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Research Article

Production and quality enhancement of wet white leather by syntan assisted polyphosphate tannage: A cleaner technological approach to the leather processing

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Abstract

Most of the leathers produced worldwide are chromium tanned. The negative environmental impact of chromium pressurizes the tanners to find out alternative tanning technologies. In this research as an alternative to the conventional chrome tanning a wet white leather was produced by commercial grade sodium Hexa Meta phosphate (SHMP) tanning in wet condition at room temperature. The quality deficiencies of the wet white leather were improved by a modified method of syntan (Basyntan DLE) assisted SHMP tanning. The optimum SHMP tanning conditions were identified as pH of the tanning bath (3), offer of the SHMP (12% based on pelt weight) and tanning time (6 hours). Shrinkage temperature and tensile strength of the SHMP tanned wet white leather were 84 °C and 19.15N/mm² respectively. In the modified system 8% offer of Basyntan DLE along with 12% SHMP was identified as best combination. In this condition shrinkage temperature of the wet white leather enhanced 6.02% from 84 °C to 89 °C. Other physical properties were also found to be increased significantly. Due to the improvement of leather quality and generation of chromium free wastewater, this syntan assisted SHMP tanning may be the potential cleaner technology as a substitute of the most practiced wet blue technology in the tanning industry.

Keywords: *Wet white leather, Tanning, Cleaner technology, Polyphosphate, Syntan.*

1. Introduction

Leather manufacturing is a traditional and wide common industry that plays a significant role in the world economy (UNIDO, 2003).Animal hides or skins are converted to leather through multifarious mechanical and chemical operations which are vindicated into three indispensible sub groups as beam house, tanning and post tanning (Stanislaw and Krystyna, 2011), (UNEP IE, 1996). In the beam house stage raw hides or skins are prepared up to the point of initiating tanning and are named as pelt. The transformation of putrescible pelt into stable material leather, capable of resisting microbial attack is occurred in tanning stage (Covington, 2011). Diversified physical properties and protective and decorative surface coatings are introduced to the leather in the post tanning operations (UNEP IE, 1996).

Today almost 90% of the leather is produced globally by chrome tanning method using basic chromium sulfate (BCS) as tanning agent and the produced leather is called wet-blue. The wastewater discharged from chrome tanning operation contains roughly 35-40% chromium of total offer (Musa and Gasmelseed, 2013). In addition the utilization technology of chrome containing tannery solid wastes to useful byproducts also discharges this heavy metal to the environment (Kanagaraj*et al*, 2006).

This high amount of chromium (Cr^{3+}) is toxic for the flora and fauna and for the soil microbiology. In addition various researchers have identified the possibilities of the conversion of chromium (III) to its hexavalent (Cr^{6+}) state during tanning. Cr^{6+} is carcinogenic for human and it has toxic and mutagenic behavior to the microorganisms and aquatic systems (Musa and Gasmelseed, 2013), (Bartlett and James, 1979), (Ajmal and Ahmad, 1984). So, possible alternatives of conventional chrome tanning method either by fully or partial replacement of chromium has long been an area of research worldwide.

Wet white leather production is a kind of cleaner technology to mitigate the environmental pollution caused specifically by conventional chrome tanning method.

Minimization of effluent pollution load, avoidance of harmful chemicals and production of easily convertible solid wastes to useable by products are the main theme of cleaner technologies. Various types of cleaner technological options for each and every unit operations of leather production processes have already been established and practiced (Ludvik, 2000). In recent

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times wet-white leather has gained advantages almost as like as wet-blue (Covington, 2011). Wet white leather is a white leather produced by tanning of hides and skins with non-chromium agents provided with the benefits of Chromium free effluents, recyclable shavings, riskless of Cr (VI) formation, metal free leathers etc. various types of tanning agents solely or in combination with others have already been used for wet white leather production (Covington, 2011). Here syntan assisted polyphosphate tanning was studied for the production of wet white leather. Synthetic tanning materials (syntans) have huge role in the tanning industry. Different syntans are used in different purposes as non swelling acids, bleaching agents, neutralizing agents; retanning agents etc (Sarkar, 2012). On the other hand phosphate tannage was first investigated by Wilson where he postulated electrovalent linking of phosphate to collagen for the production of pure white leather provided with the benefit of great tensile strength and high shrinkage temperature. Linder showed that the increase of the fixation of P_2O_5 to the collagen during phosphate tannage increases the quality of leather (McLaughlin, 1945).

In this study an endeavor has been made to produce wet white leather by tanning using low cost abundantly available commercial grade sodium Hexa Meta phosphate (SHMP). This work also highlighted the investigation of tanning performance of SHMP as a function of time, percentages of SHMP and pH of the tanning bath. This study also focused on the quality enhancement of phosphate tanned wet white leather by phenol based syntan.

2. Materials and Methods

2.1 Materials

For this study six pieces of goat skins were purchased from a slaughterhouse at Fulbarigate, Khulna, Bangladesh. Commercial grade SHMP for wet white tanning was procured from a scientific store, Dhaka. A phenol based syntan of BASF, commercially named as Basyntan DLE and all the other chemicals required for leather production were purchased from a leather chemical store at Hazaribagh, Dhaka, Bangladesh.

2.2 Methods

2.2.1 Preparations for poly phosphate tanning.

Collected raw skins were weighed and taken for the chemical operations. Table 1 represents the unit operations of the preparatory stage of poly phosphate tanning. All the percentages of chemicals of the following recipe were based on raw skins weight (soaking & painting), pelt weight (Liming) and defleshed pelt weight (Chemical wash, Deliming& Bating).

Table 1 Recipe of the preparatory stages of tanning

S. No	Process	% of water & chemicals	Remarks
1	Soaking	300% Water 0.5% Soda Ash 0.2% Preservative 0.5% Common Salt	Soaking was done in a plastic bowl for 1 hour
2	Painting	6% Lime 3% Na_2S 0.2% Lime Auxiliary 0.2% Wetting agent Water added to make paste	Applied the paste on the flesh side of the skins and kept for 6 hours.
After that the skins were scudded well for the removal of hairs and washed for 10 minutes. Now the skins are termed as pelt. The pelts were then weighed.			
3	Liming	400% Water 3% Lime 1% Sodium Sulphide 0.5% Lime Auxiliary 0.2% Wetting Agent	Liming was done in plastic bowl for 3days.
After 3 days of Liming the pelts were defleshed by a fleshing machine, washed for 10 minutes and weighed. The following operations were done in drum.			
4	Chemical wash	100% Water 0.5% Sodium Metabisulfie	Run 30 minutes. Then drained.
5	Deliming	100% Water 1% Ammonium sulphate 1% Ammonium chloride 0.5% Meta bisulfie	Run 60 minutes. Phenolphthalein-Colorless test was done to get the end of complete deliming.
6	Bating	100% Water 2% Bate powder 0.5% Wetting agent	Run 60 minutes (Bath temperature was 37 ^{0}C). Bubble test was done for getting end point of bating.
Skins were then scudded well with hand knife for the removal of hair roots and scuds. After scudding skins were washed for 10 minutes.			

After Bating two of the bated pelts were isolated, horsed-up and allowed for drying at room temperature. Shrinkage temperature and other physical properties of one of the dried bated pelt was then determined. Another one was cut into four pieces and kept for quality enhancement studies. Rests four of the bated pelts were cut into 16 small pieces, weighed separately and were allowed in the tanning using SHMP. The sizes and weights of the cut pieces were almost same. The backbone of the cut pieces were identified by cut marks.

2.2.2 Poly phosphate tanning.

The tanning experiments using SHMP was done in drum. All percentages of the chemicals used for the experiments were based on the weight of the individual pelts. The effect of different influencing parameters on the SHMP tanning was evaluated and optimized by measuring the shrinkage temperature (Ts) of the wet white leather. Shrinkage temperature is the indication of the hydrothermal stability of the leather and degree of tannage which increases with the increase of the number of additional bond formation between the tanning agent and the skin collagen (Covington, 2011), (Dutt, 1990), (Kuria*et al*, 2016).

2.2.2.1 Optimization of the tanning pH for polyphosphate tannage

Five pieces of pre weighed bated pelts were introduced in four different drums with 100% of water at room temperature. The pHs of the baths were controlled from 2.5 to 4.5 by adding required percentages of sulphuric acids (1:10 diluted) into it. Required amount of salts were also added in different drums to dispel acid swelling. After that 8% of SHMP were added in each drum followed by addition of 1% cationic fat in each drum. The mixture was allowed for 2 hours of drumming and then kept undisturbed for overnight. Next morning the wet white leathers were taken from the bath, horsed up and hung for air drying. The shrinkage temperatures of the dried leathers were measured using SATRA STD 114 test apparatus based on test method (IUP/16). The pH value where highest Ts was observed was selected as optimum and taken for the following set of experiments.

2.2.2.2 Optimization of the percentages offer of SHMP for polyphosphate tannage

The optimization experiments of SHMP dosages were performed by taking five pieces of bated pelt in to five different drums for 2 hours of tanning at room temperature by keeping the previously optimized pH of the bath. The percentages of SHMP were varied from 6-14 in the five drums. 100% water of the pelt weight, salts and 1% cationic fat were added in each drum. After tanning the wet white leathers were kept in the drum for overnight followed by air drying and Ts were measured as described previously. Optimum dosage was selected based on the highest Ts value.

2.2.2.3 Tanning time optimization of the polyphosphate tannage

For the optimization of tanning time five pieces of bated pelts were treated for 2 to 10 hours with already optimized percentage of SHMP in five different drums at room temperature at a pH which was optimized previously. Each of the drum was filled with 100% water and 1% cationic fat of the pelts weight and required amount of salts also. After tanning the white leathers were kept in drums for overnight, horsed up and then dried those at room temperature. Optimum tanning time was chosen by measuring highest shrinkage temperature.

2.2.3 Quality evaluation and enhancement studies of the polyphosphate tanned wet white leather by syntan assisted tanning.

For quality enhancement studies four pieces of bated pelts were kept in four different drums with 1% cationic fat, salts and 100% water of pelts weight in each drum. After that pH of all the drums were maintained 3 (already optimized) and previously optimized polyphosphate percentage (12% of pelt weight) were added in every drum and allowed them to run for 30 minutes at room temperature. Now different dosages of Basyntan DLE ranges from 4% to 10% of the pelt weight were added in each drum and the drums were allowed to run for further 330 minutes. After tanning the leathers were kept in the baths for overnight, horsed up in the next morning and dried in atmospheric air by hang drying. Different physical properties were measured based on various standard test methods for the non tanned pelt (bated pelt), polyphosphate tanned wet white leather (produced at the optimum tanning conditions) and syntan assisted polyphosphate tanned wet white leather. All the results were then compared and analyzed. Sampling locations for physical testing were determined according to the official method (ISO 2418:2002).

Tensile strength and tearing strength were measured using SATRA tensile tester based on the official test method (IUP/6) and (IUP/8) respectively. Thickness was measured using leather thickness gauge TG 200P (IAS, China).

According to the official method (IUP/9) the ball burst strength was measured.

3. Results and Discussion

3.1 Process optimization studies of SHMP tannage

3.1.1 Effect of tanning pH on the SHMP tannage

The change of the shrinkage temperature of wet white leather with change of pH values of the tanning bath is represented in the Fig. 1

The figure illustrates that with the decrease of the pH of the tanning bath shrinkage temperature increased up to pH 3 and further decrease of pH valueresulted a slight decrease of the value of shrinkage temperature. The maximum shrinkage temperature was observed at pH 3 and the value was 73 ^{0}C. The shrinkage temperature of leather increases due to the formation of bond between collagen and tanning agents (Dutt, 1990). Linder stated that polyphosphate is an anionic tannage and Wilson described electrovalent linking of polymeric phosphate to collagen (McLaughlin, 1945). For the formation of electrovalent bonds available positive charges from the collagen is desirable and the charges of protein is affected by pH (Bhal and Bhal, 1999). This may be due to the reason of changing shrinkage temperature of wet white leather with pH. Based on the results depicted in the Fig. 1 pH 3 was selected as optimum condition for SHMP tannage.

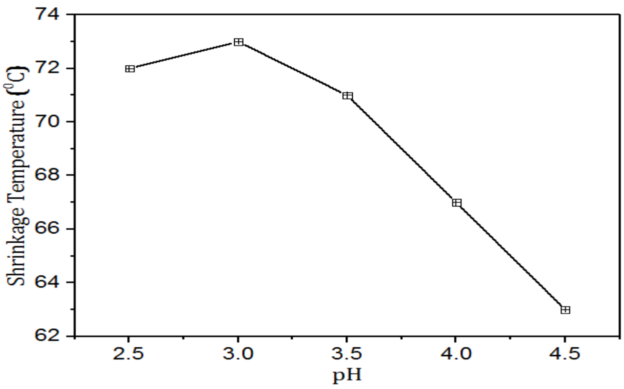

Fig.1 Effect of pH on the Ts of wet white leather (Tanning time = 2 hour, dose of SHMP = 8% of pelt weight)

3.1.2 Effect of SHMP dosages on the wet white tannage

Fig. 2 shows the results of the influence of the dosages of SHMP on the shrinkage temperature of the wet white leather

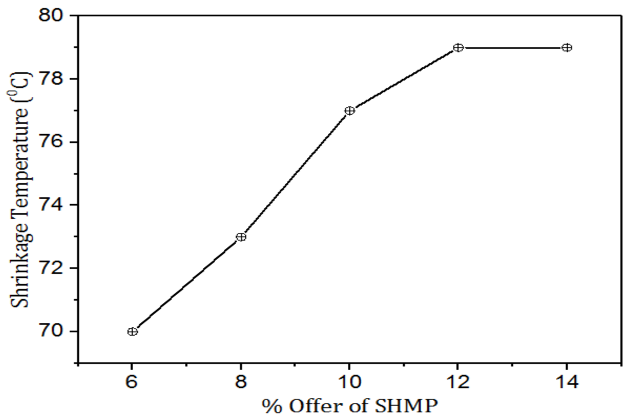

Fig.2 Effect of SHMP dosages on the Ts of wet white leather (Tanning time = 2 hour, pH of the bath = 3)

It is noticed that higher shrinkage temperature was observed at higher offer of the SHMP. It reached to maximum (79 ^{0}C) for 12% of SHMP and then remained constant even the SHMP dosage was 14%. Shrinkage temperature is the measure of the degree of tannage (Kuria*et al*, 2016). With the increase of SHMP dosages degree of tannage increased which eventually raised the shrinkage temperature of the wet white leather. This is the speculation of the results represented in the above Figure. Based on the maximum shrinkage temperature 12% offer of SHMP was optimized for this tanning.

3.1.3 Effect of time on the SHMP tannage

The results of the influence of tanning time on the shrinkage temperature of the wet white leather is given in the Fig. 3

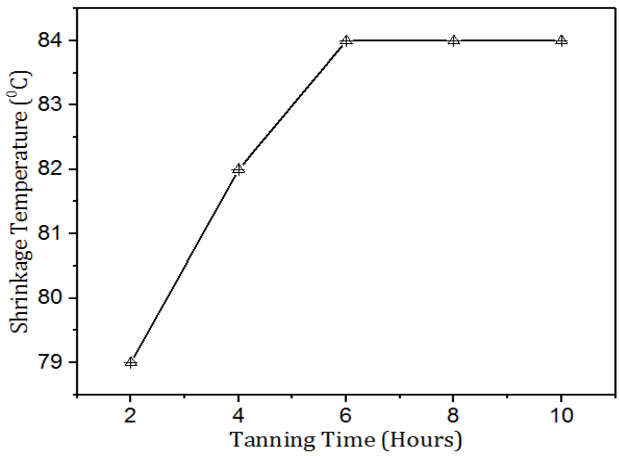

Fig.3 Effect of time on the Ts of wet white leather (dose of SHMP = 12% of pelt weight, pH of the bath = 3)

From the figure above it is seen that shrinkage temperature increased with tanning time from 2 to 6 hours and then remained unchanged. The highest shrinkage temperature of this experimental condition was 84 ^{0}C for 6 hours of tanning. All the possible bonds between collagen and SHMP may be formed for 6 hours of reaction this may be due to the cause of the constant behavior of shrinkage temperature for 8 and 10 hours of tanning.

3.2 Quality evaluation and enhancement studies

The physical –mechanical properties of the non tanned pelt and wet white leather (polyphosphate tanned at optimum condition) are shown in the Table 2.

The standard values showed in the table are based on (Kuria*et al*, 2016) and (Musa and Gasmelseed, 2013). The results of Table 2 indicate that all the physical properties of leather increased by polyphosphate tanning. The strong bondage between collagen and SHMP is the reason behind the improvement of the shrinkage temperature. The introduced SHMP give background support to the fiber and this may be the cause of the increment of the tensile strength.

Table 2 Physical characteristics of pelt and leather

S. No	Properties	Bated pelt	Wet white Leather	Standard value
1	Shrinkage temperature (°C)	59	84	75
2	Tensile strength (N/mm²)	9.41	19.15	>12
3	Tearing strength (N/mm)	9.75	15.49	>20
4	Grain crack load (kg)	8.11	14.54	20
5	Grain crack extension (mm)	3.28	5.98	7
6	Thickness (mm)	0.6-0.7	0.6-0.7	-

Table 3 Physical properties of Basyntan DLE assisted SHMP tanned wet white leather

S. No	Properties	SHMP +Syntan(4%)	SHMP +Syntan (6%)	SHMP +Syntan (8%)	SHMP +Syntan (10%)
1	Shrinkage temperature (°C)	85	87	89	88
2	Tensile strength (N/mm²)	20.25	22.33	23.75	22.88
3	Tearing strength (N/mm)	18.32	21.11	22.85	22.05
4	Grain crack load (kg)	17.03	18.23	19.35	18.75
5	Grain crack extension (mm)	6.08	7.15	8.25	8.05
6	Thickness (mm)	0.6-0.7	0.7-0.8	0.8-0.9	0.8-0.9

The presence of SHMP inside the leather is may be due to the reason for the increase of tearing strength and grain crack resistance (Dutt, 1990). The above table also illustrates that most of the physical properties of the polyphosphate tanned wet white leather did not meet the standards. This is may be due to the fact that SHMP itself is not enough to produce wet white leather with desired physical properties.

The physical characteristics of the wet white leather produced by syntan assisted polyphosphate tanning are represented in the Table 3.

It is observed from the Table 3 that with the increase of the percentage offer of the Basyntan DLE all the physical properties of the wet white leather increased significantly. The added phenolic syntanBasyntan DLE created additional bonds with skin collagen and made support to the fiber. This might be the cause of the improvement of the leather properties. From 6% to 10% offer of the DLE the values were over the standards. The highest values of all the properties were noticed for 8% dosage of Basyntan DLE. Further dosage increment could not improve the process performance. The percentage enhancement of the physical properties of the SHMP tanned leather by 8% Basyntan DLE offer is shown below.

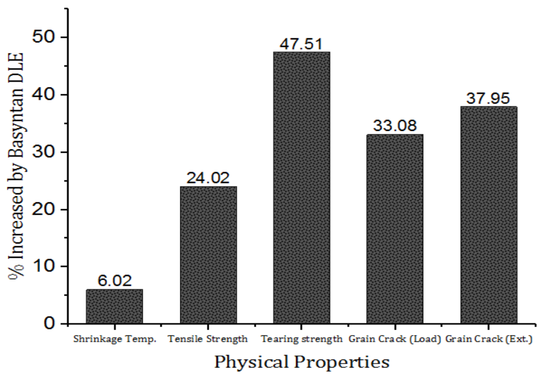

Fig.2 percentage enhancement of different physical properties of wet white leather by Bsyntan DLE assisted SHMP tanning

Conclusions

This paper is focused on the cleaner leather production as an alternative to the most practiced chrome tanning method. To do so an attempt was made to produce wet white leather by commercial grade Sodium Hexa Meta Phosphate (SHMP) tanning. The mechanical and physio-chemical properties of the wet white leather were enhanced as desirable by a modified method of syntan supported SHMP tanning. The overall outcomes of this research are represented below:

1) This study investigated the influence of different factors on the SHMP tanning and the optimum tanning conditions were identified.
2) The produced lather was pure white in color. Shrinkage temperature and tensile strength of the wet white leather increased significantly. In contrast tearing strength and Grain crack resistance were also increased but did not meet the standard value.
3) In the modified system best possible coupling of Basyntan DLE and SHMP was ascertained.
4) The momentous improvement of the SHMP tanned wet white leather was obtained by the syntan assisted system as tensile strength, tearing strength, grain crack load, grain crack extension were increased to 6.02%, 24.02%, 47.51%, 33.08% and 37.95% respectively.
5) From the attained results it could be concluded that Basyntan DLE assisted Sodium Hexa Meta Phosphate tanning may be a promising cleaner technological option to the leather processing.

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