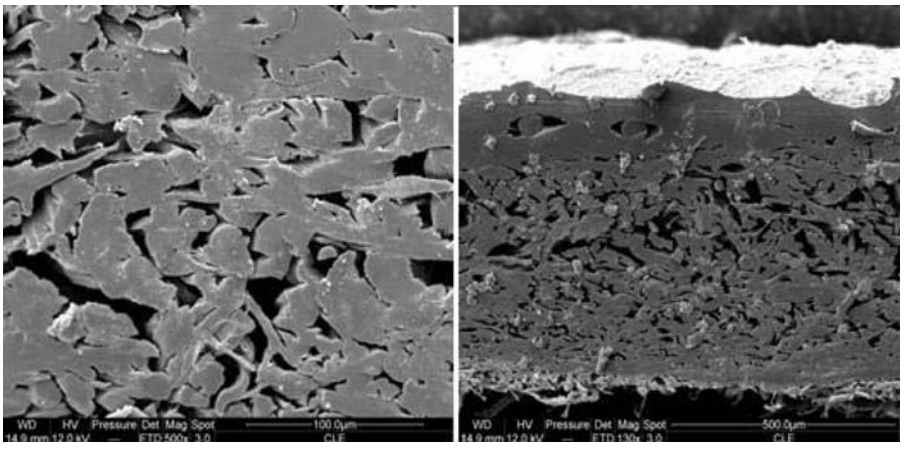

Fig. 3. Scanning electron micrographs of the pelts after fibre opening showing the cross section (×500 and ×75 magnification). Liming (fibre opening) – 20,000 ppm chloride hardness water.

Table 4
Chromium content of wet blue leathers processed with various levels of chloride hardness on soaking, liming and chrome tanning

Process	E1	E2	E3	E4	E5	E6	C % Cr_2O_3
Soaking	3.8	3.7	3.7	3.9	3.8	3.9	4.1
Liming	3.4	3.2	3.3	3.4	3.2	3.3	3.8
Chrome tanning	3.6	3.6	3.7	3.3	3.2	3.1	3.7

E1-500 ppm, E2-1000 ppm, E3-3000 ppm, E4-6000 ppm, E5-12,000 ppm, E6-20,000 ppm C-distilled water.

carried out with 20,000 ppm total hardness water. From the SEM pictures the opening up of the fibers with 20,000 ppm hardness is comparable with control showing similar characteristics. Fig. 3 shows the cross sectional view of the limed pelt processed with 20,000 ppm chloride hardness water. The opening up of fibers is viewed through the SEM picture when compared with the control.

3.4. Characteristics of leather

The characteristics of the wet blue leathers processed with various levels of total hardness and chloride hardness are visually assessed. The assessment was done based on some parameters which includes color of the wet blue, presence or absence of chrome patches, grain characteristics, grain smoothness and finally general appearance. Chrome patches are absent in all the leathers processed with chlorides and hardness water when compared with the control leathers. Figs. 5 and 6 show the visual assessment data of wet blue leathers processed with various levels of chloride hardness and total hardness water. The assessment of the leather was done based on ten point rating while 1 indicates poor characteristics and 10 for outstanding characteristics. All the experimental wet blue leathers E1, E2, E3, E4, are comparable with the control wet blue leathers. Variation is observed in the characteristics of E5 and E6. The properties like colour, surface characteristics and smoothness were affected in the wet blue

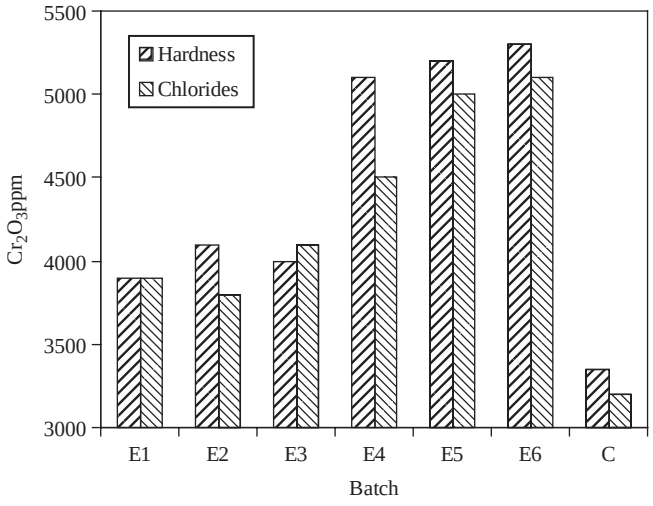

Fig. 4. Chromium content in the spent liquor processed with various levels of chlorides and hardness water.

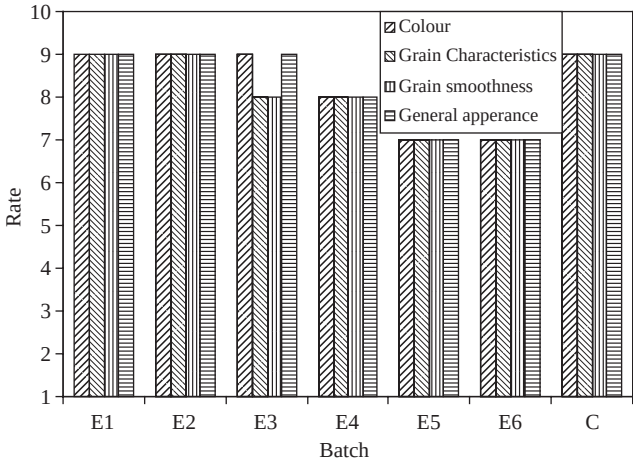

Fig. 5. Visual assessment of wet blue leathers processed with various levels of hard water.

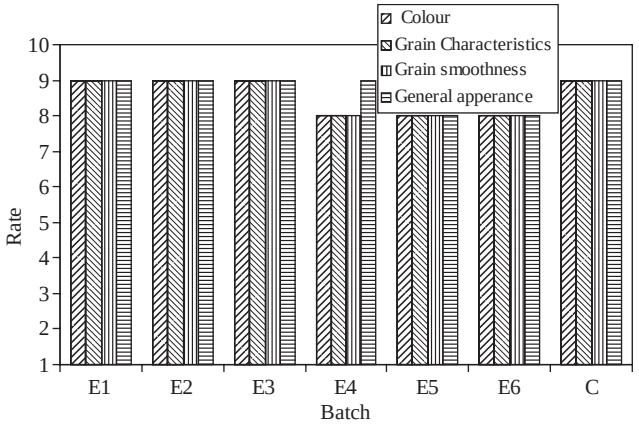

Fig. 6. Visual assessment of wet blue leathers processed with water containing various levels of chlorides.

leathers processed with 12,000 and 20,000 ppm of hardness when compared with the control leathers.

4. Conclusion

The following conclusions can be drawn based on the results obtained from the studies. It has been known for long that the hardness of water affects various pretanning and chrome tanning operation that could result in improper soaking, liming and chrome tanning.

- Presence of impurities in the form of chlorides and hardness up to 20,000 ppm does not impair soaking process.
- When liming was carried with water containing total hardness and chlorides above 20,000 ppm, opening of the fibers was comparable with control which was confirmed through SEM examination.
- The study indicates that total hardness water and the water containing chlorides can be used for pretanning in leather processing up to 20,000 ppm.
- The study indicate in the case of chrome tanning process up to 20,000 ppm of chlorides in water can be used for the process with out any adverse effect.
- Similarly water hardness up to 6000 ppm can be used in the chrome tanning process.
- The study opens up the possibilities for redefining quality parameters standards for water used in leather making.

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