

Accelerated Liming Process Using Phase Transfer Catalyst

by

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Abstract

In the present work, effect of using phase transfer catalysts (PTC) was studied in liming and re-liming processes of goat skin, for decrease in the processing time, thereby increasing productivity. Three different Phase Transfer Catalysts; Tetramethylammonium Hydroxide (TMAH), Tetraethylammonium Hydroxide (TEAH) and Tetrabutylammonium Hydroxide (TBAH) were chosen and experiments were conducted on liming and re-liming of goat skin to select suitable catalyst in comparison with the conventional liming process. The monitoring parameters were ease of hair removal and increase in pelt weight to find the maximum swelling and plumping. After determining the optimal PTC amount, studies were also carried out on reuse of liquor containing PTC with replenishment. Use of TMAH in liming process was found to bring about significant time reduction and could bring improved swelling in liming and re-liming processes.

Introduction

Liming is an important unit operation in leather making where soaked hides/skins are treated with calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution along with an unhairing agent, usually the sodium sulfide (Na_2S). It is a slow process and depending upon the type of leathers made from skins/hides, the process time varies between 5 to 48 hours. Liming process is carried out in the pit/drum/paddle where interfibrillary soluble proteins and keratinous matter get removed in addition to opening up of fiber bundles. After the unhairing process, the hides/skins are treated with $\text{Ca}(\text{OH})_2$ solution to achieve required degree of swelling and also to facilitate flesh removal. This process is also time consuming and takes nearly 14 hours to 72 hours for completion.

Phase transfer catalysis was first applied to reactions involving a water-soluble nucleophilic reagent and an organic soluble electrophilic reagent.¹ By using a PTC in a chemical reaction, one can achieve faster reactions and obtain higher conversions or yields. PTC is not only limited to systems with hydrophilic and hydrophobic reactants, it is also employed in liquid/solid and

liquid/gas reactions. PTC has been widely used for the synthesis of organic compounds for many decades. PTC can also be used in the production of pharmaceuticals, agricultural chemicals, fine chemicals and other specialty chemicals.²⁻⁵ There are many types of PTCs, such as Quaternary Ammonium Salts and Phosphonium Salts, Crown Ethers, etc. Among these, the Quaternary Ammonium Salts are most widely used in the industry because of the low cost. Several research initiatives have been made in the past to speedup liming process and to minimize the toxic waste generation. A detailed literature survey reveals the following. A very rapid liming and subsequent tanning process was reported by treating hides with sodium sulfide solution by painting followed by treatment with sodium peroxide treatment and neutralization led to subsequent tanning of hides in short span of time.⁶ Another method of very rapid liming and subsequent tanning process without effluent by dipping in sodium sulfide solution for 4 min followed by treatment with 10% sodium peroxide solution for 1 hour.⁷ A continuous automatic beamhouse processing was reported by rapid soaking of brine cured hides and unhairing using 4-6% sodium sulphide solution for 10 minutes.⁸ A lime free unhairing system has been reported by using 3% caustic soda, 1% salt, 1% DMAS, 1-2% sodium sulphhydrate.⁹ Other reports include oxidative unhairing of leathers using hydrogen peroxide, amine, enzyme,¹⁰ sulphide free unhairing using ozone,¹¹ oxidative unhairing with hydrogen peroxide,¹² rapid oxidative unhairing using calcium peroxide to avoid using sodium sulphide in unhairing process.¹³ There are few reports for optimal chemicals and reuse of chemicals during the liming process. Dima W. Nazer *et al.*¹⁴ proposed modification of the method where the un-hairing-liming liquids were reused several times after being recharged by reduced quantities of chemicals. Thanikaivelan *et al.*¹⁵ studied an approach to apply the beam-house chemicals with optimal requirement.

In the present study, an attempt has been made to use PTC to transfer ions from liquid to solid phase during the liming process, to decrease the processing time. Three different PTC's, TMAH, TBAH and TEAH were chosen and experiments on liming of goat skin were carried out to compare the effect of PTC in comparison with the conventional liming process.

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Experimental

Materials

Wet salted skins were used for the studies. TMAH (10% Aqueous Solution), TBAH (10% Aqueous Solution) and Tetraethylammonium Hydroxide (25% Aqueous Solution) used were purchased from Lab chemicals supplier, Chennai. Other chemicals used are calcium hydroxide (LR), sodium sulphide (LR) were purchased from SD fine chemicals, Mumbai, India.

Method

The wet salted goat skins were washed once with 300% water (on the weight of the skins) to remove the salt, blood stains, dirt etc. and soaked overnight in 300% water. The weight of the skin after soaking was chosen as basis for chemical addition. The skins were treated with 100% water, 10% lime, 2% sodium sulfide. The above process method is referred here as a conventional liming process. In PTC aided liming process the PTCs of required amount was added to the lime liquor containing 100% water, 10% lime, 2% sodium sulfide. The hair removal ability and increase in weight of limed skin was measured periodically with time to identify the one showing maximum swelling and plumping in comparison to conventional process.

Liming of Goat Skin Using Three Different Phase Transfer Catalysts

All experiments were repeated for thrice to check the reproducibility. A set of four soaked goat skin samples weighing about 500 g were taken in separate plastic trays. In all the four experiments 10% of lime, 100% of water and 2% of sodium sulphide was used. Three different PTCs TMAH, TEAH, TBAH

were added to an extent of 2.5% to three samples and the fourth one was a conventional liming process without PTC. The solution was applied uniformly all over the skin and the skins are place in the solution. The hair removal ability was checked for every one hour and the weight gain after each hour was measured for a period of 5 hours and percentage weight increase was calculated. Among the three PTCs based on their performance, TMAH was chosen and further experiments were conducted with TMAH only.

Optimization of Amount of TMAH Required for Liming Process

A set of four samples was taken and each was separately treated with 10% lime, 100% water and 2% sodium sulphide. In three samples different quantities of TMAH added (0.75, 1.0, 1.25) and the fourth one was a conventional liming process without TMAH. Experiments were conducted in the same manner as mentioned above and repeated thrice to check reproducibility. The hair removal ability was checked for every one hour and the weight gain after each hour was recorded for a period of 5 hours.

Reusing of Lime Liquor with Additional TMAH Replenishment

A total of two samples were taken in separately. In one sample, the lime liquor of 1% TMAH aided liming process from previous process was taken and 0.5% of TMAH was added. Additionally, 3% lime, 1.5% sulphide and 100% water was added. The sample 2 is a conventional process using 10% of lime, 100% water and 2% sodium sulphide were used. The hair removal ability was checked for every one hour and the weight gain after each hour was recorded for 5 hours.

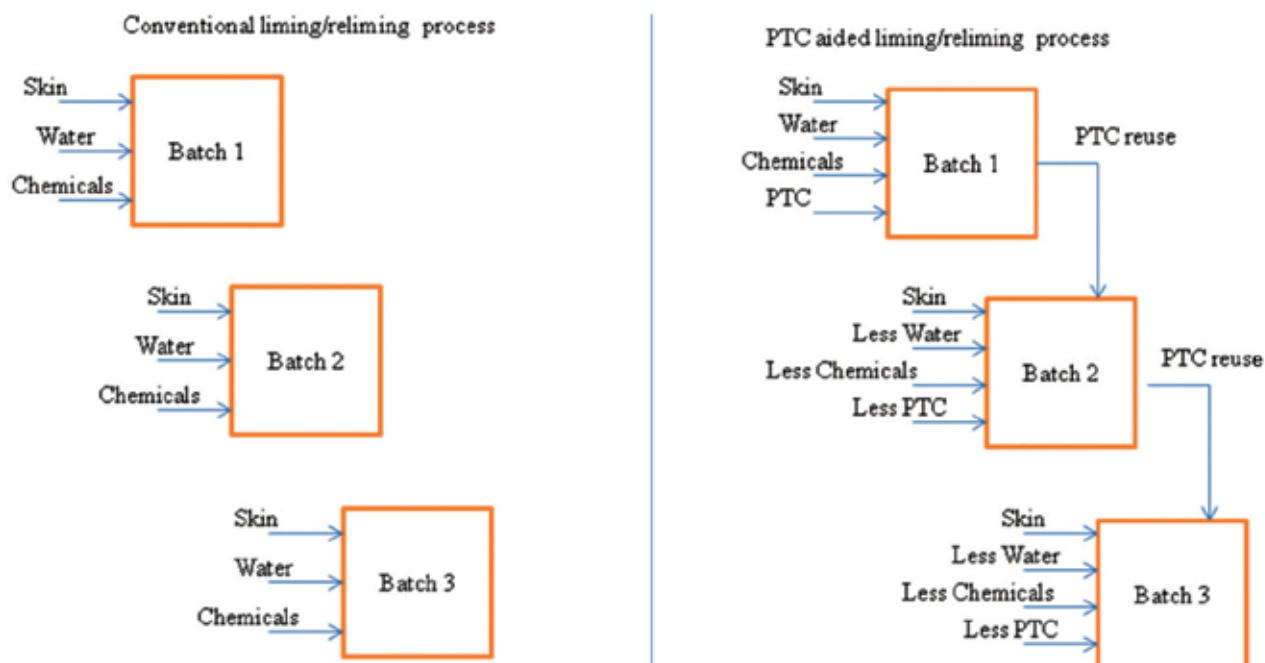


Figure 1. Flow chart showing conventional and PTC aided liming process for reuse.

The above procedure was repeated for one more subsequent batch of water soaked goat skins to study the reusability of used lime liquor containing PTC with the additional make up of 0.5% TMAH. The experimental details are schematically shown as flow chart in Figure 1.

The Effect of TMAH in Re-liming of Goat Skin

In order to study the effect of TMAH in re-liming process, a similar procedure was adopted as mentioned above, but using 200% water, 5% lime along with 0.5, 0.75, 1.0% TMAH and increase in weight was checked for every one hour for 7 hours. For comparison purpose a parallel experiment was conducted without the addition of TMAH.

Reusing of Relime Liquor with Additional TMAH Replenishment

After establishing optimum quantity for re-liming process, in order to study the reusability of used relime liquor containing PTC, sets of two samples were taken in separately. In one sample, the lime liquor of 0.75% TMAH aided re-liming process from previous process was used and 0.5% of TMAH was added and additionally 2% lime, required amount of water was added to make 200% water. The sample 2 is a conventional process using 5% of Lime, required amount of water to make 200% Water. The weight gains after each hour and recorded for a period of 5 hours.

The above procedure was repeated for one more batch of limed goat skins to study the reusability of used relime liquor containing PTC with the additional make up about 0.5% TMAH, lime 2%, and required amount water to make up to 200% float. The details are also shown in Figure 1.

Then the limed skins were processed into full chrome goat upper leathers as per the standard process given in Appendix 1. Both control and PTC aided limed leathers were converted into chrome tanned crust leathers. They were tested for different physical and chemical analysis, and the organoleptic properties were evaluated by experts.

Results and Discussion

Lime has the functional (OH) Hydroxyl group. Since this being one of the groups in the reaction, specific PTC that has OH group for compatibility was chosen. Hence these three PTCs of Quaternary Ammonium salts, having the anion OH group were selected for this work.

It was found that PTC has considerable effect in the liming process in reducing process duration. It was found that not all the PTCs have the ability to reduce the liming time as shown in Figure 2.

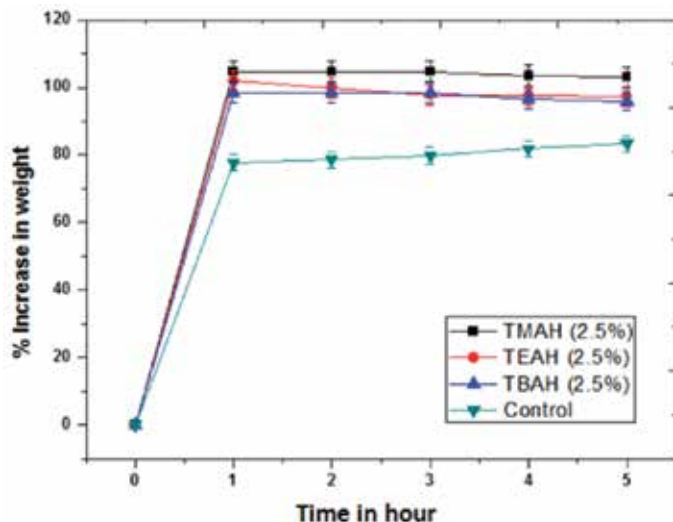


Figure 2. Effect of time in increase in weight of limed goat skin for different phase transfer catalyst.

Among three PTCs, the TMAH produced better hair removal and swelling than other PTCs and conventional process as shown in Figure 1. Hair removal was achieved in 2 hours with TMAH and 3 hours in case of TEAH, TBAH aided liming processes. For conventional process it took 5 hours for hair removal. Application of PTC in the liming process results up to 60% time reduction for liming process. The flesh was removed easily in PTC aided liming process than the conventional liming process.

Figure 3 shows 1% and 1.25% PTC aided liming process gives almost equal hair removal ability and swelling. Hair removal was achieved in 2 hours. 0.75% PTC aided liming process achieved hair removal in 3 hours and in conventional liming process hair removal achieved in 5 hours. The flesh was removed easily in the PTC aided liming process.

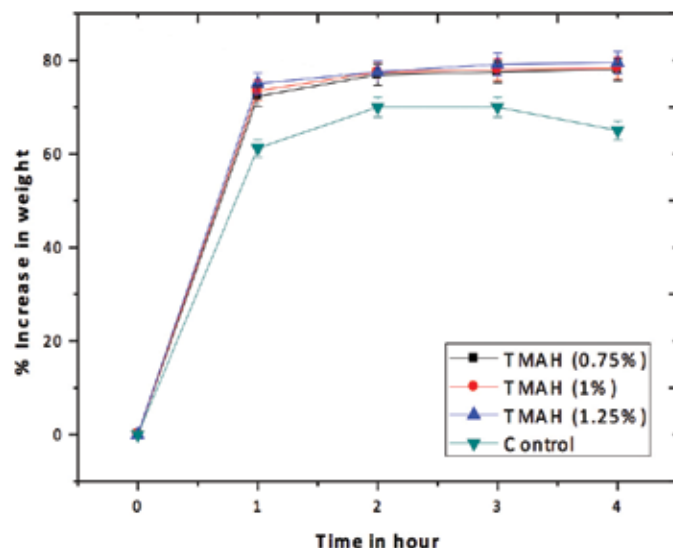


Figure 3. Effect of amount of TMAH on increase in weight of limed goat skin.

First time reusing the lime liquor of the optimum amount of PTC aided the liming process with 0.5% PTC replenishment produced comparable results as the fresh optimum amount of PTC aided liming process and the results are shown in Figure 4. Hair removal achieved in 2 hours

Second time reusing the lime liquor of the optimum amount of PTC aided the liming process with 0.5% PTC makeup produced similar results as the fresh optimum amount of PTC aided liming process. Hair removal was achieved in 2 hours. The reuse of PTC containing lime liquor reduced the amount of PTC required for each cycle process. For a set of three processes the TMAH used per process was reduced to 0.66% on soaked weight.

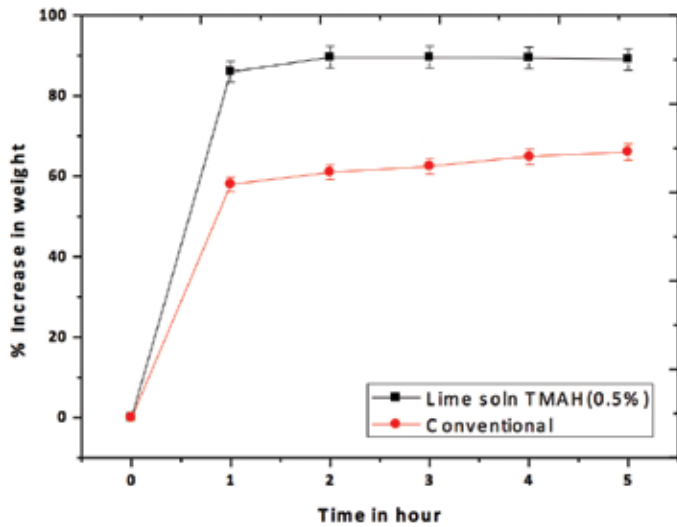


Figure 4. Effect of time on increase in weight of limed goat skin using used lime liquor containing PTC with additional replenishment.

The TMAH assisted re-liming process gives better swelling than conventional re-liming process as shown in Figure 5. Application of PTC in the re-liming process results in more than 85% reduction of time needed for re-liming. The 0.75% of TMAH applied re-liming process provides better swelling than 0.5% and comparable swelling to 1% TMAH aided re-liming process. In the TMAH aided re-liming process, the flesh was easily removed than the conventional re-liming process

First time reusing the relime liquor of optimum amount of PTC aided re-liming process with 0.5% PTC replenishment gives equal results as the fresh optimum amount of PTC aided re-liming process. It reduces the process time more than 85%. The results are shown in Figure 6.

Second time reusing the relime liquor of optimum amount of PTC aided re-liming process with 0.5% PTC makeup gives equal results as the fresh optimum amount of PTC aided re-liming process. The reuse of PTC relime liquor reduced the amount of

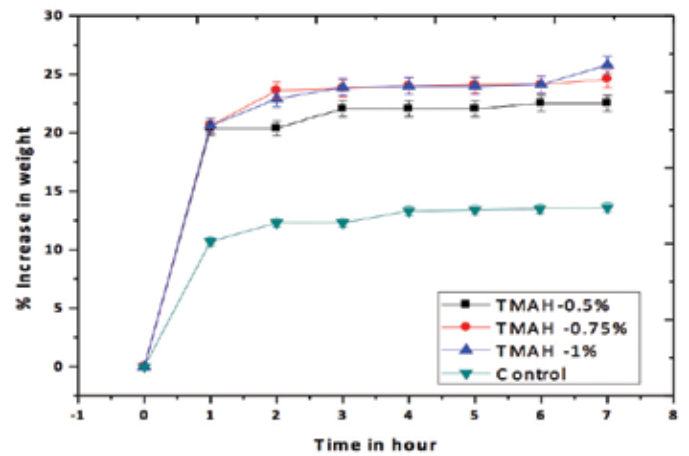


Figure 5. Effect of time in increase in weight of re-limed goat skin in optimization studies.

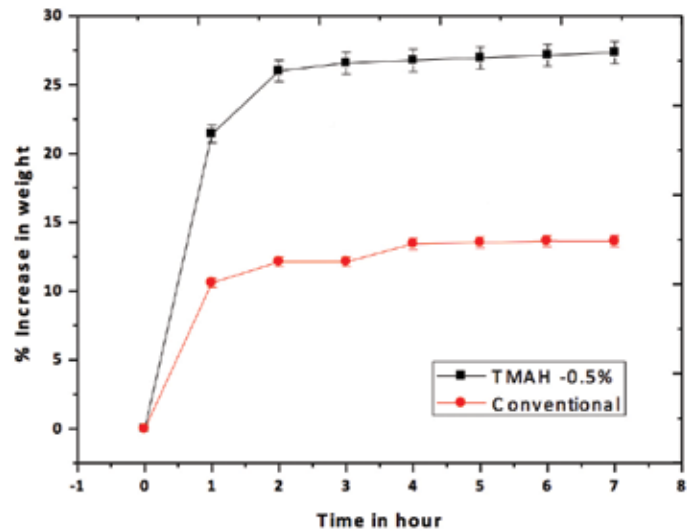


Figure 6. Effect of time on increase in weight of re-limed goat skin using used re-lime liquor containing PTC with additional replenishment.

PTC required for each process. For a set of three re-liming processes the TMAH used per process is reduced to 0.583% on soaked weight.

The effect of TMAH was also studied for re-liming process and TMAH had a similar effect. Studies on reuse of used lime liquor and re-lime liquor containing PTC with 0.5% of additional PTC make up shows that the used lime liquor can be used twice to have identical re-liming effect.

Chrome tanned crust leathers were tested for different physical and chemical analysis and the results are given in Table I. Results show that TMAH aided limed leathers has comparable properties as control leather is an additional proof that there is no adverse effect on the use of PTC during the liming process.

Average Value of Three Experiments

Table II shows the organoleptic properties of tanned leathers and the results reveal that control and experimental leathers possess similar characteristics.

Average Value of Three Evaluations

This study clearly shows that the liming and re-liming process time can be significantly reduced by employing TMAH, thereby leading to increased productivity without affecting the final leather quality.

Table I

Physical and Chemical analysis of chrome tanned crust leather produced from conventional and TMAH aided liming process.

	Chrome content, % Cr ₂ O ₃	Fat content, %	Tensile strength, N/mm ²	Tear strength N
Control	3.11±0.1	5.02±0.2	23.3±1	88±2
TMAH aided Liming	3.05±0.1	5.11±0.2	23.8±1	85±2

Average value of three experiments

Table II

Organoleptic properties of chrome tanned crust leather produced from conventional and PTC aided liming process.

	Softness	Smoothness	Grain characteristics	Overall appearance
Control	6±1	7±0.5	7±0.5	7±1
TMAH aided Liming	7±1	6±0.5	7±0.5	7±1

0- poor, 10-Excellent

Average value of three evaluations

Conclusions

Preliminary experiment on use of PTC in the liming process of goat skin in comparison with conventional liming process reveals that PTC has considerable effect on unhairing and swelling during the liming process in reducing process duration. Among three catalysts the TMAH performs better. The

conventional liming process took 5 hours for hair removal whereas TMAH aided liming process required just 2 hours and giving maximum weight gain due to swelling than the conventional liming process.

Similarly, studies carried out in re-liming process of goat skin showed that application of PTC in re-liming process results in more than 50% increase in swelling compared to conventional re-liming process. This study clearly shows that the liming and re-liming process time can be significantly reduced by employing Tetramethylammonium Hydroxide as a Phase Transfer Catalyst.

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Appendix

Process description for processing cured goat skins into leather.

Process	Quantity	Product	Duration	Remarks
Soaking I	300%	Water	30min	
Soaking II	300%	Water	Left overnight	
	0.1%	Preservative		
	0.5%	Wetting agent		
Next day washing	200%	Water		
Liming				Process details given in experimental section
Reliming				Process details given in experimental section
Washing	200%	Water	10 min	
Deliming	150%	Water	Run for 1 h	Washed and drained pH 8-8.5
	1%	Ammonium chloride		
	0.75%	Bating agent		
Washing	100%	Water	10 min	
Pickling	80%	Water	Run for 15 min 3 x 10 min, Run for 10 min 4 x 15 min, Run for 1 h	pH 2.8-3
	8%	Sodium chloride		
	1%	Formic acid		
	0.75%	Sulphuric acid		

Next day the pelts drummed for 30 min pH at cross section adjusted to 2.8- 3.0. Then 50% of pickle bath drained.

Chrome tanning	8%	Basic chromium sulphate (BCS)	2 x 30 min	Check for penetration in cross section
	1.0%	Sodium formate	10 min	
	1%	Sodium bicarbonate	3 x 20 min, run for 1 h	Check the pH to be 3.8 to 4. Drain the bath and pile overnight.

Appendix continued on following page.

Appendix continued.

Next day sammed and shaved to 1.0 mm.

Washing	200%	Water	10 min	Drain
Neutralization	150%	Water		pH 5-5.5
	0.5%	Sodium formate	10 min	
	0.5%	Sodium bicarbonate	3 x 15 min + 1 h	
Washing	100%	Water	10 min	
Retanning and Fatliquoring	100%	Water		pH 3.5 Drain, rinse, pile over night
	9%	Fatliquor	1 h	
	8%	Syntan	1 h	
	1%	Formic acid	3 x 5 min + 40 min	

Finally leathers were dried and then conditioned for testing and evaluation.